DETRITIATION REACTIONS
IN
AROMATIC SYSTEMS

A Thesis
presented for the degree of
Doctor of Philosophy in the Faculty of Science
of the
University of Leicester
by
Raymond Baker

The University, Leicester
May, 1962

ProQuest Number: U622487

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

ProQuest U622487

Published by ProQuest LLC(2015). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code.
Microform Edition © ProQuest LLC.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

X752937706

547.32
111731
23.7.62

STATEMENT

All the experimental work herein described has been carried out by the author in the laboratories of the Department of Chemistry, University of Leicester between October 1959 and the present date.

The work has not been presented, and is not being concurrently presented for any other degree.

May 1962

Signed: R Baker

I wish to express my gratitude to Dr. C. Eaborn for suggesting the topic, and for his valuable assistance whilst the work was being carried out. My thanks are also due to Mr. R. W. Bott for his help and encouragement, and to Professor L. Hunter, in whose laboratories this work was undertaken.

A maintainance grant from the Department of Scientific and Industrial Research, is gratefully acknowledged.

Finally, I should like to thank my wife for the considerable help in the typing of the thesis.

Signed: R Baker

SUMMARY

A review of the literature on electrophilic aromatic hydrogen-exchange reactions is presented.

A number of mono-tritiated substituted benzenes, heterocyclic, and polynuclear compounds have been prepared and rates of detritiation have been measured, mainly in anhydrous trifluoroacetic acid.

The results provide a measure of the reactivities of various aromatic positions of dibenzothiophen, dibenzofuran, benzothiophen, thiophen, diphenyl ether, diphenyl sulphide, 5-ethylcarbazole, naphthalene, biphenyl, fluorene, phenanthrene, and diphenylmethane. Conclusions are considered in relation to data available for the more familiar aromatic substitutions, such as bromination and nitration, and some anomalies are noted.

An analogy has been shown to exist in the detritiation of [2-^{3}H]fluorene and 9,9-dimethyl-[2-^{3}H]fluorene on the one hand, and [p-^{3}H]toluene and [p-^{3}H]-t-butylbenzene on the other; the significance of this is discussed.

Measurement of the rate of detritiation of o- and p-tritiated -toluene and -t-butylbenzene in a variety of media has shown that variations in the relative reactivities of ortho- and para- positions cannot be ascribed to steric effects.

The rates of detritiation of the compounds, 4-X-$[4'\text{-}{}^{3}\text{H}]$biphenyl (where X = 4-Me $>$ 4-Meo $>$ 4-H $>$ 4-Cl 4-Br $>$ 4-NO_2) and 2-X-$[7\text{-}{}^{3}\text{H}]$fluorene (where X = Me $>$ Meo $>$ H $>$ Cl $>$ Br $>$ CO_2H $>$ NO_2) have been measured. The effects of substituents, in analogous positions, are very similar in the fluorene and biphenyl systems, but the results do not show whether tautomeric effects are transmitted from one ring to the other in these systems. Anomalous results for the 2-Meo-$[7\text{-}{}^{3}\text{H}]$fluorene and 4-Meo-$[4'\text{-}{}^{3}\text{H}]$biphenyl indicate that some interaction, possible hydrogen bonding, occurs between the methoxy-substituent and trifluoroacetic acid.

CONTENTS

Page

Introduction

Electrophilic aromatic hydrogen-exchange

Preparation of compounds

Kinetics and Results

Discussion Page

Electrophilic aromatic hydrogen exchange

1. Evidence for the electrophilic nature of exchange

Exchange between hydrogen gas (containing deuterium) and benzene at the surface of finely divided catalysts was first observed by Horuiti, Polanyi and Ogden.[1]

Ingold, Raisin and Wilson,[2] studying qualitatively the exchange reaction of benzene and acids containing deuterium, came to the conclusion that hydrogen exchange is a typical electrophilic substitution. The reaction is reversible, being completely balanced except for isotopic differences. The evidence for regarding the process as electrophilic was threefold:-

(a) Deuterating acids were found to arrange themselves in the efficiency series $D_2SO_4 > D_2SeO_4 > D_3O > PhOD > D_2O$[3], which is obviously an acidity series.

(b) Substituent effects were similar to those observed in reactions such as nitration and chlorination, known to involve an electrophilic entity.

e.g., dimethylaniline was deuterated more rapidly than anisole by aqueous deutero-acids, i.e., by the deuteroxonium ion.

(c) Hydrogen exchange followed the usual orientation laws for electrophilic aromatic substitution, e.g., phenol, aniline, and anisole were rapidly deuterated at three positions only (assumed to be _ortho_ and _para_-positions), and this was followed by a slow deuteration (assumed to be at the _meta_-position). These assumptions were subsequently shown to be correct for phenol and aniline.[4] Further evidence obtained by Lauer and Day,[5] was that in the deuteration of anisole, the <u>ortho/para</u>-ratio decreases with decrease in temperature. In electrophilic substitutions, low temperature favours a high percentage of <u>para</u>-product.

In experiments with a number of aromatic ethers, the rate of exchange at the <u>para</u>-positions was observed to increase along the series,

PhOMe > PhOEt > PhOn-Pr > PhOi- Pr

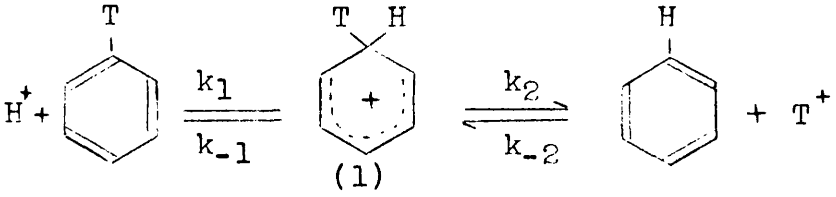
This same order is observed in other electrophilic substitutions with aromatic ethers.[6,7]

McKay,[8] and other workers,[9] have shown that the exchange of isotopic atoms between two substances follow first order kinetics, provided there is no isotope effect. Papers by Harris,[10] and later by Melander[11], showed that even where appreciable isotope effects are involved, the exchange rate approximates to first order, provided that the relative concentration of the distinguisable isotope is small enough, and there are no medium effects. Thus if k is the rate constant for the exchange reaction, and Fo and F are the relative abundances of the distinguishable isotope in one of the reactants initially and after time t, then:

$$k = \frac{\log_e}{t}\left(\frac{Fo}{F}\right)$$

2. Mechanism of hydrogen exchange.

The first detritiation reactions were carried out by Olsson and Melander.[12] Tritium (or deuterium), which had been introduced into the _ortho_-, _para_-, _meta_-, and _alpha_-positions of toluene was exchanged by shaking the isomers with 80.8% sulphuric acid. The relative exchange rates of the _ortho_-, _meta_-, and _para_-, positions were found to be (47±2), (1.00±.04) and (41±2) for tritium exchange, and (51±2), (1.00±.04) and (46±3) for deuterium exchange. They showed that if the substitution is represented by:-



and the intermediate is assumed to be present in very low concentration, the rate factor

$$\frac{k_2}{k_{-1}+k_2} = \frac{1}{k_{-1}/k_2+1}$$

determines the isotope effect in the forward reaction. This holds irrespective of whether a hydrogen acceptor is involved in reactions -1 and 2, or whether the reaction proceeds through a low stability intermediate, as assumed by Gold and Satchell,[13,14] (see below). If the σ-complex intermediate (1), behaves like an ordinary molecule the ratio k_{-1}/k_2 could be supposed to be of the order 7-10 for the tritium- protium pair, and 4-6 for the deuterium-protium pair. Consequently the ratio of protodetritiation, k_t, to that of protodedeuteration, k_d, in any medium should be given by:-

$$\frac{k_t}{k_d} = \frac{(k_{-1}/k_2)_d + 1}{(k_{-1}/k_2)_t + 1} \doteq 0.6$$

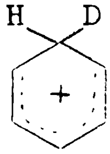
The rates k_t and k_d were measured and the ratio k_t/k_d varied between 0.65 for benzene to 0.59 and 0.52 for *meta-* and *para-* substituted toluenes respectively. Thus the isotope effect appeared to decrease with increasing reactivity of the nuclear position. It should be noted, however, that the isotope effect observed is consistent also with the synchronous S_E3 process for the breaking of a carbon-deuterium or carbon-tritium bond. Such a process would give an isotope effect of *ca.* 6 (tritium-protium), and (deuterium-protium) *ca.* 4, and $k_t/k_d \doteq 0.66$.

Gold and Satchell[13,14] examined kinetically the loss of deuterium from *p*-nitro$[o\text{-}^2H]$phenol, *p*-chloro$[o\text{-}^2H]$phenol, $[o\text{-}^2H]$*p*-cresol and $[^2H]$benzene in various sulphuric acid - water mixtures. Plots of the logarithm of the exchange rate against the Hammett acidity *Ho* were approximately straight lines of slopes 0.94, 0.90, 1.08, and 1.36 respectively. After considering the concentrations of H_3O^+ and HSO_4^- present in the various concentrations of sulphuric acid, they regarded the dependence of reaction velocity on *Ho* as established, in spite of the difference between the experimental slopes and the expected slope of unity. The marked deviation in the case of benzene was attributed to the salting out of the compound by sulphuric acid. A proportionality in rate constant and *Ho* has been interpreted by Hammett as implying a rate-determining reaction of the conjugate acid of a substrate, the protonation occurring rapidly to a small extent, with no water molecule taking part in the rate-determing step.

$$HA + S \underset{}{\overset{\text{fast}}{\rightleftharpoons}} SH^{+} + A^{-} \quad \ldots\ldots\ldots\ldots(1)$$

$$SH^{+} \xrightarrow{\text{slow}} \text{products} \quad \ldots\ldots\ldots\ldots(2)$$

In applying this idea to the loss of deuterium from a substrate in an acidic medium, Gold and Satchell noted that SH^{+} could not be identified with (11), (an intermediate of the type commonly assumed in electrophilic aromatic substitution), in which the H and D atoms occupy identical positions.



(11)

The appropriate equations for the hydrogen exchange reactions are as follows:-

$$H_3O^{+} + ArD \overset{\text{fast}}{\rightleftharpoons} ArHD^{+} + H_2O \quad \ldots\ldots(i)$$

$$ArHD^{+} \overset{\text{slow}}{\rightleftharpoons} ArH + D^{+} \quad \ldots\ldots\ldots\ldots(ii)$$

$$D^{+} + H_2O \overset{\text{fast}}{\rightleftharpoons} DOH_2^{+} \quad \ldots\ldots\ldots\ldots\ldots\ldots(iii)$$

The attachment of a proton (step i) is fast and involves a molecule of water. The removal of the deuteron (step ii) is a slow rate-determining step and involves no molecule of water. If the two isotopic atoms occupy equivalent positions in the intermediate, then their attachment and removal must take place in identical steps. They suggested therefore that SH$^+$ must be identified with a conjugate acid of the aromatic molecule, and must have a structure such that the added proton does not occupy an equivalent position to the deuterium to be replaced. Three possible structures were considered:-

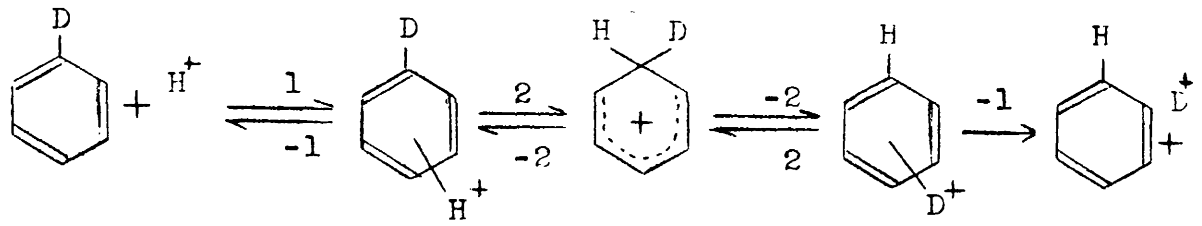
(i) linked less tightly than the deuterium to the carbon atom at which substitution occurs.

(ii) attached elsewhere in the same molecule.

(iii) attached to a different molecule to the one undergoing exchange.

The intermolecular mechanism (iii) implies that the entity ØH$^+$ (where Ø is an unspecified composition of a deuterated and protonated phenol molecule) is in preference to H$_3$O$^+$, responsible for most of the reaction converting RD into the conjugate acid RDH$^+$. Conversely, Ø would be more effective than H$_2$O in removing the proton from RDH$^+$. They rejected this mechanism since it is known that H$_2$O is a stronger base than Ø.

Gold and Satchell considered therefore, that the mechanism must be intramolecular and formulated it thus:-



RD c (111) c' RH ..(3)

This mechanism involves a rapid, reversible, loose attachment of a proton to the deuterated molecule to give a low concentration intermediate (c). This undergoes a slow rearrangement to the low concentration intermediate (c'). (c) and (c') were said to have the structure of outer-complexes, intermediate (III) the structure of an inner complex; they quote the work of Brown and Brady[15] in support of these structures. They discussed the mechanism put forward by de la Mare, Hughes, Ingold and Pocker[16] for the hydration of olefins, which envisaged a rapid equilibrium between acidic species and protons in a "freer form". The "freer" protons then combine with the substrate in the rate determing step. Although their experimental results were compatible with any form of "freer" proton, Gold and Satchell advanced strong arguments against this mechanism.

The rates of deuterium exchange in *p*-cresol with hydrochloric acid and sulphuric acid, and in *p*-chlorophenol with sulphuric acid and with phosphoric acid have also been measured by Gold and Satchell.[17] They found that although, in each case, the rate of exchange followed the acidity function, the slope of logk against $\underline{H}o$ varied for the same compound in the two different acids. They attributed this to the variation of the salting-out effect in the different media.

Satchell[18] observed that in the exchange with *ortho*- and *para*- deuterated anisoles in acetic acid-sulphuric acid there was a linear correlation of the logarithm of the exchange rate with the *H*o acidity function. He concluded that the exchange mechanism was identical with that in aqueous sulphuric acid.

Gold and Satchell[19] compared directly the rates of exchange at the nuclear positions in toluene with that of benzene. The partial rate factors for *ortho*-, *meta*-, and *para*-positions of toluene were found to be 83, 1.9, 83, these figures agreeing well with those obtained by Olsson and Melander. A linear plot of log(rate of exchange) against *H*o was again obtained.

Mackor, Smit and Van der Waals[20] measured the rates of dedeuteration of a number of compounds in a trifluoroacetic acid - sulphuric acid medium. These included $[^{2}H]$benzene, [*o*-^{2}H]toluene, [*m*-^{2}H]toluene, [*p*-^{2}H]toluene, and [*p*-^{2}H]-t-butylbenzene. A plot of the logarithm of exchange rates against *H*o acidity function for the acidic media revealed straight line correlations of slope 1.0 for benzene and [*p*-^{2}H]toluene. Partial rate factors of 234, 3.16 and 347 for the *ortho*-, *meta*-, and *para*-position of toluene and 363 for the *para*-position of t-butylbenzene were obtained. Some interesting points arose from this work:-

1) These partial rate factors for the several positions of toluene differ greatly from those obtained by Gold and Satchell for hydrogen exchange reactions in the aqueous sulphuric acid medium.

2) The ratio of the reactivities of the *ortho*- and *para*-positions of toluene differ from those obtained by Melander

and by Gold and Satchell in aqueous sulphuric acid. Mackor *et al.* considered these differences to be attributed to changes in the medium or experimental errors.

3) The aromatic ring is activated in dedeuteration by the *para*-t-butyl group to a greater extent than by the *para*-methyl group, indicating that hyperconjugation does not play an important part in the activating mechanism in trifluoroacetic acid.

4) Mackor suggested that the substituent effects were due to entropy effects and not through the activation energy, but Eaborn and Deans[64] critisized this and believe it to be incorrect.

Tiers[21] measured, by a competition method, the rates of dedeuteration of the *ortho*- and *para*-positions of toluene by aqueous perchloric acid (70.8%), and also by heptafluorobutyric acid. He observed that the *ortho/para* reactivity ratio in the former medium was 1.09, whilst in the later it was 0.4. He considered the higher ratio was an unambiguous example of +I inductive activation but pointed out that the same effect could be attributed to hyperconjugation, as argued by the molecular orbital treatment of Crawford.[22] Tiers also suggested that the reduction in *ortho/para* ratio on going to heptafluorobutyric acid is a consequence of the steric requirement of the bulky acid molecule.

Lauer *et al.*[23] carried out the deuteration of toluene in a mixture of trifluoroacetic acid and deuterium oxide. The partial rate factors were fo = 250, fm = 4, and fp = 420. The factors for the *ortho*- and *para*-positions and the *ortho/para* rate ratio are in close agreement with the results obtained by Smit, Mackor, and Van der Waals.

Lauer *et al*.[24] also measured the deuteration of t-butylbenzene in the same medium and obtained the following partial rate factors:

fo = 198, fm = 7, fp = 490.

which are again in agreement with those of Smit, Mackor, and Var der Waals. Further, the similarity in the *ortho/para* rate ratio for toluene and t-butylbenzene indicated that the steric requirement of the attacking entity is small, and therefore the fact that the *ortho/para* ratio for toluene <1 may not be due to a steric effect.

The rates of detritiation of $\left[{}^{3}H\right]$benzene, *m*- $\left[{}^{3}H\right]$toluene and *p*- $\left[{}^{3}H\right]$toluene in 68.80wt% sulphuric acid at 25° were measured by Eaborn and Taylor.[25] In 73-75wt% they obtained rate factors of fp= 250 and fm= 5.0; these factors differed from those of Gold and Satchell for dedeuteration in 68wt% (viz. fp = 83 and fm = 1.9). Eaborn and Taylor pointed out that their rate factors were based on direct comparison of the three compounds in the same acid, whereas Gold and Satchell compared rates for *m*- and *p*-$\left[{}^{2}H\right]$toluene with those derived for $\left[{}^{2}H\right]$benzene by interpolation. The ratio fp/fm for detritiation in 73-75% acid (viz.,50), agrees satisfactorily with that, (viz.,44) reported by Gold and Satchell, and with those (viz., 46±3 and 41±2) reported by

Olsson and Melander[12] for dedeuteration and detritiation in 80.8%sulphuric acid under heterogeneous conditions.

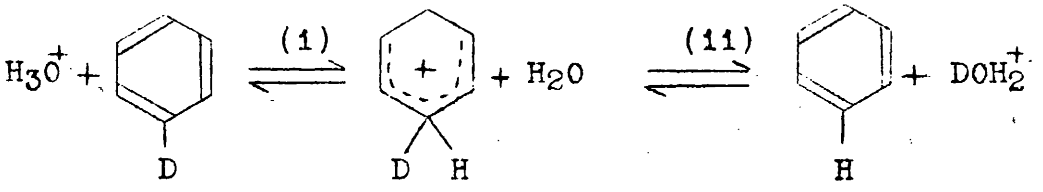
Eaborn and Taylor attributed the apparent disagreement between their value for benzene and that of Gold and Satchell to experimental error. They believed their value to be correct because:-

i) they had checked their work and investigated all the possible errors, because of the disagreement with the dedeuteration results.

ii) the dependence of the rate of detritiation of $[^{3}H]$ benzene on acid concentration, while being different from that reported by Gold and Satchell, was very similar to that for *m*- $[^{2}H]$toluene.

iii) for many electrophilic substitutions, Stock and Brown[26] noted that the ratio log fp/logfm lies between 3.18 and 4.72. Their figures correspond to a ratio of 3.42 and Gold and Satchell's to 6.88. Rate factors determined for detritiation in acetic acid - water - sulphuric acid[27] correspond to a ratio of 3.65, and those for dedeuteration in aqueous trifluoroacetic acid with a ratio of 4.3±0.8.

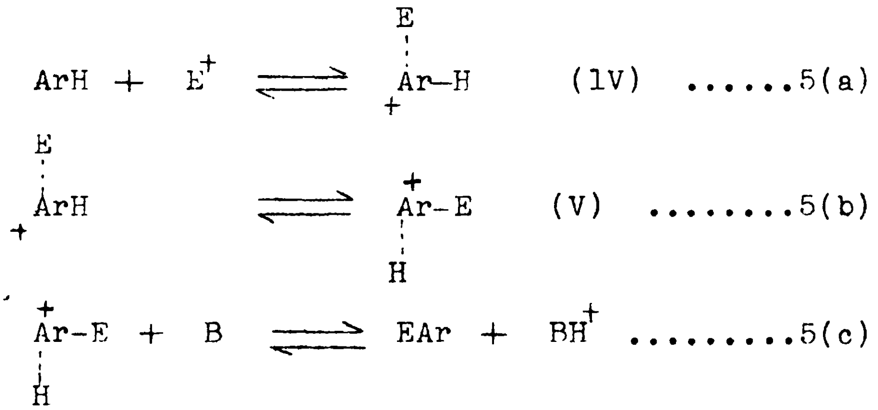
Eaborn and Taylor put forward a mechanism different from Gold and Satchell's :-



..(4)

Both of steps (i) and (ii) must contribute to the determination of the overall rate in hydrogen exchange. Gold and Satchell reject this mechanism since both transition states of steps (i) and (ii) would involve a solvent molecule (or entity A of the acid HA) partly bound covalently. They considered this to be ruled out by their observation of a linear dependence of the logarithm of the rate constants for dedeuteration on the Hammett acidity function, H_o. Eaborn and Taylor were unable to accept that there is any significant correlation between rate of exchange and H_o. The plot of log rate against H_o for the detritiation of benzene, leads to a curve of slope varying from *ca* -1.5 to *ca* -2.2; the plot for *m*-$[^3H]$ toluene is very similar. They considered Gold and Satchell's results for dedeuteration of benzene could be presented as a straight line of slope -1.5 or as a curve whose slope varied from *ca*.-1.2 to *ca*-1.7. The plots were found to have different slopes if the values of H_o employed were those selected by Gold and Satchell from the Hammett and Deyrup[28] data, rather than those selected by Long and Paul[29] from the previous data. For some other aromatic compounds, particularly phenols, more satisfactory log k_d-H_o correlations appear to be[30,13,17] obtained. Eaborn and Taylor, however, pointed out there is considerable uncertainty about the precise mechanistic significance of linear log k- H_o plots even when these have unit slopes.[31] It is their opinion that there is no firm ground for the belief that such plots exclude the possibility of covalent participation of a solvent molecule in the rate-determing step. In support of their mechanism they quote the work of Kresge and Chiang[32] who demonstrated that detritiation of 1,3,5-trimethoxy$[^{3}H]$benzene by weak acids is general acid catalysed, so that proton transfer from catalysing acid to substrate is involved in the rate-determing step; they consider it unlikely that a different mechanism operates for less reactive aromatic compounds in concentrated strong acids.

Eaborn and Taylor considered the general mechanism (5) for electrophilic substitution suggested by R.D.Brown,[33] in which σ-complexes (Wheland intermediates), of type (V1) are not involved.

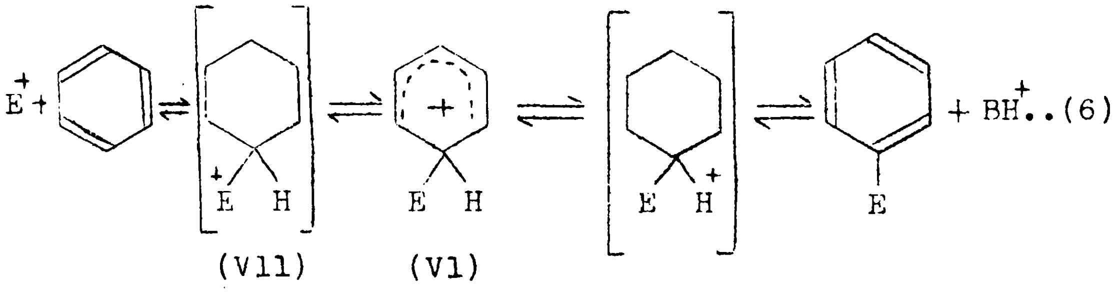


$$\mathrm{ArH} + E^{+} \rightleftharpoons \underset{+}{\overset{\overset{E}{\vdots}}{\mathrm{Ar{-}H}}} \qquad (\mathrm{1V}) \quad ......5(a)$$

$$\underset{+}{\overset{\overset{E}{\vdots}}{\mathrm{ArH}}} \rightleftharpoons \underset{\underset{H}{\vdots}}{\overset{+}{\mathrm{Ar{-}E}}} \qquad (\mathrm{V}) \quad ....5(b)$$

$$\underset{\underset{H}{\vdots}}{\overset{+}{\mathrm{Ar{-}E}}} + B \rightleftharpoons \mathrm{EAr} + \mathrm{BH}^{+} \quad ....5(c)$$

The intermediates (1V) and (V) are charge-transfer complexes, E^{+} is an electrophil and B is a base



(V11) (V1)

Any one of the steps (a),(b) or (c) may be rate-determining, and the structure (Vl) is considered to represent a point of maximum potential energy between the complexes lV and V.

R.D.Brown lists six features of electrophilic aromatic substitution which have to be taken into account in devising a mechanism. All but one of these are, in the opinion of Eaborn and Taylor, equally consistent with their mechanism (6), (the entities in brackets are transition states). The one exception is Gold and Satchell's conclusion that a linear dependence of logk on $\underline{H}o$ rules out the possibility of a solvent molecule's being covalently involved in the transition state in aromatic hydrogen exchange. Eaborn and Taylor stress that the rate-determining transition state does not coincide in structure with the intermediate (Vl), but is removed to a greater or lesser extent from it towards reactants or products. They consider it difficult to see how rate studies can distinguish between the two theories.

Kresge and Chiang[34] present evidence in support of the mechanism of Eaborn and Taylor. The loss of tritium from 1,3,5-trimethoxy-$\left[2-{}^{2}H\right]$benzene is an "h_o-dependent" reaction in the usual sense. The interpretation of this observation, that the transition state is a fully protonated species in which the transfered proton has lost all specific interaction with the conjugate base of the catalysing acid, is based on the assumption that the substrate is a Hammett base, i.e.,that it's degree of protonation in concentrated aqueous acid is governed by h_o. They showed that this assumption was false for 1,3,5-trimethoxybenzene in aqueous perchloric acid, i.e., the degree of protonation is proportional not to h_o, but to the different acidity function $h_R^{\prime}$ [35].

If the transition state for exchange in 1,3,5-trimethoxybenzene was a fully protonated species unassociated with the conjugate base of the catalysing acid, the rate of exchange would be proportional to $h_R^{\prime}$ ($h_R^{\prime} = h_R.a_{H_2O}$). Since in the range of acid concentration, the empirical relation $h_R^{\prime} = (h_o)^2$ holds to a good degree of approximation, this would appear as a linear plot of log k against $\underline{H}o$ of slope 2.0. On the other hand, had proton transfer not yet occurred to any appreciable extent at the transition state, composed of an aromatic molecule and a nearly intact hydronium ion, then a rate dependence on c_{H_3O} would be observed. This would give an $\underline{H}o$ plot of considerable less than slope 1.0. Kresge and Chiang consider the mechanism of this reaction to be the orthodox one for electrophilic substitution and the actual situation at the transition state must be intermediate between no transfer and complete transfer of the proton. The observed acidity-dependence is intermediate between that predicted for these extremes. They consider that results obtained with other aromatic substrates (log k - $\underline{H}o$ for phenol and arylethers with slopes 1.0, ranging to 1.5 and 2.0 for the hydrocarbons toluene and benzene) are consistent with a single mechanism for all aromatic hydrogen exchange, similiar to that established for trimethoxybenzene, but with varying degrees of proton transfer at the transition state. They consider it is also consistent with a single mechanism, but different acidity-dependencies, for the degree of protonation of different aromatic compounds.

General acid catalysis has also been observed by Colapietro and Long[65] for the deuterium exchange of azulene-$\left[{}^{2}H\right]$(1,3) in water as the solvent.

In a recent publication, Gold[37] suggests that the theory of Kresge and Chiang does not explain the absence of even a vague connection between the velocity of hydrogen exchange and the chemical composition of an acidic medium (i.e., the concentration of H_3O^+, H_2SO_4, $CH_3CO_2H_2^+$, in strongly acidic solutions of water and acetic acid.). In the view of Gold this is the only salient experimental result requiring a mechanistic explanation. Gold poses the question, "how can different and additive contributions from catalysing Bronsted acids (i.e.,general acid catalysis) be observed in weakly acidic buffer solutions but not in strongly acidic media ?".

He proposes that the two kinds of solvent system considered differ in the transferability of protons, i.e., the frequency with which protons are exchanged between their possible sites on different acid molecules. Data available[38] on the speed of proton transfers suggests that the reaction between sulphuric acid and water, or that between the hydronium ion and water, is several powers of ten times faster than the proton transfer from the acetic acid molecule to water. Gold suggests that general acid catalysis is observed in a process when the proton remains attached to a molecule of the catalysing acid, HA, for a time which is long compared with some time interval characteristic of the molecular motions during the formation of the transition state; the transition state will have the definite composition (ArH.HA). An example of this situation is the acetic acid catalysed aromatic hydrogen exchange in dilute aqueous solution. On the other hand, in a strongly acid medium, supposing the proton switch to be fast compared with other rearrangements of atoms during the formation of the transition state, the origin of the proton taken up by the substrate will be "blurred." The transition state can then be represented by a protonated substrate in association with several molecules of base between which the proton switch can occur. The concentration of the transition state may then be controlled by the thermodynamic availability of protons in the system (i.e., by an acidity function), and will not bear a simple relationship to a concentration of catalysing acids.

Gold pointed out that in formulating a mechanism for proton transfer the difference in mass between the proton and other entities involved in the process must be considered. In aromatic hydrogen exchange, which involves proton transfer from strongly acidic solvent systems to organic substrates, the potential proton donors build up a hydrogen-bonded network which permits very rapid and frequent proton switches amongst its members[39]. In the transfer of a proton from this system to an aromatic molecule, the motions of heavy particles to be considered are :-

i) the deformation of the aromatic substrate,

ii) the relative adjustment of the solvent network and the aromatic molecule for solvation of the electric charge on the protonated substrate,

iii) a rotation or translation to attain a disposition which places the aromatic molecule in suitable relation to the network for proton transfer to take place.

On these considerations a proton will become attached to the aromatic molecule as the motions produce an optimum configuration. The immediate origin of the proton is the neighbouring member of the solvent network, but the chemical identity of this molecule is unimportant if a replacement proton can be rapidly transfered to it by chain conduction across hydrogen bridges[39]. Weak acids, however, retain their chemical identity during the whole proton transfer and, therefore, form transition states of indisputable composition.

Eaborn and Taylor[40] measured the rates of detritiation of $[^3H]$benzene, o-, m, and p-tritio- toluene and t-butylbenzene in one or more of the following solvents; aqueous sulphuric acid, acetic acid containing aqueous sulphuric acid, and trifluoroacetic acid containing aqueous sulphuric acid. The main features of their results were:-

i) the spread of rates varies markedly with the medium, probably increasing as the solvating power of the media decreases.

ii) the activating influence of p-methyl and p-t-butyl groups can follow either the Baker-Nathan order Me > Bu^t, or the inductive order Bu^t > Me, depending on the solvent.

iii) for meta-substituents the activation order in all media is clearly Bu^t > Me.

They do not attempt to explain completely the variation in the spread of rates as the medium is changed because so many factors vary together, but they do indicate what results are expected if one property of the medium is changed independently of the others. The results can be explained by use of the concept of hyperconjugation. The greater inductive effect of the t-butyl group results in an inductive order for the meta-group, but hyperconjugation from the methyl groups brings the overall effects of the para-groups near to equality, and allows the p-methyl group to have a greater activating effect than the p-butyl group in some media. The change from a Baker-Nathan order to an inductive order as the dielectric constant of the medium is lowered may simply reflect the increase in the direct-field component of the inductive effect.

Eaborn and Taylor note the objections to relying on C-H hyperconjugation; spectral transition energies indicating that electron release by t-butyl group is about equal to or rather greater than that by the methyl group,[41] and this has led to suggestions that the Baker-Nathan order in chemical reactions results from steric hindrance to solvation by the t-butyl group of electron deficient centres in the transition state.[41,42] They regard it unsatisfactory when considering chemical reactivities to regard the t-butyl and methyl groups as having similar electron-releasing properties, particularly in view of the greater activation of the meta-position by a t-butyl group. Explaining the results in terms of steric hindrance to solvation meets with difficulties since it has to be assumed that there is negligeable steric hindrance by the meta- but considerable hindrance by the p-t-butyl group. The change in the activation order $p\text{-Me} > p\text{-Bu}^t$ to $p\text{-Me} < p\text{-Bu}^t$ could then follow as the medium is changed in the direction of decreasing solvating power, but they regard this as unsatisfactory.

They conclude that both hyperconjugation and steric effects operate to determine the effects of p-methyl and p-t-butyl groups in detritiation.

3. Substituent effects in aromatic hydrogen exchange.

The rates of detritiation of mono tritio-benzene and -halogenobenzenes in trifluoroacetic acid containing either aqueous sulphuric acid or aqueous perchloric acid were measured by Eaborn and Taylor.[43] They obtained accurate rate factors for detritiation ortho- and para- to the halogens along with approximate values for the reaction meta- to the halogens. The results are shown in Table 1 as partial rate factors (f).

Table 1

Detritiation of $X.C_6H_4[^3H]$ compounds at 25°.

	$CF_3CO_2H-H_2O-H_2SO_4$	$CF_3CO_2H-H_2O-HClO_4$	$CF_3CO_2H-H_2O-HClO_4$
X	*f*	*f*	*f*
H	1	1	1
p-F	1.73	1.79	-
p-Cl	0.127	0.161	-
p-Br	0.072	0.098	0.085
p-I	0.0865	0.112	-
o-F	-	0.136	0.126
o-Cl	-	0.035	0.036
o-Br	-	0.027	0.027
o-I	-	0.043	0.041
m-F	-	-	0.002
m-Cl	0.002	-	0.001
m-Br	-	-	0.001
m-I	-	-	0.003

The composition of the media in Table 1 are given in the tables of classified media on pages 31-35.

The main features of the results were:-

i) The spread of rates were dependent upon the medium in the manner previously noted with aromatic compounds.[25,40] A plot of log *f* in one medium against log *f* in either of the other media was a straight line.

ii) Fluorine activates the *para*-position in detritiation as it does in molecular bromination and chlorination,[44] the

+T effect outweighing the -I effect. In many reactions fluorine deactivates but the activation in detritiation is consistent with the observation that the demand on the electromeric effect of substituents is large in this reaction.[54] Additional results for the p-F atom, are that it activates 2.18 times in 76.29wt% aqueous sulphuric acid, 1.7 times in CF_3CO_2H (92.04) - H_2O (5.45) - $HClO_4$ (2.51) and 2.4 times in CF_3CO_2H (85.08) - H_2O (6.42) - H_2SO_4 (8.50).

iii) The deactivation order p-Cl $<$ p-I $<$ p-Br applies in detritiation as in molecular bromination in nitromethane.[45]

iv) Deactivation by the *ortho*-substituents is in the order F $<$ I $<$ Cl $<$ Br . The reduction in rate on moving the halogen from the *para*- to the *ortho*- position decreases in the order F $>$ Cl $>$ Br $>$ I , which is consistent with increased importance of the -I effect at the *ortho*-position. It is noteworthy that the importance of the +T effect for the o-F substituent is still sufficient to make this atom less deactivatig than a p-Br substituent.

v) A plot of log *f* for detritiation of $X.C_6H_4[^3H]$ compounds in CF_3CO_2H(96.77) - H_2O(0.82) - $HClO_4$(2.41) against log k_{rel} for hydrolysis of $X.C_6H_4.CMe_2Cl$ compounds in 90% aqueous acetone at 25°[46] is a good straight line for the *meta*- and *para*- halogens (that is the substituent effects in these detritiations are related to the σ^+ constants of Brown[47]). A similiar relation also applies for the *ortho*- halogens, but the appropriate line lies well away from that for the *meta*- and *para*- substituents.

The rates of detritiation *meta*- to the halogens could be measured only very roughly because of side-reactions but Eaborn and Taylor reached the conclusion that *meta*-halogens deactivate markedly more than *ortho*- and *para*-halogens, as in other electrophilic aromatic substitutions.

Olsson[48] obtained rates of exchange of 0.00186, 0.252, 0.0088 and 0.288 for deuterium exchange and 0.00121, 0.144, 0.00317 and 0.118 for tritium exchange for benzene and the *o*, *m*, and *p*-positions in toluene in 80.66% aqueous acid in heterogeneous solution.

The rates of dedeuteration of a number of polyalkylbenzenes in mixtures of deuterium oxide and trifluoroacetic acid have been measured.[49] The effects of methyl groups in compounds such as toluene, xylene, hemimellitene, and durene were found to be additive, thus providing further evidence for the small steric requirement of deuteration in trifluoroacetic acid. Similar work[50] on the reactivities of three polyiso-propylbenzenes relative to the corresponding polymethylbenzene gave the figures:-

meta-di-isopropylbenzene : xylene = 1.04;

para-di-isopropylbenzene : xylene = 2.16 and 1,3,5-tri-isopropylbenzene : mesitylene = 0.27.

Partial rate factors were obtained for *o*, *m*, and *p*-isopropylbenzene:- $f_o = 250 \pm 10$, $f_m = 6.16 \pm 0.20$, $f_p = 483 \pm 21$ and also ethylbenzene, $m_f = 4.52$.

Shatenshtein[51] investigated the deuteration of *ortho*- and *para*- $[^2H]$ toluenes in liquid hydrogen halides; his results are given in Table 11.

Table 11

Comparison of rate constants (sec^{-1}) of deuterium exchange with hydrogen halides at 25°.

	HI	HBr	HF
[o-^{2}H] toluene	2×10^{-6}	5×10^{-5}	2×10^{-2}
[p-^{2}H] toluene	4×10^{-6}	2×10^{-4}	-

Previously, earlier work of Shatenshtein[52] on the deuteration of toluene, ethylbenzene, t-butyl- and n-butylbenzene in liquid hydrogen bromide (containing 1-5% deuterium bromide) had indicated, that for all the monoalkylbenzenes, the partial rate factors are in the ratio:-

$K_p : K_o : K_m = 6000 : 1000 : 5$, with benzene = 1.

Qualitative studies on m-xylene, mesitylene, durene and pentamethylbenzene showed there was no exchange of the hydrogens of the alkyl groups.

Deuterium-hydrogen exchange of phenol, anisole and ethoxybenzene in liquid "deuterium bromide" at 25° was also studied by Shatenshtein[53]; exchange with these compounds took place rapidly in the ortho- and para- positions.

4. Hydrogen exchange in polynuclear and heterocyclic compounds.

The rates of detritiation of (2-, 3- and 4-^{3}H) biphenyl and of (α- and β-^{3}H) naphthalene in trifluoroacetic acid containing aqueous sulphuric acid or aqueous perchloric acid were measured by Eaborn and Taylor.[54] The results are shown in Table 111 as partial rate factors f, composition of the media is given in mole%.

Table 111

Detritiation at 25°

Compound	CF_3CO_2H - H_2O - H_2SO_4 (95.31):(2.21):(2.48)	CF_3CO_2H - H_2O - $HClO_4$ (92.04):(5.45):(2.51)
	f	f
[^{3}H] benzene	1	1
[p-^{3}H] toluene	702	313
[2-^{3}H] biphenyl	133	52
[3-^{3}H] biphenyl	-	0.68
[4-^{3}H] biphenyl	143	52
[α-^{3}H] naphthalene	1079	370
[β-^{3}H] naphthalene	127	62

The spread of rates varied markedly with the medium as with alkylbenzenes.[27,25,40] The 2- and 4- positions of biphenyl were equally reactive, but the α-position of naphthalene was considerably more activated than the β-position in agreement with calculations.[55,56] The values of the ratio of $\left(\frac{\log f_p^{Me}}{\log f_p^{Ph}}\right)$ showed a general tendency to fall from reaction to reaction as f_p^{Me} rises,[57] probably as the electron-demand rises and calls forth increasingly the +E effect of the p-Ph group.[57,58] They concluded that, in electrophilic aromatic substitution, no single substituent constant can satisfactorily represent the effect of a p-Ph or the

3,4-C_4H_4 group.

Deuteration of a number of polynuclear compounds have been studied by Dallinga, Verrijn Stuart, Smit and Mackor.[55] They employed a mixture of trifluoroacetic acid (deuterium content 96%), sulphuric acid (100%) and carbon tetrachloride. The partial rate factors for the <u>ortho</u>-, <u>meta</u>-, and <u>para</u>-position of biphenyl were 37.2, 0.3, 37.2 respectively and the α- and β- positions in naphthalene were 178, 23.4 respectively; these results are in good agreement with those of Eaborn and Taylor.

Rice[59] studied deuterium-exchange of a number of polynuclear hydrocarbons. The dedeuteration of biphenyl isomers in aqueous trifluoroacetic acid gave partial rate factors for the 2-, 3-, and 4-positions of 82, 0.49, and 130 respectively. Similarly the partial rate factors for the 2'-, 3'- and 4'- positions of 4-methylbiphenyl were found to be 360, 3.2 and 490. He determined the initial rates of dedeuteration of a number of hydrocarbons in trifluoroacetic acid and deuterium oxide. In the series of compounds toluene, biphenylmethane, triphenylmethane, tetraphenylmethane and benzene, the relative reactivities per aromatic ring were found to be 158 ; 37 : 11 : 7 : 1.

The following rate constants for the dedeuteration of biphenyl and naphthalene , compounds in liquid hydrogen iodide and liquid hydrogen bromide have been obtained by Shatenshtein,[51,52] and are shown in Table lV.

Table lV

Rate constants for deuterium exchange at 25° in liquid hydrogen halides.

	HI	HBr
[o-^{2}H] biphenyl	1×10^{-6}	3×10^{-5}
[p-^{2}H] biphenyl	4×10^{-6}	1×10^{-4}
[α-^{2}H] naphthalene	5×10^{-6}	2×10^{-3}
[β-^{2}H] naphthalene	-	6×10^{-5}

Shatenshtein[52] also found partial rate factors for the dedeuteration of p-terphenyl in liquid HBr, 6×10^{-5} for the *ortho*- and 7×10^{-4} for the *para*-positions. These figures were calculated from experimental data assuming no exchange in the *meta*- position. From initial rates of deuteration, partial rate factors were obtained of 8×10^{-6} for the *para*- position of triphenylmethane and 6×10^{-5} for the *para*- position of diphenylmethane.

Shatenshtein *et al.*[60] have also studied hydrogen-deuterium exchange of other polynuclear compounds in liquid hydrogen bromide, *viz.*, naphthalene, anthracene, phenanthrene, pyrene and chrysene, and also the deuteration of substituted naphthalenes in liquid deuterium bromide.[61] Results obtained by Shatenshtein[62] on the deuteration of phenylated alkanes in liquid deuterium bromide indicated that phenyl groups, separated by aliphatic carbon atoms exert an effect on each other.

Liquid deuterium fluoride has also been used by Shatenshtein[63] as a deuterating medium. This was chosen as a solvent because of it's high dielectric constant, and rates of exchange in liquid deuterium fluoride are much greater than in liquid deuterium bromide (i.e., 10^4 for benzene).

The detritiation of $[2-{}^3H]$ thiophen and $[3-{}^3H]$ thiophen has been studied in 59.4% aqueous sulphuric acid at 25°. The compounds were prepared by shaking thiophen[66] with suitable concentrations of tritiated sulphuric acid. The rate of detritiation of the 2- position was found to be 955 ± 140 times faster than the 3- position.

5. Use of catalysts in hydrogen exchange.

Aluminium tribromide was used as a catalyst in the deuteration of aromatic compounds in liquid deuterium bromide.[53] The rate of deuterium-exchange was greatly increased in many cases, but interesting results were obtained with some aromatic amines. With no catalyst, rapid exchange took place at the ortho- and para- hydrogen atoms, with diphenylamine slow exchange of the ortho- and para- hydrogens occurred, but no exchange occurred with dimethylaniline. This difference in behaviour was ascribed to the dissimilar basicity of the compounds, they decrease in the order:-

dimethylaniline > diphenylamine > triphenylamine.

This is clearly shown by the formation of a salt with dimethylaniline but not with triphenylamine. The absence of exchange in dimethylaniline is, therefore, explained by lack of conjugation into the ring of the lone pair of electrons, which are taken up in salt formation. Triphenylamine forms no salt so that π-conjugation of the lone pair can take place. On addition of aluminium tribromide to the solution, the exchange rate of diphenylamine is actually decreased. This is explained by the formation of a salt, due to the increased acidity of the solution:-

$$(C_6H_5)_3\overset{+}{N}D\ Al\overset{-}{Br_4}$$

and the absence of any π-conjugation from the lone pair on the nitrogen.

The catalysis of deuterium exchange in liquid hydrogen iodide by iodine has also been studied by Shatenshtein.[51] The exchange rate of deuterated biphenyl compounds was found to increase proportionally with the concentration of iodine. The electrical conductivity of hydrogen iodide did not increase appreciably with the solution of iodine, or with the addition of mesitylene or hexamethylbenzene to the solution, indicating the absence of appreciable ionisation in the system. Mesitylene and a solution of iodine in hydrogen iodide had a red-violet colour and hexamethylbenzene had a red-brown colour. This was explained by the probable formation of a molecular compound between the hydrocarbon and iodine.

$$ArH + I_2 \rightleftharpoons ArH.I_2$$

Shatenshtein considered the catalytic activity of iodine in deuterium exchange to be due to the equilibrium:-

$$ArD + HI + I_2 \rightleftharpoons ArD.....HI.I_2$$

(he did not exclude the possibility that instead of ArD it's complex with iodine, ArD..I_2 is involved). This equilibrium is analogous to :-

$$ArD + HHal + AlHal_3 \rightleftharpoons ArD + \overset{\delta+}{H}.AlHal_4^{\delta-}$$

in which systems isotopic exchange occurs. The efficiency of the catalyst was thought to depend upon the degree which it polarises the H-Hal bond. Further support for this explanation was obtained by comparing electrophilic bromination, which is catalysed by metal halides and iodine. ($AlBr_3 > FeBr > I_2$)

$$ArH + Br_2 + I_2 \rightleftharpoons ArH.....\overset{\delta+}{Br}-\overset{\delta-}{Br}.I_2$$

The positively charged bromine reacts with the hydrocarbon at a position of high electron density. Therefore the iodine acts by facilitating the approach of a proton to the hydrocarbon.

Shatenshtein[63] has also shown that BF_3 added to liquid hydrogen fluoride accelerates the rate of hydrogen-deuterium exchange.

The substituent effects measured prior to the present work are summarised, classified under types of media, in the next five pages.

AQUEOUS SULPHURIC ACID

Composition	Exchange	Compound	Partial rate factor			Ref.
(mole%)			$\underline{f}_o$	$\underline{f}_m$	$\underline{f}_p$	
80.8%	tritium	toluene	47	1.00	41^a	12
80.8%	tritium	"	51	1.00	46^a	"
68.0%	deuterium	"	83	1.9	83	19
73.24%	tritium	"	-	5.0	254	25
75.30%	tritium	"	-	5.0	253	"
71.34%	tritium	"	250	5.0	250	40
71.34%	tritium	t-butyl-benzene	170	-	180	"
			2-	3-		
59.4%	tritium	thiophen	955	1.0^a		66

a- relative rates

ACETIC ACID - SULPHURIC ACID - WATER

Composition	Exchange	Compound	Partial rate factor			Ref.
(mole%)			$\underline{f}_o$	$\underline{f}_m$	$\underline{f}_p$	
CH_3CO_2H (26.0) H_2SO_4 (40.0) H_2O (34.0)	tritium	toluene	305	5.0	313	40
	tritium	t-butyl-benzene	-	9.3	230	"

SULPHURIC ACID - TRIFLUOROACETIC ACID - WATER

Composition (mole%)	Exchange	Compound	Partial rate factors			Ref.
			f_o	f_m	f_p	
CF_3CO_2H	deuterium	toluene	234	3.16	347	20
H_2SO_4(0.25m)	"	t-butylbenzene	-	-	363	"
CF_3CO_2H	tritium	toluene	541	9.2	702	40
(95.31) H_2SO_4	"	t-butylbenzene	-	32	863	"
((2.48) H_2O	tritium	biphenyl	133	-	143	54
(2.21)			f_α	f_β		
	tritium	naphthalene	1079	127		54

Detritiation of $X.C_6H_4[^3H]$ compounds

Composition (mole%)	Exchange	X	Partial rate factor of position relative to X			Ref.
			o	m	p	
CF_3CO_2H	tritium	F	-	-	1.73	43
(83.40) H_2SO_4	"	Cl	-	.002	0.127	"
	"	Br	-	-	0.072	"
(14.62) H_2O	"	I	-	-	0.00865	"
((1.98)						

TRIFLUOROACETIC ACID - PERCHLORIC ACID - WATER

Composition (mole%)	Exchange	Compound	Partial rate factors			Ref.
			f_o	f_m	f_p	
CF_3CO_2H (92.04) $HClO_4$ (2.51) H_2O (5.45)	tritium	toluene	330	7.2	313	40
	tritium	t-butylbenzene	393	23.7	387	40
	tritium	biphenyl	52	0.68	52	54
			f_α	f_β		
	tritium	naphthalene	370	62		54

Detritiation of $X.C_6H_4[^3H]$ compounds

Composition (mole%)	Exchange	X	Partial rate factors of position relative to X			Ref.
			o	m	p	
CF_3CO_2H (96.77) $HClO_4$ (2.41) H_2O (0.82)	tritium	F	0.136	-	1.79	43
	tritium	Cl	0.035	-	0.161	43
	tritium	Br	0.027	-	0.098	43
	tritium	I	0.043	-	0.112	43
CF_3CO_2H (89.50) $HClO_4$ (5.95) H_2O (4.55)	tritium	F	0.126	0.002	-	43
	tritium	Cl	0.036	0.001	-	43
	tritium	Br	0.027	0.001	0.085	43
	tritium	I	0.041	0.003	-	43

AQUEOUS TRIFLUOROACETIC ACID.

Exchange	Compound	Partial rate factors			Ref.
		f_o	f_m	f_p	
deuterium	isopropylbenzene	250	6.16	483	50
deuterium	ethylbenzene	-	4.52	-	50
deuterium	biphenyl	82	0.49	130	59
deuterium	toluene	250	4	420	23
deuterium	t-butylbenzene	198	7	490	24
		f_2	f_3	f_4	
deuterium	4'-methylbiphenyl	360	3.2	490	59

AQUEOUS PERCHLORIC ACID.

Composition	Exchange	Compound	Relative Reactivities			Ref.
			o	*m*	*p*	
70.8wt.%	deuterium	toluene	1.09	0.065	1.00	21

ANHYDROUS HEPTAFLUOROBUTYRIC ACID

Exchange	Compound	Relative Reactivities			Ref.
		o	*m*	*p*	
deuterium	toluene	0.4	0.065	1.00	21

TRIFLUOROACETIC ACID-SULPHURIC ACID-CARBON TETRACHLORIDE

Exchange	Compound	Partial Rate factors			Ref.
		f_o	f_m	f_p	
deuterium	biphenyl	37.2	0.3	37.2	55
			f_α	f_β	
deuterium	naphthalene		178	23.4	55

LIQUID HYDROGEN HALIDES

Hydrogen Halide	Exchange	Compound	Rate constants (sec.$^{-1}$)		Ref.
			2	4	
HI	deuterium	biphenyl	1×10^{-6}	4×10^{-6}	52
HBr	deuterium	biphenyl	3×10^{-5}	1×10^{-4}	52
HI	deuterium	toluene	2×10^{-6}	4×10^{-6}	51
HBr	deuterium	toluene	5×10^{-5}	2×10^{-4}	51
HF	deuterium	toluene	2×10^{-2}	-	51
HBr	deuterium	*p*-terphenyl	6×10^{-5}	7×10^{-4}	52
HBr	deuterium	triphenyl-methane	-	8×10^{-6}	52
HBr	deuterium	diphenyl-methane	-	6×10^{-5}	52
			α	β	
HI	deuterium	naphthalene	5×10^{-6}	-	51
HBr	deuterium	naphthalene	2×10^{-3}	6×10^{-5}	51

PREPARATION OF COMPOUNDS.

1.Preparation of tritiated aromatic compounds.

Most of the tritiated materials were prepared by hydrolysis of the appropriate Grignard or organolithium reagents with tritiated water.

(a) Grignard Reagents.

Reactions involving Grignard reagents were carried out in a three-necked flask with a stirrer, dropping-funnel and water cooled condensor. Moisture was excluded from the apparatus by means of sulphuric acid "bubblers" connected, by a T-piece, to the top of the condensor and the dropping-funnel. The apparatus and the magnesium turnings were dried for at least one hour at 110° before use. The ether was supplied as "anhydrous ether" by McFarland and Co. and not dried further.

Enough ether was added to the flask to cover the magnesium turnings and a small percentage of the bromo-compound was added, the remainder of the bromo-compound being dissolved in ether in the dropping funnel. Initiation of the reactions, where necessary, was carried out by heating, or by the addition of a few drops of ethylene dibromide. Once the reaction had commenced the bromo-compound was added during a period of about one hour to the rapidly stirred contents of the flask. After addition was complete the reaction was refluxed for one hour.

In some cases the Grignard reagent was prepared using the "entrainment" method.[67] This involves entraining the halogen compound with ethylene dibromide instead of the more usual ethyl bromide; the advantage of the new method is that only the required Grignard reagent is formed, the ethylene dibromide reacting to give ethylene and magnesium bromide. The method involves the addition of all the bromo-compound to a large excess of magnesium in ether. The solution is then refluxed and ethylene dibromide added, dropwise, from a Hirshberg[68] dropping-funnel over a period of at least 12hours.

Tritiated water (supplied by the Radiochemical Centre, Amersham, and of activity 1curie/5ml., or 1curie/10ml.), was added slowly, in a quantity calculated to give a product of the required activity, to the rapidly stirred, and cooled Grignard reagent. The reagent always needed much more water than the calculated amount, due to the hygroscopic nature of the basic magnesium halide, formed by decomposition of the Grignard reagent. In all the preparations, therefore , the addition of the tritiated water was followed by the addition of excess distilled water. The magnesium salts were dissolved by adding 20% hydrochloric acid, or a saturated solution of ammonium chloride, the strength of the acid being insufficient to cause appreciable change in the tritiated product. The ether layer was separated, washed succesively with water, sodium carbonate solution, water, and then dried by standing overnight over anhydrous sodium sulphate. The ether was removed through an 80cm. heated Vigreaux column.

(b) Organolithium reagents.

Organolithium compounds were prepared in an apparatus similiar to that, described above, for Grignard reagents. Reactions were carried out in an atmosphere of oxygen-free nitrogen, which had been dried by passage through sulphuric acid bubblers. The lithium was prepared by beating small lumps of the metal into thin foil, oxidation being minimised by covering the surface with liquid paraffin. The lithium sheets were then washed in petroleum ether and cut into small pieces in an atmosphere of nitrogen. The organolithium compound formed in the reaction was filtered from the unreacted lithium before hydrolysis. All other stages in the preparation were identical with those in the Grignard preparations.

2. Preparation of tritiated benzene derivatives.

p-$[^3H]$ toluene, p-$[^3H]$ t-butylbenzene and $[^3H]$ benzene, all of 5mc./g., were kindly donated by Dr.R.Taylor.

t-Butylbenzene was prepared in 70% yield by the method of Huston et. al.[70]

Nitration of t-butylbenzene.[71]

Nitric acid,(200g.,d.1.52), was gradually added to an equal weight of vigorously stirred t-butylbenzene at room temperature. The reaction was complete after 2hours, the mixture was poured into water and the product isolated by ether extraction. The ethereal solution was washed, dried (Na_2SO_4) and concentrated. Fractional distillation gave p-nitro-t-butylbenzene in 70% yield, b.p. 132-133°/14mm.

2-Bromo-4-nitro-t-butylbenzene.[71]

p-Nitro-t-butylbenzene (202g.) was heated with bromine (236g.) in the presence of finely divided iron (40g.), to about 96°. After 30mins., more bromine (236g.) was added and the mixture heated for 7hours. The product was isolated by distillation in a current of super-heated steam. Crystallisation from alcohol gave 2-bromo-4-nitro-t-butylbenzene (14%, 40g.), m.p. 94.5°.

4-Amino-2-bromo-t-butylbenzene.[71]

The nitro-compound (40g.) was dissolved in a mixture of alcohol (175ml.) and concentrated hydrochloric acid (5.5ml.), and finely divided iron (27.5g.) added in four equal portions. The mixture was refluxed for 2hours and the amine precipitated as the hydrochloride. The free amine was liberated with alkalis, and extracted with ether. The ethereal solution was washed, dried (Na_2SO_4) and concentrated. Fractional distillation gave 4-amino-2-bromo-t-butylbenzene (24.5g.,70%), b.p. 153-155°/11mm.

o-Bromo-t-butylbenzene.[71]

4-amino-2-bromo-t-butylbenzene (24.5g.,0.125moles) was diazotised at 0° and added to 50%w/w. hypophosphorous acid, cooled to -5°.The mixture was allowed to stand at 0° for 24hours and ether extracted. After washing and drying (Na_2SO_4), fractional distillation of the ethereal layer gave o-bromo-t-butylbenzene (14g.,61.5%), b.p.109°/27mm.

[*o*-^{3}H]-t-butylbenzene (6.5mc./g. activity)

The Grignard reagent was formed from *o*-bromo-t-butylbenzene (14g., 0.065mole), magnesium (1.6g., 0.7g.-atom),in ether. The reagent was hydrolysed with tritiated water (1.2ml. of 100mc/ml. followed by excess of distilled water. Treatment with 20% hydrochloric acid followed by separation, drying (Na_2SO_4) and fractionation of the ethereal layer gave [*o*-^{3}H]-t-butylbenzene (6g.,69%),b.p.169°/759mm., n_D^{20}= 1.4915

Bromomesitylene was prepared by the method of Smith[72] in 75% yield, b.p. 226°/760mm.

[2-^{3}H]-1,3,5-trimethylbenzene (5mc./g. activity).

Mesitylbromide (20g.,0.1mole), in ether solution, was treated with magnesium (0.11g.-atom). The Grignard reagent was hydrolysed with tritiated water (1.20ml. of 100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [2-^{3}H]-1,3,5-trimethylbenzene in 45% yield, b.p. 164°, n_D^{20}= 1.4967

Propylene sulphide.[69]

Propylene oxide (30g.), thiourea (42g.), ice (60g.) and water (90ml.) were stirred at 0° for 30mins. and at 20° for a further hour. The mixture was ether extracted and the ethereal solution washed, dried and concentrated. Fractionation gave propylene sulphide (23g.,60%), b.p. 75°.

[*p*-^{3}H]-bromobenzene (6.7mc./g. activity).

p-Dibromobenzene (30g., 0.096mole) was reacted, in ether, with magnesium (2.3g.,0.096 g.-atom) at -30°. The Grignard reagent was hydrolysed with tritiated water (3.0ml. of 100mc./ml.) Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal extract gave [*p*-^{3}H] bromobenzene (12g., 54%), b.p.157°

[*p*-^{3}H]-thiophenol (ca. 6.7mc./ml. activity)

[*p*-^{3}H] bromobenzene (12g.) was reacted with lithium[69], in ether, and propylene sulphide (5.9g.) added over 30mins. The stirring was continued for 2hours and the reaction allowed to stand overnight, before hydrolysis. The mixture was extracted with ether and the ethereal solution washed, dried (Na_2SO_4) and concentrated. Fractional distillation gave [*p*-^{3}H] thiophenol (5g., 62%), b.p. 169°.

[*p*-^{3}H]-thioanisole (ca. 6.7mc./g. activity).

[*p*-^{3}H]-thiophenol (5g., 0.052mole) was methylated with dimethylsulphate (5g.) in sodium hydroxide (1.65g.) and water (16ml.). The mixture was refluxed for 1hour; the product was ether extracted and the ethereal solution washed, dried (Na_2SO_4) and concentrated. Fractionation gave [*p*-^{3}H]-thioanisole (3g., 53%), b.p. 187-8°

[*m*-^{3}H]-thioanisole (7mc./g. activity) was prepared by a similiar method.

[*m*-^{3}H] anisole (8.4mc./g. activity).

m-Bromoanisole (14g., 0.075mole) was reacted with magnesium (2.0g., 0.083 g.-atom), the Grignard complex was hydrolysed with tritiated water (1.35ml., 100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave

$[\underline{m}\text{-}^{3}H]$ anisole (7g.,86%), b.p. 154°

$[p\text{-}^{3}H]$ anisole (8mc./g.,activity) was prepared in an analogous way. Yield: 83%, b.p. 154°

3. Preparation of heterocyclic compounds.

Dibenzothiophen was prepared in 65% yield from biphenyl by the method of Gilman and Jacoby;[73] the final purification was by distillation under reduced pressure,followed by crystallisation from alcohol, m.p.99°

$[4\text{-}^{3}H]$ dibenzothiophen (7mc./g. activity).

Dibenzothiophen (0.1mole), in ether, was reacted with n-butyllithium (0.1mole)for 24hours[74] before hydrolysis with tritiated water (2.7ml.,100mc./ml.). Treatment with aqueous ammonium chloride followed by separation,washing, drying (Na_2SO_4), and distillation of the ethereal layer gave $[4\text{-}^{3}H]$dibenzothiophen (17g., 92%),b.p. 152-154° /3mm. A sample for kinetics, after crystallisation several times from alcohol, had a m.p. 99°.

3-Aminodibenzothiophen.

Dibenzothiophen (100g.,0.55mole) was converted to 3-aminodibenzothiophen(m.p.120°) in 50% yield by oxidation, nitration, and reduction,by the method of Brown, Christiansen, and Sandrin.[75]

3-Bromodibenzothiophen.[76]

3-Aminodibenzothiophen (30g.,0.15mole), in glacial acetic acid, was diazotised using nitrosylsulphuric acid, and converted by a Sandmeyer reaction in 25% yield to 3-bromodibenzothiophen (m.p. 95-96°).

[3-^{3}H]-dibenzothiophen (7mc./g. activity).

3-Bromodibenzothiophen (8g., 0.03mole) was allowed to react with n-butyllithium (0.03mole) for 10mins., in ether, at room temperature[76] before the solution was hydrolysed with tritiated water (0.8ml.,100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave [3-^{3}H]-dibenzothiophen (3.6g., 66%), b.p. 141-3°/2mm. The product was crystallised several times from alcohol and had a m.p. 99°.

2-Bromodibenzothiophen was prepared by the direct bromination of dibenzothiophen (30g., 0.161mole) in carbon tetrachloride.[77] It was necessary to distil the product under reduced pressure to obtain pure 2-bromodibenzothiophen (26g., 60%), b.p. 175-7°/3mm., m.p. 125° (from ethanol).

[2-^{3}H]-dibenzothiophen (6.7mc./g. activity).

2-Bromodibenzothiophen (14.3g., 0.05mole) was treated with n-butyllithuim (0.05mole) in ether for 10 mins. at room temperature, before the solution was hydrolysed with tritiated water (1.35ml.,100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4), and distillation of the ethereal layer gave [2-^{3}H]-dibenzothiophen (8g.,88%), b.p. 153-5°/3mm., m.p. 99° (alcohol).

1-Acetamidodibenzothiophen was prepared from dibenzothiophen by the method of Gilman and Jacoby[73] by nitration, reduction, and acetylation.

1-Bromodibenzothiophen was prepared in 22% yield by the method of Gilman and Wilder.[78]

$[1-^{3}H]$dibenzothiophen (8 mc./g. activity).

1-Bromodibenzothiophen (6 g.,0.0228mole) was reacted with n-butyllithium (0.023mole) for 10 mins. at room temperature, followed by hydrolysis with tritiated water (0.7ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[1-^{3}H]$dibenzothiophen (2.5g., 60%), b.p. 141-3°/2mm., m.p. 99° (from alcohol).

Dibenzofuran supplied by Messrs. B. D. H. Ltd., had a m.p. 86° and was used without further purification.

$[4-^{3}H]$dibenzofuran (8mc./g. activity)

Dibenzofuran (16.8g.,0.1mole) was reacted with n-butyllithium[79] (0.1mole) in refluxing ether for 24 hours and followed by hydrolysis with tritiated water (2.7ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[4-^{3}H]$dibenzofuran (90%), b.p. 145°/3mm., m.p. 86° (from alcohol).

3-Nitrodibenzofuran was prepared in 76% yield by direct nitration of dibenzofuran by the method of Gilman, Bywaters and Parker.[80]

3-Aminodibenzofuran was prepared in 80% yield by reduction of the nitro-compound with stannous chloride in glacial acetic acid, by the method of Gilman and Avakian.[81]

3-Bromodibenzofuran[82]

3-Aminodibenzofuran (37g.,0.2mole) was converted by a Sandmeyer reaction to 3-bromodibenzofuran (9g.,18%),m.p. 121°

[3-^{3}H]dibenzofuran (8mc./g. activity).

3-Bromodibenzofuran was reacted with n-butyllithium, in ether, for 10 mins. at room temperature before hydrolysis with tritiated water (0.9ml./100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying(Na_2SO_4) and fractionation under reduced pressure gave [3-^{3}H]dibenzofuran (4g.,66%). A kinetic sample, crystallised from alcohol, had a m.p. 86°.

2-Bromodibenzofuran.

Dibenzofuran (30g., 0.18mole), in glacial acetic acid, was treated with bromine (0.36mole) for 4 hours at 50°, no reaction was obtained at 0° as advised by Bui and Royer.[83] The product was poured into water, extracted with benzene, washed, dried (Na_2SO_4) and distilled to give 2-bromodibenzofuran (20g., 45%), which had a m.p. 107-8° after crystallisation from alcohol.

[2-^{3}H]dibenzofuran (8mc./g. activity).

2-Bromodibenzofuran (12.3g., 0.05mole) was reacted with n-butyllithium (0.05mole) in refluxing ether for 20 mins; the lithium reagent formed was hydrolysed with tritiated water (1.35ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [2-^{3}H]dibenzofuran (6.5g.,78%), b.p. 131-3°/2mm.. A sample had a m.p. 86° after crystallisation from alcohol.

4-Aminodibenzofuran.

Dibenzothiophen (126g.,0.75mole) was converted to 4-aminodibenzofuran (39g., 0.75 mole) by the method of Gilman and Ingram.[84] The product had the m.p. 81-83°.

1-Bromodibenzofuran was obtained in 40% yield (m.p. 68°), by the method of Gilman and Ess.[85]

$[1-{}^{3}H]$ dibenzofuran (8mc./g. activity).

1-Bromodibenzofuran (6.2g.,0.025 mole) was reacted, in ether, with a slight excess of n-butyllithium. After stirring at 0° for 10 mins., the solution was hydrolysed with tritiated water (0.07ml., 100mc./ml.). Treatment with dilute acid hydrochloric acid followed by separation, washing,drying (Na_2SO_4) and distillation of the ethereal layer gave $[1-{}^{3}H]$ dibenzofuran (2g., 48%), b.p. 119°/1mm.. A sample was crystallised from alcohol and had a m.p. 86°.

$[2-{}^{3}H]$ furan (5mc./g. activity).

Furan (6.8g.,0.2mole), in dry tetrafuran, was treated with n-butyllithium (0.2 mole)[86], stirred for two hours and allowed to stand overnight. The addition of aqueous ammonium chloride followed by separation,washing,drying (Na_2SO_4) and fractionation of the ethereal layer gave $[2-{}^{3}H]$ furan (4g., 60%), b.p. 32°.

$[2-{}^{3}H]$ thiophen (10mc./g. activity).

Thiophen (8.4g.,0.1 mole) was treated with n-butyllithium , in ether, and the mixture allowed to stand overnight. The solution was hydrolysed with tritiated water (1.8ml., 100mc./ml.) followed by the addition of aqueous ammonium chloride, separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[2-{}^{3}H]$ thiophen (6g.,60%),b.p. 83°

$[3-{}^3H]$thiophen (ca. 9mc./g. activity).

Thiophen (10g.) and sulphuric acid [6ml., 69%, consisting of concentrated sulphuric acid (4.2ml.) and tritiated water (1.8ml.,100mc./ml.)] were shaken vigorously for 26.5 hours at 25°[66], and the thiophen separated, washed with water, dried ($CaCl_2$) and distilled. The product was shaken with perchloric acid (20ml.,53.7%) for 19 hours and ether added. Separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[3-{}^3H]$thiophen (6g.,60%), b.p. 83°.

$[2-{}^3H]$ benzothiophen (8mc./g. activity).

n-Butyllithium (10.2g.,0.075mole), in ether, was added to benzothiophen (10.2g.,0.075 mole), in dry tetrafuran, at -10°[88] and the volume made up to 150ml. with ether. The solution was stirred at room temperature for 2 hours and hydrolysed with tritiated water (1.6ml., 100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation under reduced pressure gave $[2-{}^3H]$ benzothiophen (8g.,78%), b.p. 90-1°/10 mm., m.p. 32° after several crystallisations from alcohol.

3-Bromobenzothiophen.

Direct bromination of benzothiophen in boiling carbon tetrachloride gave 3-bromobenzothiophen[89,90] in 74% yield, b.p. 146-8°/22mm.

$[3-{}^3H]$ benzothiophen (8mc./g. activity).

3-Bromobenzothiophen (16g.,0.083 mole), in ether solution, was treated with magnesium (4.5g.,0.185 mole) under "entrainment" conditions; ethylene dibromide (18.5g.,0.1 mole being added to complete the reaction. The Grignard reagent was hydrolysed with tritiated water (1.6ml.,100mc./ml.). Addition of dilute hydrochloric acid followed by separation, washing, drying (Na_2SO4) and fractionation of the ethereal layer gave [3-^{3}H]benzothiophen (7g.,69%), b.p. 104-6°/20mm., m.p. 32° after several crystallisations from alcohol.

[2-^{3}H]benzofuran (8mc./ml. activity) .

Benzofuran (8.9g.,0.075 mole) was treated with n-butyllithium (0.075 mole) in ether, and the reaction stirred for 4 hours at room temperature and allowed to stand overnight.[91] The solution was hydrolysed with tritiated water (1.4ml.,100mc./ml. Addition of aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [3-^{3}H] benzofuran (6g.,68%), b.p. 66°/16mm., n_D^{20}= 1.5620.

[1-^{3}H]-5-ethylcarbazole (8mc./ml. activity).

5-ethylcarbazole (10.3g.,0.05 mole), in ether, was refluxed for 20 hours with n-butyllithium (0.05 mole), an additional 0.05 mole of the lithium regent was added and the refluxing continued for a further 24 hours.[79] The solution was hydrolysed with tritiated water (1.6ml., 100mc./ml.). Addition of aoueous ammonium chloride followed by separation, washing, drying (Na_2SO4) and distillation of the ethereal layer gave [1-^{3}H]-5-ethylcarbazole (8g.,78%). The product was crystallised from alcohol and had a m.p. 67°.

3-Bromo-5-ethylcarbazole

A solution of 5-ethylcarbazole (30g.,0.154 mole), potassium bromide (12.3g.), water (23ml.), and acetic acid (400ml.) was kept at 25-30° with a cooling bath while finely powdered potassium bromate (19.3g., 0.115 mole) was added dropwise over 30mins.[79] The resulting mixture was stirred for 3 hours at 25° and filtered. Crystallisation from alcohol gave 3-bromo-5-ethylcarbazole (15g., 36%) , m.p. 83°.

[3-^{3}H]-5-ethylcarbazole (7.5mc./g. activity).

3-Bromo-5-ethylcarbazole (14.3g.,0.05 mole) was reacted with n-butyllithium (0.05 mole) in a mixture of dry ether and benzene. The solution was hydrolysed with tritiated water (1.35ml.,100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing,drying (Na_2SO_4) and distillation of the ethereal layer gave [3-^{3}H] 5-ethylcarbazole (7g., 68%). The final purification was by crystallisation from alcohol and the product had a m.p. 67°

4. Preparation of fluorene compounds.

2-Bromofluorene was obtained in 68% yield by the bromination of fluorene in chloroform.[94]

[2-^{3}H] fluorene (10mc./g. activity).

2-Bromofluorene (80g.,0.3 mole) was reacted with magnesium (24.3g.,1.0g.-atom) in ether under "entrainment" conditions and dibromoethane (70g.,0.3 mole) added over 12 hours, to the refluxing solution, to complete the reaction. The solution was hydrolysed with tritiated water (5.4ml.,100mc./ml. Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation under reduced pressure gave $[2-^{3}H]$ fluorene (21g., 40%). The product had a m.p. 114-115° after crystallisation from alcohol and vacuum sublimation.

9-Methyl-$[2-^{3}H]$ fluorene (ca. 10mc./g. activity).

$[2-^{3}H]$ fluorene (14g.,0.09 mole) in ether was treated with a slight excess of n-butyllithium. After heating under reflux for 2 hours an excess of methyl iodide was added and the mixture heated overnight. Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave 9-methyl-$[2-^{3}H]$ fluorene (11.5g.,76%), b.p. 159-162°/12mm. Crystallisation from methanol gave a product with a m.p. 49°, (other workers[92] report 46°).

9,9-Dimethyl-$[2-^{3}H]$ fluorene (ca. 10mc./g. activity).

9-Methyl-$[2-^{3}H]$ fluorene (11.5g., 0.064 mole) in ether was treated with n-butyllithium and methyl iodide as described in the previous preparation.

Fractionation and crystallisation from methanol gave 9,9-dimethyl-$[2-^{3}H]$ fluorene (7g., 57%), b.p. 147°/10mm., m.p. 96°.

Removal of tritium from the 9-position of fluorene.

When the $[2-^{3}H]$ fluorene, prepared above, was used in exchange reactions it was found that about 8% of the tritium remained in the molecule after 10 times the approximate half-life of the exchange in the 2-position. When the 2-9-methyl- derivative was exchanged, about 5% of the tritium similarly remained unchanged, but none of the 9,9-dimethylderivative. It was concluded that some tritium had entered the 9-position when the Grignard reagent, from the 2-bromofluorene, was hydrolysed, and, in agreement with this, it was found that when the tritio-fluorene and -9-methylfluorene were boiled with 10% aqueous-ethanolic alkali for 2 hours, the recovered samples retained no activity after acid exchange. These samples were used in the measurement of the reported rate constants.

$[9-{}^3H]$ fluorene (6mc./g. activity).

Fluorene (8.3g., 0.05 mole), in ether, was reacted with n-butyllithium (0.05 mole) and the solution hydrolysed with tritiated water (1.0ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[9-{}^3H]$ fluorene (7.5g., 90%), m.p. 114-115° (from acetic acid).

7-Bromo-$[2-{}^3H]$ fluorene (ca, 5 mc./g. activity).

This was prepared by direct bromination of $[2-{}^3H]$ fluorene in chloroform.[94] The product had a m.p. 112° after distillation under reduced pressure and crystallisation from alcohol.

7-Nitro-$[2-{}^3H]$ fluorene (low activity).

This was prepared by the method of Kuhn[93] from $[2-{}^3H]$ fluorene but more than the expected loss (a half) of activity occurred, probably due to the exchange of the tritio-fluorene in the nitrating acid. The product (yield 90%) was crystallised from acetic acid and had a m.p. 156°.

2,7-Dibromofluorene was prepared by direct bromination[111] of 2-bromofluorene in chloroform and when crystallised from alcohol had a m.p. 163°.

2-Carboxy-$[7\text{-}^{3}\mathrm{H}]$fluorene (5mc./g. activity).

2-Bromo-$[7\text{-}^{3}\mathrm{H}]$fluorene (8.5g., 0.058 mole), in ether, was reacted with magnesium (0.18g.-atom) under "entrainment" conditions and dibromoethane (0.06 mole) added to the refluxing solution over 12 hours. The Grignard reagent was poured onto a slurry of crushed, solid carbon dioxide in dry ether . The ethereal solution was treated with dilute hydrochloric acid and extracted several times with 0.2 M aqueous sodium hydroxide, the extracts being added to an excess of hydrochloric acid. The 2-carboxy-$[7\text{-}^{3}\mathrm{H}]$fluorene (2g., 27%) was purified by dissolving in alkali and reprecipitating with acid, and finally by sublimation.

7-Bromo-2-nitrofluorene.

2-Bromofluorene was nitrated in acetic acid by the method of Campbell and Temple.[95] 7-Bromo-2-nitrofluorene (63%), m.p. 236° was crystallised from acetic acid.

2-Amino-7-bromofluorene.

7-Bromo-2-nitrofluorene (91g., 0.3 mole) was reduced by iron powder (73g.) in a mixture of ethanol (1300ml.) and (1800ml hydrochloric acid by the method of Campbell and Temple.[95] 2-Amino-7-bromofluorene (49g., 60%), m.p. 140° was crystallised from aqueous alcohol.

7-Bromo-2-hydroxyfluorene. was prepared from 2-amino-7-bromofluorene by the method of Gray and Hartley.[96]

7-Bromo-2-methoxyfluorene.

7-Bromo-2-hydroxyfluorene (18g., 0.067 mole) was methylated by dimethylsulphate (16.9g., 0.134 mole) in a solution of sodium hydroxide (8g.) in water (200ml.). The mixture was kept at 70° for 30mins., and the cooled alkaline solution filtered. The 7-bromo-2-methoxyfluorene (4g., 20%), m.p. 111° was purified by chromatography on an alumina column with petroleum ether (40-60°) and several crystallisations from alcohol.

Found C 61.54%: H 4.27%

$C_{14}H_{11}BrO$ requires C 61.11%; H 4.04%

2-Methoxy-[7-^{3}H]fluorene (9mc./g. activity).

7-Bromo-2-methoxyfluorene (2.5g., 0.009 mole), in ether, was reacted with magnesium (0.54g.-atom) under "entrainment" conditions, the dibromoethane (0.3 mole) was added to the refluxing solution over 12 hours. The solution was hydrolysed with tritiated water (0.3ml.,100mc./ml. Treatment with aqueous ammonium chloride followed by separation,washing, drying (Na_2SO_4) and distillation of the ethereal layer left the crude solid product. The 2-methoxyfluorene (1.0g., 56%), m.p. 108° was purified by chromatography on an alumina column with petroleum ether (40-60°) and crystallisation from alcohol but found to be inactive.

A second attempt, with the refluxing time of the Grignard reagent only 2 hours, gave the required active compound.

7-Bromo-2-chlorofluorene was prepared in 51% yield by the method of Bachmann and Boatner.[97] The product, m.p.157-8°, was purified by chromatography on alumina with petroleum ether (40-60°) and crystallisation from alcohol.

2-Chloro-[7-^{3}H]fluorene (7.5mc./g. activity).
7-Bromo-2-chlorofluorene (2.5g., 0.009 mole), in ether, was reacted with magnesium (0.3g.-atom) under "entrainment" conditions and dibromoethane added to the refluxing solution over 2 hours. The solution was hydrolysed with tritiated water (0.3ml.,100mc./ml.) and after separation, washing, and drying (Na_2SO_4) of the ethereal layer the solvent was removed. The 2-chloro-[7-^{3}H]fluorene (1g.,56%), m.p. 96°, was purified by chromatography (alumina) with petroleum ether (40-60°) and crystallisation from alcohol.

2-Methylfluorene was obtained by the Willgerodt-Kindler[98] conversion of 2-acetylfluorene to fluorenyl-2-acetic acid;[99] the latter was decarboxylated by distilling with calcium oxide.[99]

2-Methyl-7-nitrofluorene, m.p. 180-181, was prepared in 62% yield by the method of Sawicki.[100]

7-Amino-2-methylfluorene.
2-Methyl-7-nitrofluorene (15g.,0.067 mole), calcium chloride (4.4g.) in water (90ml.), and zinc dust (130g.) were refluxed in alcohol for 6 hours.[100] Filtration,and cooling of the alcoholic solution gave 7-amino-2-methylfluorene (10g.,77%), which had a m.p. 104° after crystallisation from aqueous alcohol.

7-Bromo-2-methylfluorene
This was prepared from 7-amino-2-methylfluorene (10g.) by the method of Bachmann and Boatner.[97] 7-Bromo-2-methylfluorene (6g., 45%) was purified by chromatography (alumina)

with petroleum ether (40-60°) and after several crystallisations from alcohol had a m.p. 129.5-130°.

Found: C 65.10%; H 4.26%; Br 30.64%

$C_{14}H_{11}Br$ requires: C 64.90%; H 4.28%; Br 30.84%

2-Methyl-[7-^{3}H] fluorene (8mc./g. activity).

7-Bromo-2-methylfluorene (4g.,0.016 mole), in ether, was reacted with magnesium (0.5g.-atom) under "entrainment" conditions and dibromoethane added to the refluxing solution over 2 hours. The Grignard reagent was hydrolysed with tritiated water (0.4ml., 100mc./ml.). After treatment with aqueous ammonium chloride the ethereal layer was separated, washed and dried (Na_2SO_4) and the solvent removed. 2-Methyl-[7-^{3}H] fluorene (2.0g.,73%), m.p. 104° was purified by chromatography on alumina with petroleum ether (60-80°) and crystallisation from alcohol.

[2-^{3}H] fluorene was used as the starting point of a first attempt to prepare 2-methyl-[7-^{3}H] fluorene and the procedure was identical to that described above for 2-methylfluorene. When kinetic measurements were made on this compound, however, it was found that the loss in tritium was not the expected first order. A probable explanation is that tritium displaced from the fluorene nucleus by acetylation, exchanged with acetic anhydride so that tritium was incorporated into the acetyl group of the 2-acetyl-[7-^{3}H] fluorene produced. The evidence suggests that some of this tritium remained in the conversion of the acetyl compound into 2-methyl-[7-^{3}H] fluorene. This tritium would then be located in the methyl group, and the hydrogens of this group have been shown to be not exchanged in acidic media.[101]

5. Preparation of biphenyl compounds.

[o- and p-^{3}H] biphenyl were kindly donated by Dr.R.Taylor.

4,4'-Dibromobiphenyl was prepared by Dr.P Greasley.

4-Bromo-[4'-^{3}H] biphenyl (4mc./g. activity).

4,4'-Dibromobiphenyl (50g., 0.16 mole), in dry benzene, was reacted with n-butyllithium (0.16 mole), in ether, for 15 mins, at C°. The solution was hydrolysed with tritiated water (2.9ml.,100mc/ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave 4-bromo-[4'-^{3}H] biphenyl (20g.,54%), b.p. 172-4°/8mm., m.p. 90°, after crystallisation from alcohol.

4-Carboxy-[4'-^{3}H] biphenyl (4mc./g. activity).

4-Bromo-[4'-^{3}H] biphenyl (0.05 mole), in ether, was reacted with n-butyllithium (0.05 mole), for 1 hour at room temperature. The solution was poured onto a slurry of solid carbon dioxide, in ether, and the solution treated with dilute hydrochloric acid and extracted several times with aqueous sodium hydroxide, the extracts being added immediately to an excess of hydrochloric acid. The organic acid was purified by dissolving in alkali and reprecipitating with acid and finally sublimation under reduced pressure gave 4-carboxy-[4'-^{3}H] biphenyl (30%), m.p. 228°.

4-Bromo-4'-trimethylsilylbiphenyl.

4,4'-Dibromobiphenyl (50g.,0.16 mole), in dry benzene, was reacted with n-butyllithium (0.16 mole) and after stirring at 0° for 15 mins., trimethylchlorosilane (0.2 mole) was added to the solution, which was refluxed for 1 hour. Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave 4-bromo-4'-trimethylsilylbiphenyl (28g.,58%) which after crystallisation from methanol had a m.p. 80°.

[4-^{3}H]-4'-trimethylsilylbiphenyl. (5mc./g. activity).

4-Bromo-4'-trimethylbiphenyl (28g., 0.085 mole), in dry benzene, was treated with n-butyllithium (0.085 mole), in ether, for 30 mins. at 0°. The solution was hydrolysed with tritiated water (2.2ml.,100mc./ml.). Addition of aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave [4-^{3}H]-4'-trimethylsilylbiphenyl (12g.,57%). The product had a m.p. 55° after several crystallisations from methanol.

[4-^{3}H]-4'-nitrobiphenyl (ca. 5mc./g. activity).

This was prepared by Mr.K. Leyshon from [4-^{3}H]-4'-trimethyl-biphenyl by nitrodesilylation.

4-Methylbiphenyl, b.p. 113°/1mm. was prepared in 29% yield by the method of Elks and Hey.[102]

4-Bromo-4'-methylbiphenyl , m.p. 133° was prepared by direct bromination of 4-methylbiphenyl in carbon tetrachloride by the method of Gomberg and Pernert.[103]

4-Methyl-$[4'\text{-}^{3}\text{H}]$biphenyl (6.5mc./g. activity).

4-Bromo-4'-methylbiphenyl (17g.,0.o65 mole), in dry benzene, was treated with n-butyllithium (0.065 mole), in ether, and the reaction was stirred for 1 hour at room temperature. The solution was hydrolysed with tritiated water (1.5ml.,100mc./ml.). Addition of aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave 4-methyl-$[4'\text{-}^{3}\text{H}]$ biphenyl (8g., 69%) which had a m.p. 46° after crystallisation from alcohol, (the b.p. of the compound was 124°/2mm.).

4-Chlorobiphenyl[102], m.p.77° was kindly donated by Dr.K.Shipley .

4-Bromo-4'-chlorobiphenyl, m.p.157°, was prepared in 78% yield, by the direct bromination of 4-chlorobiphenyl, in glacial acetic acid, by the method of Turner and Shaw.[104]

4-Chloro-$[4'\text{-}^{3}\text{H}]$biphenyl (6mc./g. activity).

4-Bromo-4'-chlorobiphenyl (10g., 0.037 mole), in ether, was treated with n-butyllithium (0.037 mole),for 1 hour at room temperature. The solution was hydrolysed with tritiated water (0.8ml.,100mc./ml.). Addition of aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4)and distillation of the ethereal layer gave 4-chloro-$[4'{}^{3}\text{H}]$biphenyl (5g.,71%), b.p. 145°/0.5mm. The product had a m.p. 77° after crystallisation from alcohol.

4-Methoxybiphenyl.

4-Hydroxybiphenyl (90g.) was dissolved in 10% sodium hydroxide (300ml.) and dimethylsulphate (120ml.) added in portions over an hour. The mixture was heated on a steam-bath for 1 hour and the solid filtered. After drying the 4-methoxybiphenyl (85g., 88%) was distilled, b.p. 132°/1mm.

4-Bromo-4'-methoxybiphenyl, m.p. 143-144° was brominated directly in chloroform in 13% yield by the method of Abernethy and Pollock.[105]

4-Methoxy- [4'-^{3}H] biphenyl (7mc./g. activity)

4-Bromo-4'-methoxybiphenyl (7.5g.,0.03 mole) was reacted with n-butyllithium (0.03 mole) for 1 hour, at room temperature, in a mixture of ether and benzene. The solution was hydrolysed with tritiated water (0.75ml. 100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave 4-methoxy-[^{3}H] biphenyl (3g.,57%). The product had a m.p.89° after several crystallisations from alcohol.

3-Nitrobiphenyl, b.p. 152°/2mm., was prepared in 59% yield from m-nitroaniline by the method of Elks, Haworth and Hey.[102]

4-Bromo-3'-nitrobiphenyl, m.p. 95° was prepared in 90% yield by direct bromination of 3-nitrobiphenyl by the method of Blakey and Scarborough.[106]

3-Amino-4'-bromobiphenyl

4'-Bromo-3-nitrobiphenyl (100g.), in alcohol, was refluxed for 6 hours with stannous chloride (600g.) in concentrated hydrochloric acid (600ml.).[106] 3-Amino-4-bromobiphenyl (12g., 14%), m.p. 105° was obtained pure only after six crystallisations from alcohol.

4-Bromo-3'-chlorobiphenyl.

3-Amino-4'-bromobiphenyl (12g.), in water (300ml.) and concentrated hydrochloric acid (50ml.), was diazotised with a slight excess of sodium nitrite. The addition took 10 mins. and the solution was stirred at 0° for a further 30 mins. Freshly prepared cuprous chloride (18g.) was added in concentrated hydrochloric acid (75ml.) and the mixture allowed to reach room temperature after 2 hours. Ether was added and the ethereal layer separated, washed, and dried (Na_2SO_4). Distillation gave 4-bromo-3'-chlorobiphenyl (5g.,32%),b.p. 140°/1mm., n_D^{25} = 1.6496

Found C 54.58%; H 3.27%

$C_{12}H_8BrCl$ requires C 53.85%; H 3.01%

3-Chloro-[4'-^{3}H] biphenyl (6mc./g. activity).

4-Bromo-3'-chlorobiphenyl (10g.,0.037 mole), in dry tetrahydrofuran, was reacted with magnesium (0.04g.-atom) and the mixture refluxed for 2 hours. The solution was hydrolysed with tritiated water (0.8ml.,100mc./ml.). Addition of aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave 3-chloro-[4'-^{3}H] biphenyl (5g., 71%), b.p. 155°/6mm.

6. Preparation of Miscellaneous Compounds.

[α- and β-^{3}H] naphthalene were kindly donated by Dr. R. Taylor.

Diphenyl ether was supplied by Messrs. B.D.H. Ltd.

[2-^{3}H] diphenyl ether (8mc./g. activity).

Diphenyl ether (8.5g.,0.05 mole) was reacted with n-butyllithium (0.05 mole) in refluxing ether for 24 hours.[107] The solution was hydrolysed with tritiated water (1.4ml., 100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[2-^3H]$ diphenyl ether (7g., 83%), b.p. 125°/14mm., m.p.28°

4-Bromodiphenyl ether was prepared by direct bromination and kindly donated by Dr. K.C. Pande.

$[4-^3H]$ diphenyl ether (8mc,/g., activity).

4-Bromodiphenyl ether (14.1g.,0.057 mole), in ether, was reacted with magnesium (1.5g.-atom) under "entrainment" conditions. The reaction was completed by the addition of dibromoethane (15.9g.,0.075 mole) to the refluxing solution over 12 hours and then hydrolysed with tritiated water (1.5ml.,100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave $[4-^3H]$ diphenyl ether (7.9g., 83%), b.p. 118°/9mm., m.p. 28°

3-Nitrodiphenyl ether.

Sodium hydroxide (1 mole, 90%) was added to phenol (1 mole) and warmed to form the sodium salt. A copper catalyst (1g., freshly prepared from copper sulphate and zinc in concentrated hydrochloric acid) and m-nitro-bromobenzene (1 mole) were added and the mixture heated on an oil-bath at 180° for 6 hours. Addition of ether followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave 3-nitrodiphenyl ether (64g., 30%), b.p. 169°/5mm.

3-Aminodiphenyl ether.

3-Nitrodiphenyl ether (64g.,0.296 mole), in glacial acetic acid (500ml.) was refluxed with stannous chloride (250g., 1.1 mole), in concentrated hydrochloric acid (175ml.), for 5 hours. The cooled solution was made alkaline and the amine extracted with ether; the solvent was removed leaving the crude product but this was not purified further.

3-Bromodiphenyl ether.

3-aminodiphenyl ether (60g.), in concentrated hydrobromic acid (250ml.) and water (150ml.) was diazotised with sodium nitrite (30g.) and water (150g.). The solution was added to cuprous bromide (120g.) in concentrated hydrobromic acid (300ml.) and refluxed for 2 hours. The mixture was poured into water and ether added. Separation, washing, drying (Na_2SO4) and fractionation of the ethereal layer gave 3-bromodiphenyl ether (8g., 10%), b.p. 144°/6mm.

[3-^3H] diphenyl ether.

3-Bromodiphenyl ether (8g.,0.032 mole), in ether, was reacted with magnesium (0.065 mole) under "entrainment" conditions. The reaction was completed by adding dibromoethane to the refluxing solution over 12 hours and then hydrolysed with tritiated water (0.9ml.,100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [3-^3H] diphenyl ether (4g., 73%), b.p. 137°/18mm., m.p. 28°

Diphenyl sulphide was prepared as in Organic Syntheses.[108]

[2-^{3}H] diphenyl sulphide (8mc./g. activity).

Diphenyl sulphide (9.3g.,0.05 mole) and n-butyllithium (0.05 mole) were refluxed in ether for 24 hours[107] and the cooled solution hydrolysed with tritiated water (1.5ml., 100mc./ml.). Treatment with aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [2-^{3}H] diphenyl sulphide (8g.,86%), b.p. 145°/11mm., n_D^{20} = 1.6346.

4-Bromodiphenyl sulphide.

Diphenyl sulphide (30g., 0.162 mole) was brominated[112] directly in glacial acetic acid to give 4-bromodiphenyl sulphide (29g., 69%), b.p. 184°/10mm.

[4-^{3}H] diphenyl sulphide (8mc./g. activity).

4-Bromodiphenyl sulphide (16g.,0.06 mole), in ether, was reacted with magnesium under "entrainment" conditions and dibromoethane (0.06 mole) added to the refluxing solution over 12 hours. The solution was hydrolysed with tritiated water (1.8ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [4-^{3}H] diphenyl sulphide (7g., 63%), b.p. 152°/18mm., n_D^{20}= 1.6345.

4-Bromodiphenylmethane was kindly provided by Dr.J. Sperry.

[4-^{3}H] diphenylmethane (6mc./g. activity).

4-Bromodiphenylmethane (12.4g., 0.05 mole) was reacted, in ether, with magnesium (0.12 mole) under "entrainment" conditions and dibromoethane (0.05 mole) added to the refluxing solution over 12 hours. The Grignard complex was hydrolysed with tritiated water (1.0ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and fractionation of the ethereal layer gave [4-^{3}H] diphenylmethane (6g.,71%), b.p. 105-7°/5mm., m.p. 24-5° (from alcohol).

9-Bromophenanthrene was kindly donated by Dr. J. Sperry.

[9-^{3}H] phenanthrene (8.2mc./g. activity).

9-Bromophenanthrene (12.4g., 0.05 mole), iodine (0.1g.), ethyl bromide (0.3g.) and an excess of magnesium turnings were refluxed in a mixture of ether and benzene (30ml. of each) for 5 hours. The mixture was hydrolysed with tritiated water (1.4ml., 100mc./ml.). Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4) and distillation of the ethereal layer gave [9-^{3}H] phenanthrene (6g.,71%), b.p. 172-4°/2mm., m.p. 101°

KINETICS AND RESULTS

1. The measurement of the relative activities of tritiated materials.

The method used was that first described by Eaborn and Matsukawa,[126] and consists of a simple integrating method for determining the relative activities of tritiated materials, dispensing with the complex counting equipment normally employed. A liquid scintillation system is used but the direct current output of the photomultiplier is measured with a suitably shunted galvanometer. The apparatus consists of a photomultiplier tube and head, high tension unit, high sensitivity galvanometer, lamp and scale and sample cell. A linear relation, between observed current output and sample activity, was shown to exist by Eaborn and Matsukawa,[126] for tritiated water in dioxan containing terphenyl, and later for tritiated toluene with the liquid scintillator consisting of a saturated solution of *p*-terphenyl in toluene.[127]

The scintillation counter head.

The circuit of the counter head (type no. 653/A, Isotopes Development Ltd.), was modified to that shown in the Figure I. The galvanometer leads, F and G, were taken through a hole in the lower casing of the photomultiplier head in such a way that they did not touch the casing: this ensured leakage was kept to a minimum. The leads were of cotton-

A - High tension supply

E - Galvanometer

F,G - Galvanometer leads

S - Switch

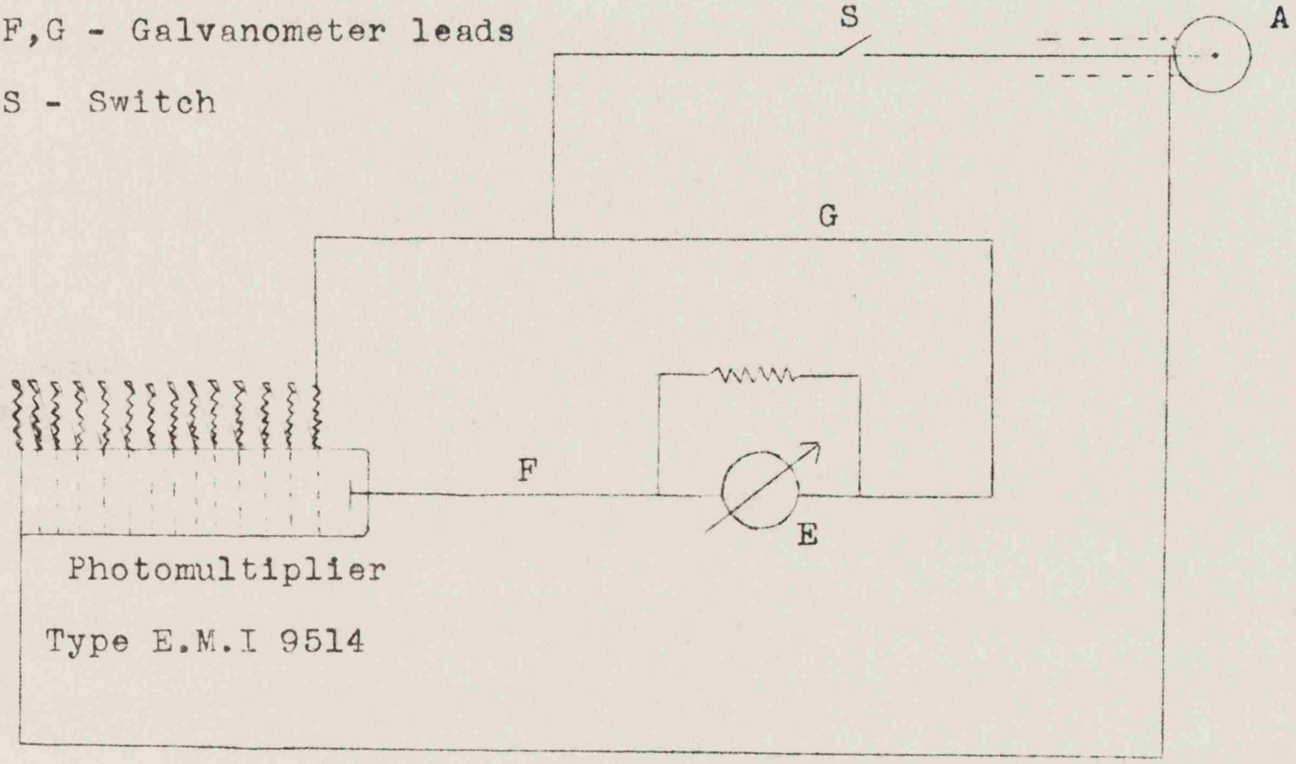


Figure I

covered copper wire, sufficiently rigid to support its own weight without contacting any earthed object. The resistance chain, as supplied by I.D.L. Ltd., consisted of eleven 470K, and 1M high resistances of 5% tolerance. The resistances across the first, and the last three stages were altered to 1M, since an E.M.I specification indicated that this would increase the signal strenght over the dark current. A further modification was the insertion of two additional 470K resistances to accommodate the thirteen stage tube. The resistance chain is shown in Figure II, looking from above the photomultiplier head

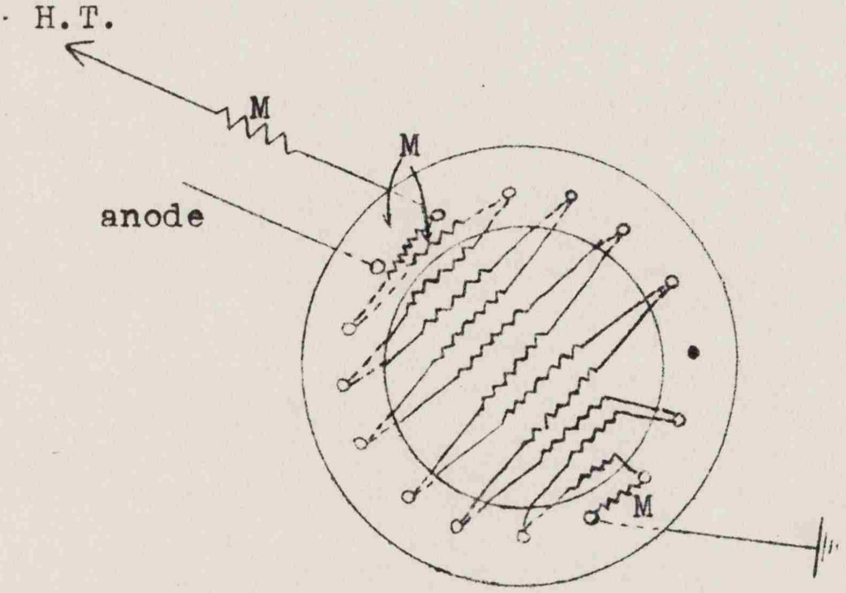


Figure II

(the resistance chain consisting of 4 x 1M and 10 x 470K resistances)

The light-tight cap (type 'A', Isotopes Development Ltd.) was lengthened by 18cm. to accommodate the scintillation cell which was placed on the top of the photomultiplier tube (Figure III).

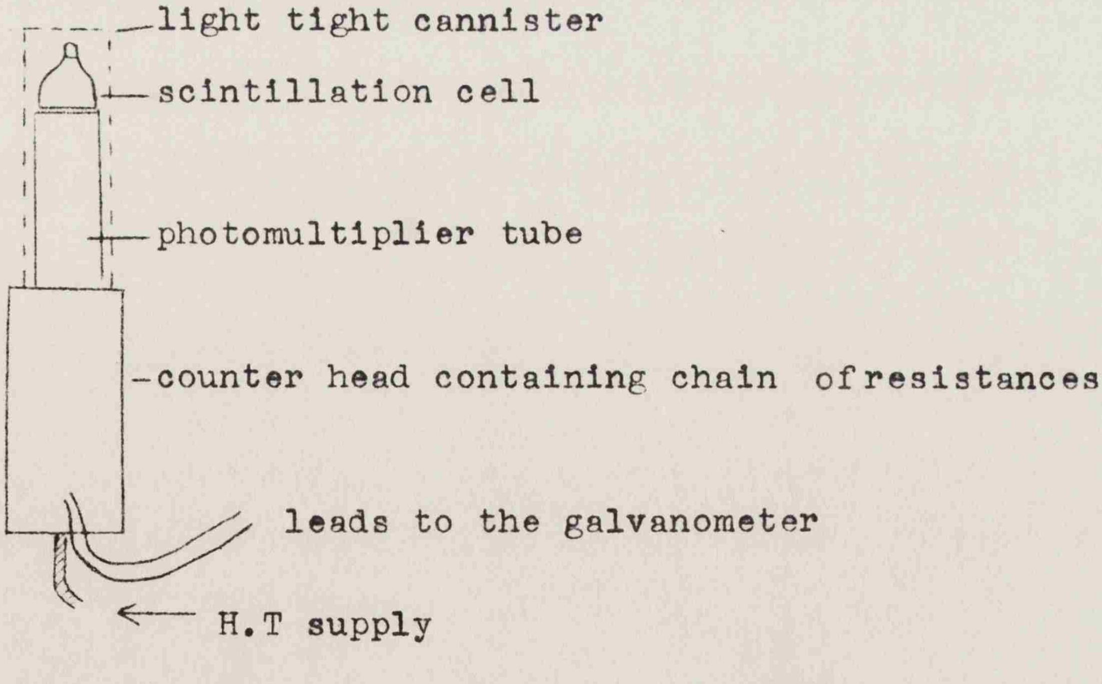


Figure III

<u>The high tension unit</u> (Type 532, Isotopes Development Ltd.)

The output voltage was regulated to better than 0.02% for a 10% change in mains imput voltage (including variations in mains frequency). Short term drift of voltage was less than 0.02% per twentyfour hours, and long term drift was better than 0.01% per one hundred hours. Positive polarity was used throughout the experimental work.

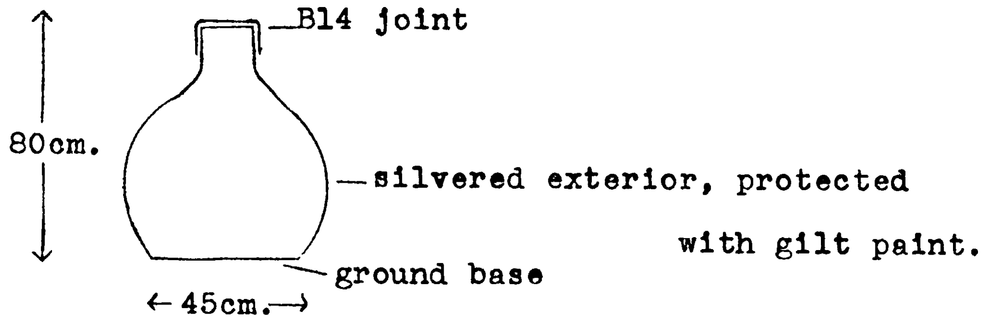
<u>The galvanometer</u> (Type no. 7943, Pye and Co. Ltd.)

The galvanometer was of the moving plane mirror variety, with a built-in window lens such as to give a focussed image at a distance of one metre. At this distance the sensitivity of the galvanometer was 1509mm./μamp, or 1175mm./μ coulomb. The galvanometer was slightly overdamped and a high sensitivity was obtained. The galvanometer legs were supported on polythene sheet to reduce the possibility of current leakage from the galvanometer, which was high potential.

<u>Photomultiplier tube</u> (E.M.I. type 9415S)

Once installed this was not exposed to illumination except to a darkroom safelight, during the changing of samples. This practice resulted in a very low, constant (except on humid days) dark current. The tube, having a S-type cathode was insensitive to moderate temperature variations.

Scintillation cell



The scintillation cell used is shown in the diagram, the base was glassblown as flat as possible and then ground. The silvering on the exterior, to reflect the maximum amount of light from the scintillating solution onto the light-sensitive cathode, was protected with paint, which was insoluble in organic solvents.

Scintillating solutions

A scintillating solution of p-terphenyl (4g./litre) and wavelength shifter (1,4-di-[2-(5-phenyloxazolyl)]-benzene) (0.01g./litre), in toluene, was used throughout this work. Since the phosphors and solutions are decomposed by ultra-violet light[128] they were kept in the dark. Ultra-violet light also causes the solutions to phosphoresce, an effect which can give rise to anomalous deflections.[129]

The toluene (sulphur-free grade), used in the solutions, was passed down an alumina column since Hayes, Anderson and Langham[130] state that this increases its optical transparency.

During all sets of measurements, constant weights of solutions were measured into the cell, together with a constant volume (ca. 20ml.) of scintillator from an automatic burette. This procedure eliminates any quenching or dilution effects.

The measurement of relative activities.

The cell, containing the solution of tritiated material together with the scintillating solution, was placed on the photomultiplier tube and silicone fluid (MS 550) was used to make optical contact between the cell base and the photomultiplier window. When samples were changed, during a day's series of measurements, the E.H.T. set was left on, but isolated from the tube by a simple throw switch. After allowing two minutes for the cell to settle on the tube, the current was switched on and the current passing, as measured by the deflection in centimetres of the spot of light on the galvanometer scale, was recorded. The process was then repeated, with the cell containing only scintillator solution, to give the dark current deflection of the instrument. The difference between the first deflection and the dark current deflection then gave a measure of the radioactivity of the sample. The deflections were noted within 20 seconds of applying the potential since Pringle, Turchinetz and Funt[131] have stated that the dark current of a photomultiplier tube increases with the time of application of the potential.

The deflections obtained were not steady, but showed a pulsation. This is due, in part, to background radiation interacting with the scintillator, and part due to interaction of cosmic and gamma radiation with the materials of the phototube (thereby releasing electrons in the tube and, possibly also, causing fluorescence in the glass of the tube[132]). The pulsation did not interfere seriously with the reading of the "steady" deflection.

Humidity was found to affect the deflections produced by the tube. Since the deflections were observed to increase with humidity it was assumed that leakage was caused by condensation of moisture upon the leads and the galvanometer. On very humid days, when a large dark current deflection was obtained, measurements were not attempted.

The lower limit of measurement was found to be about $3 \times 10^{-2} \mu$ curies for an accuracy of 2%.

2. Preparation of the acids for kinetic studies.

Seven types of acidic media were used in this work. These were aqueous sulphuric acid, trifluoroacetic acid-aqueous sulphuric acid, trifluoroacetic acid-aqueous perchloric acid, acetic acid-sulphuric acid-water, trifluoroacetic acid-acetic acid, anhydrous trifluoroacetic acid and heptafluorobutyric acid.

For kinetic studies in acetic acid-sulphuric acid-water medium, the tritiated material was dissolved in acetic acid (99.2%), and 10ml. portions of this solution were mixed with 50ml. portions of acetic acid-sulphuric acid-water at the commencement of the rate measurements. For studies in the other media the tritiated material was introduced into the medium just before the rate measurements were carried out.

Aqueous sulphuric acid.

Roughly weighed amounts of 98% sulphuric acid (Medical and Lab. Supplies, Derby) and distilled water were mixed and cooled and accurately weighed portions were made up to 500ml. with distilled water. These solutions (in 25ml. aliquots) were titrated against standard borax solutions, using screened methyl orange as indicator. From the titration figures the strength of the individual acid mixtures were calculated.

98% sulphuric acid (g.)	water (g.)	Solution made up to 500ml water (g.)	Strength of borax (N)	Average titre of borax (ml.)	Strength of acid wt.%
2000	800	3.0347	0.1140	19.20	70.70
2000	700	3.7125	0.1059	26.21	73.25
2000	676	3.2305	0.1112	22.02	74.36
2000	840	3.3196	0.1112	20.99	69.00
2000	740	3.2826	0.1112	21.48	71.41
980	505	2.849	0.1112	16.84	64.50

Acetic acid-sulphuric acid-water.

The sulphuric acid was the same as employed above. The acetic acid was May and Baker "reagent grade" (99.6% pure), and was further purified by the method of Orton and Bradfield.[109] Acetic acid (2.51.) was refluxed for 1.5 hours with chromium trioxide (60g.), and then distilled through a column, 40cm. long, 2cm. in diameter, packed with glass helices. The first 200ml. of distillate were discarded and the next 21. were collected. The water content of the acetic acid was determined by measuring the freezing point since it is known that a depression of 0.2° in the freezing point is equivalent to 0.1% water.[87]

Melting point of pure acetic acid = 16.60°

Melting point of acid used = 15.00°

Therefore water content = 0.8%

		Wt.		Molar Composition
Distilled water	=	526g.	=	34.43%
Sulphuric acid (97.6%)	=	4713g.	=	44.74%
Acetic acid (99.2%)	=	1320g.	=	20.83%

Trifluoroacetic acid-sulphuric acid- water.

Trifluoroacetic acid (supplied by "Kodak Ltd.") was purified by fractionation from 98% sulphuric acid and was estimated as indicated later. The sulphuric acid used was shown by Dr. R. Taylor (by titration against standard borax) to be of strength 97.6%.

		Wt.		Mol. Comp.
Trifluoroacetic acid (100.0%)	=	147.60g.	=	93.00%
Sulphuric acid (97.6%)	=	2.57g.	=	1.88%
Distilled water	=	0.40g.	=	5.12%

Trifluoroacetic acid-perchloric acid-water.

The perchloric acid was shown to be of strength 72.02wt-%.

		Wt.		Mol. Comp.
Trifluoroacetic acid (100.0%)	=	159.05g.	=	99.962%
Perchloric acid (72.02%)	=	0.0250g.	=	0.0102%
Distilled water	=	-	=	0.0278%

Anhydrous trifluoroacetic acid.

Anhydrous trifluoroacetic acid (500ml.) was prepared by fractionally distilling the Eastman Kodak "White Label" acid, first from concentrated sulphuric acid (50ml.) and then from silver trifluoroacetate (5g., kindly donated by Dr. P. Greasley). Titration against standard alkali showed it to be 100.0% pure, and a Karl Fischer titration, in the presence of excess pyridine, indicated that less than 0.01% of water was present.

This was the medium most widely used in the present work and the rate of exchange of [p-^{3}H] toluene was measured in each batch. The rate was found to vary by less than 1%, so that the medium was reproducible

Anhydrous heptafluorobutyric acid.

This was purified by a procedure simillar to the previous acid.

Trifluoroacetic acid-acetic acid-water.

Media of different compositions were prepared by accurate weighing of the two components, trifluoroacetic acid and acetic acid (99.2%), of purity previously discussed.

3. Exchange-rate measurements

Aqueous sulphuric acid.

The medium was used only in the detritiation reactions of [o- and p-^{3}H]-toluene and -t-butylbenzene. To about 260ml. of sulphuric acid, in a 1 litre flask, was added a small quantity of [^{3}H] toluene (0.065ml.) or [^{3}H] t-butylbenzene (0.015ml.). The amounts of aromatic compound used were always less than these quantities so as not to exceed the solubility limit and to ensure the solutions were homogeneous. The flask was sealed, and shaken mechanically for 10 mins., after which five aliquot parts were transfered to boiling tubes of 51-53ml. by means of a 50ml. pipette. (The vapour space above the solution was always small.) A pipette drainage time of 2.5 min. was necessary to give delivery of a constant quantity. The tubes were sealed with Teflon-sleeved stoppers and placed (all at the same time) in a thermostat at 24.84°, maintained to within ±0.02°; the first tube was removed after about 20 min, and others at appropriate time intervals. The contents of each tube were transfered quickly, at a recorded time, to a 250ml. long-necked, conical flask which containing a fixed amount of toluene (10ml.) and about 100g. of crushed ice; the last traces being washed from the reaction tube with water. The flask was sealed with a Teflon-sleeved glass stopper and, held upright, was shaken mechanically for 15 min. The toluene layer was then separated, washed (successively with water, aqueous 10% sodium hydroxide, and water), and dried over sodium sulphate. A weighed amount of the extract (usually 2-5g.) was placed in the counting vessel together with 20ml. of scintillator and the galvanometer reading noted.

Acetic acid-aqueous sulphuric acid

50ml. of the acid mixture was added (a pipette drainage time of 2.5 min. was allowed) to 10ml. of a solution of the tritiated aromatic (ca. 1g./500ml.) in 99.2% acetic acid contained in a tube of 62-63ml.capacity (the vapour space above the solution was as small as possible). Five such tubes were used for each run and treated as described for the previous medium.

Trifluoroacetic acid and heptafluorobutyric acid.

For all runs in anhydrous trifluoroacetic acid alone, or containing sulphuric acid, perchloric acid or acetic acid, and also in anhydrous heptafluorobutyric acid a common technique was used.

A weighed amount of the tritiated aromatic compound was dissolved in a weighed amount of the acid medium (*ca*.5.5ml.). Aliquot parts (1ml.) were pipetted into drawn-out glass tubes of about 1.2ml. capacity, and the tubes were sealed and placed in the thermostat. The residue of the solution was then weighed so that the weight per aliquot part was known. When removed from the thermostat each tube was broken under 10ml. of toluene and 100ml. of 3% aqueous sodium hydroxide. Subsequent procedure was as before, except that, since the mole-ratio of aromatic compound to solvent was larger than the other media, it could not be assumed that a negligible amount of tritium would remain in the aromatic compound at equilibrium.

The exchange reactions in these media were followed at one or more of the following temperatures -10.0° ± 0.02; 24.84° ± 0.02; 40.0° ± 0.05; 70.11° ± 0.05; 110.15° ± 0.05

At -10.0° the aromatic compound was introduced into the acid at -10.0°, samples (*ca*. 1ml.) were then removed at appropriate times with an automatic pipette.

4. Tabulation of Kinetic Results.

Aqueous sulphuric acid.

The rate constants were calculated from the formula $kt = 2.303 \log \frac{D_o}{D_t}$ where D_o is the deflection for the first sample, and D_t that for a sample removed at a time t. Kinetic runs were normally taken to more than 70% completion. Individual rate coefficients varied from the mean by less than ±2% and the mean rate coefficients (determined graphically) could be reproduced to within ±1.5%.

For each run, after giving the compound, the composition of the medium, and the temperature, the results are tabulated as deflection D, in mm., and time T, in hours. The deflection, D, was obtained from the observed galvanometer deflection by subtracting the small deflection (ca.2mm.), resulting from the dark current of the tube, and adjusted to a constant weight of toluene extract (8.8g.- the total toluene extract). All the measurements were made with a potential of 1200 volts across the photomultiplier tube unless otherwise stated.

Run 1 $[o\text{-}^3H]$ toluene

a) 70.7wt.-% 24.84°

T	0.0	0.75	1.85	3.5	5.75
D	132.2	108.0	80.5	51.2	27.5

$k = 751 \times 10^{-7}$ (sec.$^{-1}$)

b) 70.7wt.-% 24.84°

T	0.0	0.75	1.85	3.5	5.75
D	141.2	114.9	86.7	53.5	29.3

$k = 753 \times 10^{-7}$

Run 2 $[p\text{-}{}^{3}\text{H}]$ toluene

a) 70.70wt.-% 24.84°

T	0.0	0.75	2.1	4.6	6.4
D	260.5	213.5	148.5	76.5	47.3

$k = 752 \times 10^{-7}$

b) 70.70wt.-% 24.84

T	0.0	0.75	2.1	4.6	6.4
D	283.0	231.0	159.4	81.6	50.0

$k = 754 \times 10^{-7}$

Run 3 $[p\text{-}{}^{3}\text{H}]$ toluene

a) 73.25wt.-% 24.84°

T	0.0	0.2	0.55	1.0	1.5
D	179.5	147.2	104.2	74.7	39.2

$k = 2715 \times 10^{-7}$

b) 73.25wt.-% 24.84°

T	0.0	0.2	0.55	1.0	1.55
D	179.7	147.8	105.0	69.3	41.3

$k = 2704 \times 10^{-7}$

Run 4 $[o\text{-}{}^{3}\text{H}]$ toluene

a) 73.25wt.-% 24.84°

T	0.0	0.25	0.75	1.5	2.25
D	107.8	84.1	50.7	23.8	11.0

$k = 2793 \times 10^{-7}$

b) 73.25wt.-% 24.84°

T	0.0	0.33	0.75	1.65	2.1
D	35.3	25.2	16.4	6.7	4.3

$k = 2810 \times 10^{-7}$

Run 5 [*p*-^{3}H] toluene

a) 69.00wt.-% 24.84°

T	0.0	1.5	4.35	9.5	22.17
D	113.5	95.5	67.8	38.0	8.73

k = 323 x 10^{-7}

b) 69.00wt.-% 24.84°

T	0.0	1.5	4.35	9.5	22.17
D	120.5	101.5	73.4	39.7	9.4

k = 317 x 10^{-7}

Run 6 [*o*-^{3}H] toluene

a) 69.00wt.-% 24.84°

T	0.0	1.24	3.53	8.28	18.62
D	123.0	106.9	81.5	47.0	14.8

k = 316 x 10^{-7}

b) 69.00wt.-% 24.84°

T	0.0	2.15	6.35	9.2	21.5
D	177.0	138.8	85.5	63.4	16.7

k = 316 x 10^{-7}

Run 7 [*p*-^{3}H]-t-butylbenzene

a) 71.41wt.-% 24.84°

T	0.0	0.75	1.5	3.75	6.0
D	32.0	25.7	20.9	11.55	5.6

k = 806 x 10^{-7}

b) 71.41wt.-% 24.84°

T	0.0	0.7	1.4	2.55	5.5
D	32.3	26.3	21.7	15.3	6.75

k = 804 x 10^{-7}

Run 8 $[\underline{o}\text{-}{}^{3}H]$-t-butylbenzene

a) 71.41wt.-% 24.84°

T	0.0	0.8	1.85	3.23	5.85
D	46.8	37.4	28.2	19.3	9.35

k = 766 x 10^{-7}

b) 71.41wt.-% 24.84°

T	0.0	1.25	2.35	3.8	5.97
D	48.9	34.3	25.8	16.8	7.7

k = 770 x 10^{-7}

Run 9 $[\underline{p}\text{-}{}^{3}H]$ toluene

a) 71.41wt.-% 24.84°

T	0.0	0.75	1.5	2.37	4.65
D	162.5	119.6	91.2	64.4	28.0

k = 1095 x 10^{-7}

b) 71.41wt.-% 24.84°

T	0.0	0.75	1.5	2.37	4.65
D	171.2	126.0	94.5	67.5	28.3

k = 1095 x 10^{-7}

Run 10 $[\underline{p}\text{-}{}^{3}H]$ toluene

a) 74.85wt.-% 24.84°

T	0.0	0.2	0.4	0.6	1.1
D	120.4	84.3	58.7	42.3	17.6

k = 4900 x 10^{-7}

b) 74.85wt.-% 24.84°

T	0.0	0.2	0.4	0.6	0.8
D	127.5	89.4	62.8	44.2	30.5

k = 4930 x 10^{-7}

Run 11 $[o\text{-}^{3}H]$ toluene

a) 74.85wt.-% 24.84°

T	0.0	0.2	0.4	0.617	0.8
D	78.4	54.0	37.0	25.0	17.7

k = 5190 x 10^{-7}

b) 74.85wt.-% 24.84°

T	0.0	0.2	0.4	0.6	0.8
D	84.7	58.4	39.4	27.8	19.1

k = 5180 x 10^{-7}

Run 12 $[p\text{-}^{3}H]$ toluene

a) 64.50wt.-% 24.84°

T	0.0	9.05	21.55	32.9	48.8
D	133.0	112.5	90.2	72.7	56.2

k = 50.7 x 10^{-7}

b) 64.50wt.-% 24.84°

T	0.0	9.05	21.55	32.9	48.8
D	151.0	127.8	102.1	82.6	62.7

k = 50.7 x 10^{-7}

Run 13 $[o\text{-}^{3}H]$ toluene

a) 64.50wt.-% 24.84°

T	0.0	8.95	21.55	35.15	45.65
D	97.9	83.2	66.8	52.2	43.3

k = 49.6 x 10^{-7}

b) 64.50wt.-% 24.84°

T	0.0	8.95	21.55	35.15	45.65
D	104.5	88.9	71.5	55.8	46.3

k = 49.6 x 10^{-7}

Acetic acid - sulphuric acid - water

The tables of runs follow the same form as used in aqueous sulphuric acid. All the runs were measured in the medium: acetic acid (20.83%) - sulphuric acid (44.74%) - water (34.43%), where the figures indicate molar composition.

Run 14 $[2\text{-}^{3}\text{H}]$fluorene

a) 25.0°

T	0.0	0.25	0.5	0.75	1.25
D	73.7	52.0	36.7	26.0	14.0

$k = 3870 \text{ x } 10^{-7}$

b) 25.0°

T	0.0	0.25	0.5	0.75	1.25
D	49.4	34.7	24.2	17.1	8.6

$k = 3930 \text{ x } 10^{-7}$

Run 15 9-methyl-$[2\text{-}^{3}\text{H}]$fluorene

a) 25.0°

T	0.0	0.25	0.5	0.75	1.25
D	76.9	53.7	38.5	27.7	14.4

$k = 3800 \text{ x } 10^{-7}$

b) 25.0°

T	0.0	0.2	0.4	0.75	1.25
D	23.4	17.9	13.4	8.55	4.3

$k = 3790 \text{ x } 10^{-7}$

Run 16 9,9-dimethyl-$[2\text{-}^{3}\text{H}]$fluorene

a) 25.0°

T	0.0	0.25	0.5	0.75	1.25
D	35.7	25.7	18.8	13.8	7.5

$k = 3570 \text{ x } 10^{-7}$

b) 25.0°

T	0.0	0.25	0.50	0.75	1.25
D	29.1	21.2	15.0	10.95	5.9

$k = 3600 \times 10^{-7}$

Run 17 $[9\text{-}^{3}\text{H}]$fluorene

a) 25.0°

T	0.0	14.3	25.2	37.6	49.0
D	47.7	28.3	19.0	11.8	6.45

$k = 102 \times 10^{-7}$

For all the preceding runs on fluorene compounds, solutions of .05g. of the aromatic in acetic acid (250ml.) were used.

Run 18 $[p\text{-}^{3}\text{H}]$toluene

a) 25.0°

T	0.0	0.817	3.05	4.73	7.32
D	99.5	83.8	52.4	37.2	21.3

$k = 582 \times 10^{-7}$

b) 25.0°

T	0.0	0.82	3.05	4.73	7.32
D	45.6	38.6	24.1	17.1	6.8

$k = 580 \times 10^{-7}$

Trifluoroacetic acid - sulphuric acid - water

As previously mentioned the mole-ratio of compound to solvent was larger than in the previous media. The reactions, therefore, did not go to completion and residual deflections were obtained at infinite time (taken, according to the usual practice in kinetic work, as ten half-lifes). It was necessary to deduct from each deflection an amount equal to the deflection at equilibrium. Since some of the half-lifes were very long it was more convenient to calculate the deflection at equilibrium. It was assumed that:-

a) Two hydrogen atoms are available for exchange in each molecule of water and of sulphuric acid.

b) One hydrogen atom is available for each molecule of trifluoroacetic acid.

c) A number of hydrogen atoms are available for exchange in each aromatic molecule. This was estimated in each case by considering the number of hydrogen atoms which would exchange, in the time that it takes for a given position to detritiate. For example:- (i) in benzene, all six positions are available for the tritium at equilibrium, (ii) in *m*-tritiotoluene and *m*-tritio-t-butylbenzene, five positions are available, (iii) but in *p*-tritiotoluene only three positions are available (since tritiation of the *meta*-position will not be appreciable in ten times the half-life of the detritiation). The error in neglecting isotope effects on the equilibrium is insignificant.

The general method of calculating the equilibrium deflection was as follows. The ratio of the number of equivalents of the medium and the aromatic compound were predetermined in each run, by weighing each component (the equivalent weight is obtained by dividing the molecular weight by the number of exchangeable hydrogen atoms). The deflection due to the known weight of aromatic compound dissolved in the medium was calculated (to within about 5%) from a knowledge of the specific deflection of the aromatic compound; the specific deflection was determined for a weight of aromatic compound of the order of that dissolved in the medium since the specific deflection alters with weight of tritiated material. It was possible, therefore, to calculate the deflection that would be obtained from the total toluene extract (8.8g.) if the extraction was performed immediately after the aromatic compound was dissolved in the acidic medium; hence it was possible to calculate the equilibrium deflection for a 10ml. extracted sample. This equilibrium deflection was then deducted from the deflection actually obtained for each extracted 10ml. sample. Since the equilibrium deflection was general less than 5% of the observed deflections during kinetic runs, any errors due to the approximations would have little affect on the corrected deflections.

The mole percentages of the acid medium were:- trifluoroacetic acid (93.00%)-sulphuric acid (1.88%)-water(5.12%), so that the number of equivalents per gram of the medium was 0.00983.

The result tables are given as in the previous media, but details for the calculation of the equilibrium deflection are recorded. For simplification the results are given in the following form:- A: Temperature at which the run was measured, B: The number of hydrogen atoms in the aromatic compound that can exchange in ten times the half life of the detritiation reaction, C: Weight of acid mixture in g., E: Weight of the tritiated aromatic compound, F: Weight remaining after sealing the five samples, G: The specific deflection of the tritiated aromatic compound (deflection in mm./weight of aromatic compound in g.), H: The calculated percentage reaction at equilibrium, I: The calculated equilibrium deflection.

The results are tabulated as deflection D, in mm., and time T, in hours. The deflection, D, was obtained from the observed galvanometer deflection by subtracting the small dark current deflection and adjusting to a constant weight of toluene extract, the measured or calculated equilibrium deflection has then been subtracted to give the true deflection (D). All the measurements were made with a potential of 1200 volts across the photomultiplier tube unless otherwise stated.

The calculation of the equilibrium deflection is recorded in detail for the first run in this medium.

Run 19 $\left[\underline{o}\text{-}{}^{3}H\right]$-t-butylbenzene

Temperature (A) - 24.84°. The number of hydrogen atoms in $\left[\underline{o}\text{-}{}^{3}H\right]$-t-butylbenzene that can exchange in 10 x the half life of the detritiation reaction = 3. (B)

Weight of acid mixture (C) = 7.8353g. = 0.07703 equivalents

Weight of $\left[\underline{o}\text{-}{}^{3}H\right]$-t-butylbenzene (E) = 0.065g. = 0.00146 equivs.

Weight remaining after sealing five samples (F) = 0.4085g.

Thus the average weight per sample = 1.498g.

The deflection due to 0.0092g. of [o-^{3}H]-t-butylbenzene = 217.5 (mm.)

Thus the initial deflection per sample = $\frac{217.5 \times 1.498 \times 0.065}{7.89 \times 0.0092}$

= 292.0mm.

Since the reaction goes $\frac{0.07703}{0.07849} \times 100\%$ = 98.1%, then the equilibrium deflection = $\frac{292 \times (100-98.1)}{100}$ = 5.6mm.

T	0.0	0.75	1.5	2.583	4
D	230.6	150.6	100	52.6	25.0

$k = 1558 \times 10^{-7}$

b) A = 24.84°, B = 3, C = 7.8095g., E = 0.0599g.,

F = 0.3984g., G = 217.5mm./0.0092g., H = 98.3%, I = 4.6mm.

T	0.0	0.75	1.5	2.35	4.1
D	189.2	123.6	79.3	49.9	19.0

$k = 1573 \times 10^{-7}$

Run 20 [p-^{3}H]-t-butylbenzene

a) A = 24.84°, C = 7.8181g., B = 3, E = 0.0713g.

F = 0.4373g., G = 215.1mm./0.0084g., H = 98.0%, I = 6.4mm.

T	0.0	0.4	1.0	1.5	2.25
D	234.4	169.6	106.9	71.9	40.6

$k = 2170 \times 10^{-7}$

b) A = 24.84°, B = 3, C = 7.8184g., E = 0.0650g.

F = 0.4042g., G = 215.1mm./0.0084g., H = 98.1%, I = 5.5mm.

T	0.0	0.4	1.0	1.5	2.25
D	223.5	162.0	100.8	69.1	37.6

k = 2200 x 10-7

Run 21 $[\underline{p}\text{-}^{3}\mathrm{H}]$ toluene

a) A = 24.84°, B = 3, C = 7.8296g., E = 0.0603g.

F = 0.0430g., G = 368.6mm./0.0183g., H = 98.3%, I = 3.9mm.

T	0.0	0.4	1.0	1.5	2.5
D	273.1	210.4	145.1	105.4	55.9

k = 1765 x 10^{-7}

b) A = 24.84°, B = 3, C = 7.8412g., E = 0.0632g.,

F = 0.3014g., G = 285.7mm./0.0096g., H = 98.2%, I = 6.5mm.

T	0.0	0.5	1.1	1.5	2.0
D	277.8	200.5	136.3	109.0	79.2

k = 1775 x 10^{-7}

Run 22 $[\underline{o}\text{-}^{3}\mathrm{H}]$ toluene

a) A = 24.84°, B = 3, C = 7.7920g., E = 0.0813g.,

F = .3328g., G = 368.6mm./0.0183g., H = 97.7%, I = 7.4mm.

T	0.0	0.5	1.0	1.5	2.5
D	267.1	211.6	167.6	131.9	85.6

k = 1295 x 10^{-7}

b) A = 24.84°, C = 7.8287g., B = 3, E = 0.0616g.,

F = 0.4433g., G = 368.6mm./0.0183g., H = 98.2%,. I = 4.3mm.

T	0.0	0.4	1.0	1.83	2.50
D	213.9	176.9	133.3	89.0	66.0

k = 1295 x 10^{-7}

Trifluoroacetic acid - perchloric acid - water

The equilibrium deflections in this medium were calculated in the same way as the previous medium. It was assumed that one hydrogen atom was available for exchange in each molecule of perchloric acid.

The molar composition of the medium was trifluoroacetic acid (99.962%) - perchloric acid (0.0102%) - water (0.0278%); the number of equivalents per gram of this medium was 0.008817.

Run 23 $[2\text{-}^{3}\text{H}]$fluorene

a) A = 25.0°, B = 3, C = 7.5729g., E = 0.0153g.,
F = 0.4777g., G = 159.6mm./0.0052g., H = 99.6%, I = 0.35mm.

T	0.0	0.25	0.50	0.75	1.25
D	59.65	45.45	35.25	26.65	16.2

$k = 2975 \times 10^{-7}$

b) A = 25.0°, B = 3, C = 7.6644g., E = 0.0125g.,
F = 0.5035g., G = 159.6mm./0.0052g., H = 99.6%, I = 0.6mm.

T	0.0	0.25	0.50	0.75	1.25
D	59.2	45.3	35.2	26.5	15.8

$k = 2930 \times 10^{-7}$

Run 24 $[2\text{-}^{3}\text{H}]$-9-methylfluorene

a) A = 25.0°, B = 3, C = 7.5567g., E = 0.0166g.,
F = 0.4672g., G = 310.4mm./0.0109g., H = 99.6%, I = 0.6mm.

T	0.0	0.25	0.50	0.75	1.25
D	49.85	37.65	27.75	21.75	12.4

$k = 3110 \times 10^{-7}$

b) A = 25.0°, B = 3, C = 7.6347g., E = 0.0139g.,
F = 0.4835g., G = 310.4mm./0.0109g., H = 99.6%, I = 0.6mm.

T	0.0	0.25	0.50	0.75	1.25
D	55.5	41.9	31.6	23.6	13.6

$k = 3120 \times 10^{-7}$

Run 25 9,9-dimethyl-$[2\text{-}^{3}H]$fluorene

a) A = 25.0°, B = 3, C = 7.5989g., E = 0.0183g.,

F = 0.4570g., G = 152.2mm./0.0049g., H = 99.6%,, I = 0.4mm.

T	0.0	0.2	0.4	0.6	0.8
D	54.1	40.6	30.1	22.8	16.9

$k = 4010 \times 10^{-7}$

b) A = 25.0°, B = 3, C = 7.5800g., E = 0.0171g.,

F = 0.4593g., G = 152.2mm./0.0049g., H = 99.6%, I = 0.6mm.

T	0.0	0.2	0.417	0.65	0.9
D	50.5	38.1	27.5	20.4	14.0

$k = 3950 \times 10^{-7}$

Run 26 $[p\text{-}^{3}H]$toluene

A = 25.0°, B = 3, C = 7.6157g., E = 0.0502g.,

F = 0.5183g., G = 155.2mm./0.0056g., H = 97.6%, I = 0.6mm.

T	0.0	2.0	4.5	7.9	20.5
D	201.0	167.3	133.3	95.7	29.6

$k = 256 \times 10^{-7}$

Anhydrous heptafluorobutyric acid

The equilibrium deflections were calculated as previously described; it was assumed that one hydrogen atom was available for exchange in each molecule of heptafluorobutyric acid.

Run 27 $[p\text{-}^{3}H]$toluene

a) A = 70.11°, C = 8.3982g., E = 0.0367g., B = 3,

F = 0.8110g., G = 288mm./0.0088g., H = 97.2%, I = 6.1mm.

T	0.0	118.7	224.2	297.7	387.4
D	153.9	112.9	87.2	71.7	57.6

$k = 7.10 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 8.4145g., E = 0.0343g.,

F = 0.3166g., G = 266.4mm./0.0072g., H = 97.2%, I = 6.8mm.

T	0.0	75.3	195.2	362.4	530.7
D	179.0	146.2	109.2	72.1	46.2

$k = 7.06 \times 10^{-7}$

Run 28 [p-^{3}H]-t-butylbenzene

a) A = 70.11°, B = 3, C = 8.4108g., E = 0.0439g.,

F = 0.3524g., G = 232.7mm./0.0104g., H = 97.6%. I = 4.7mm.

T	0.0	73.5	194.1	361.6	529.5
D	199.3	156.8	108.6	63.0	36.2

$k = 8.90 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 8.3374g., E = 0.0418g.,

F = 0.2107g., G = 232.7mm./0.0104g., H = 97.6%, I = 4.4mm.

T	0.0	72.3	239.4	335.1	498.5
D	210.4	162.1	97.3	70.1	41.9

$k = 8.98 \times 10^{-7}$

Run 29 [o-^{3}H] toluene

a) A = 70.11°, B = 3, C = 8.4554g., E = 0.0498g.,

F = 0.2573g., G = 210.0mm./0.0096g., H = 96.1%, I = 8.4mm.

T	0.0	169.3	337	673.5	1057
D	178.6	151.0	127.3	89.3	63.7

$k = 2.79 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 8.4483g., E = 0.0377g.,

F = 0.3225g., G = 210.0mm./0.0096g., H = 97.0%. I = 4.7mm.

T	0.0	168.3	335.9	687.5	984.7
D	148.3	125.5	104.6	74.5	56.7

$k = 2.79 \times 10^{-7}$

Run 30 $[\underline{o}\text{-}^{3}\text{H}]$-t-butylbenzene

a) A = 70.11°, C = 8.4181g., B = 3, E = 0.0457g.,

F = 0.2931g., G = 228.2mm./0.0101g., H = 97.5%, I = 5.0mm.

T	0.0	168.0	335.5	687.5	984.7
D	206.0	168.0	137.0	90.9	62.4

$k = 3.36 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 8.4990g., E = 0.0425g.,

F = 0.3399g., G = 228.2mm./0.0101g., H = 97.7%, I = 4.2mm.

T	0.0	173	341.5	677.4
D	193.1	156.9	129.1	85.9

$k = 3.32 . \times 10^{-7}$

Run 31 $[\underline{p}\text{-}^{3}\text{H}]$ biphenyl

a) A = 70.11°, B = 4, C = 10.2197g., E = 0.0212g.,

F = 1.5217g., G = 420.0mm./0.0040g., H = 98.3%, I = 7.2mm.

T	0.0	335.8	672.2	1006	1335
D	418.8	252.4	151.6	91.8	55.3

$k = 4.22 \times 10^{-7}$

b) A = 70.11°, B = 4, C = 9.5370g., E = 0.0212g.,

F = 0.8010g., G = 370.0mm./0.0040g., H = 98.1%, I = 7.5mm.

T	0.0	334.1	669.5	1006	1335
D	382.0	230.0	132.7	79.4	47.0

$k = 4.34 \times 10^{-7}$

Run 32 $[\underline{o}\text{-}^{3}\text{H}]$ biphenyl

a) A = 70.11°, B = 6, C = 9.2610g., E = 0.0239g.,

F = 0.4610g., G = 154.5mm./0.0040g., H = 97.9%, I = 3.7mm.

T	0.0	344.3	847.5	1345	1729
D	168.3	135.1	95.5	69.0	53.7

$k = 1.84 \times 10^{-7}$

b) A = 70.11°, B = 6, C = 8.8203g., E = 0.0317g.,
F = 0.0203g., G = 136.4mm./0.0040g., H = 97.2%, I = 6.1mm.

T	0.0	552	800	1032	1536
D	214.0	149.7	128.1	112.2	78.4

$k = 1.80 \times 10^{-7}$

Anhydrous trifluoroacetic acid

The equilibrium deflections were calculated as described for previous media assuming that one hydrogen atom was available for exchange in each molecule of trifluoroacetic acid.

Run 33 $[p\text{-}^{3}\text{H}]$ toluene

a) A = 70.11°, B = 3, C = 7.6611g., E = 0.0505g.,
F = 0.5692g., G = 155.8mm./0.0056g., H = 97.0%, I = 0.6mm.

T	0.0	47.9	120.1	191.7	284.9
D	212.7	96.5	31.7	9.45	1.75

$k = 43.0 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 7.5378g., E = 0.0478g.,
F = 0.4914g., G = 109.0mm./0.0054g., H = 97.7%, I = 0.5mm.

T	0.0	1588	25.25	47.95	73.65
D	197.7	154.0	134.7	94.1	66.1

$k = 42.4 \times 10^{-7}$

Run 34 $[p\text{-}^{3}\text{H}]$-t-butylbenzene

a) A = 70.11°, B = 3, C = 7.5452g., E = 0.0491g.,
F = 0.5025g., G = 174.5mm./0.0089g., H = 98.4%, I = 0.5mm.

T	0.0	14.15	23.6	46.25	71.85
D	157.6	120.6	102.1	68.7	42.9

$k = 51.0 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 7.6133g., E = 0.0584g.,
F = 0.0633g., G = 174.5mm./0.0089g., H = 98.5%, I = 0.5mm.

T	0.0	10.65	23.9	35.15	54.95
D	135.8	112.2	88.0	71.5	48.4

$\underline{k = 50.8 \text{ x } 10^{-7}}$

<u>Run 35</u> [$\underline{o}$-^{3}H]-t-butylbenzene

a) A = 70.11°, B = 3, C = 7.6220g., E = 0.0479g.,
F = 0.5380g., G = 170.4mm./0.0093g., H = 98.4%, I = 2.6mm.

T	0.0	75.35	152.2	246.8	248.8
D	146.9	78.9	40.2	18.9	18.55

$\underline{k = 23.0 \text{ x } 10^{-7}}$

b) A = 70.11°, B = 3, C = 7.6319g., E = 0.0584g.,
F = 0.5869g., G = 147.1mm./0.0068g., H = 98.1%, I = 0.5mm.

T	0.0	23.50	47.65	82.65	143.8
D	180.6	146.1	118.4	88.6	53.5

$\underline{k = 23.0 \text{ x } 10^{-7}}$

<u>Run 36</u> [$\underline{o}$-^{3}H] toluene

a) A = 70.11°, B = 3, C = 7.6484g., E = 0.0460g.,
F = 0.5813g., G = 171.2mm./0.0090g., H = 97.7%, I = 0.6mm.

T	0.0	76.9	153.8	247.4	250.5
D	138.3	74.1	42.1	20.7	21.1

$\underline{k = 20.8 \text{ x } 10^{-7}}$

b) A = 70.11°, B = 3, C = 7.5470g., E = 0.0496g.,
F = 0.5022g., G = 181.8mm./0.0094g., H = 97.6%, I = 0.5mm.

T	0.0	23.75	47.95	82.8	144.1
D	166.2	139.6	114.2	90.5	56.3

$\underline{k = 20.8 \text{ x } 10^{-7}}$

Run 37 $[2\text{-}^{3}H]$dibenzothiophen

a) A = 70.11°, B = 2.5, C = 7.6486g., E = 0.0105g.,

F = 0.1739g., G = 247.3mm./0.0069g., H = 99.8%, I = 0.7mm.

T	0.0	5.2	17.9	29.35	43.45
D	74.3	53.7	23.4	11.84	5.27

$k = 174 \times 10^{-7}$

b) A = 70.11°, B = 2.5, C = 7.6612g., E = 0.0100g.,

F = 0.1612g., G = 247.3mm./0.0069g., H = 99.8%, I = 0.2mm.

T	0.0	5.0	10.45	23.3	27.1
D	71.5	52.5	37.5	16.6	13.1

$k = 174 \times 10^{-7}$

Run 38 $[4\text{-}^{3}H]$dibenzothiophen

a) A = 70.11°, B = 8, C = 7.7938g., E = 0.0092g.,

F = 0.3438g., G = 172.4mm./0.0092g., H = 99.4%, I = 0.2mm.

T	0.0	17.7	43.75	89.8	100.9
D	31.4	24.9	18.0	10.35	9.13

$k = 34.4 \times 10^{-7}$

b) A = 70.11°, B = 8, C = 8.4236g., E = 0.0088g.,

F = 1.0076g., G = 172.4mm./0.0092g., H = 99.5%, I = 0.1mm.

T	0.0	26.05	50.2	73.65	96.8
D	26.1	18.8	14.05	10.4	8.04

$k = 34.4 \times 10^{-7}$

Run 39 $[2\text{-}^{3}H]$dibenzofuran

a) A = 70.11°, B = 2.5, C = 9.9213g., E = 0.0163g.,

F = 0.9866g.(6 samples), G = 113.3mm./0.0032g., H = 99.8%,

I = 0.2mm.

T	0.0	1.6	4.2	6.9	10.25
D	74.5	60.8	44.3	31.8	21.3

$\underline{k = 345 \times 10^{-7}}$

b) A = 70.11°, B = 2.5, C = 7.6072g., E = 0.0165g.,
F = 0.1866g., G = 113.3mm./0.0032g., H = 99.6%, I = 0.5mm.

T	0.0	1.9	5.9	10.45	22.65
D	84.7	66.5	40.3	22.2	4.07

$\underline{k = 353 \times 10^{-7}}$

Run 40 $[4\text{-}{}^{3}H]$dibenzofuran

a) A = 70.11°, B = 8, C = 7.8394g., E = 0.0177g.,
F = 0.4230g., G = 253.2mm./0.0048g., H = 99.0%, I = 1.8mm.

T	0.0	48.0	94.9	168.7	213.0
D	107.5	79.9	62.0	41.8	32.6

$\underline{k = 15.0 \times 10^{-7}}$

b) A = 70.11°, B = 8, C = 7.8469g., E = 0.0185g.,
F = 0.4344g., G = 253.2mm./0.0048g., H = 99.1%, I = 1.7mm.

T	0.0	27.2	63.85	99.0	166.7
D	122.7	105.6	83.3	69.9	51.2

$\underline{k = 15.4 \times 10^{-7}}$

Run 41 $[2\text{-}{}^{3}H]$diphenyl ether

a) A = 70.11°, B = 6, C = 7.7039g., E = 0.0224g.,
F = 0.2429g., G = 262.0mm./0.0037g., H = 98.9%, I = 3.4mm.

T	0.0	0.9	2.1	4.0	6.0
D	211.1	168.6	127.3	81.9	51.8

$\underline{k = 660 \times 10^{-7}}$

b) A = 70.11°, B = 6, C = 7.8110g., E = 0.0265g.,
F = 0.3466g., G = 262.0mm./0.0037g., H = 98.7%, I = 4.7mm.

T	0.0	1.0	2.50	4.0	6.0
D	232.3	182.0	128.6	91.1	57.6

k = 656 x 10^{-7}

Run 42 [4-^{3}H] diphenyl ether

a) A = 70.11°, B = 2.5, C = 7.7596g., E = 0.0237g.,
F = 0.3369g., G = 288.4mm./0.0044g., H = 99.5%, I = 1.5mm.

T	0.0	0.25	0.50	1.0	1.50
D	187.2	143.3	110.1	64.2	38.6

k = 2950 x 10^{-7}

b) A = 70.11°, B = 2.5, C = 7.7538g., E = 0.0274g.,
F = 0.3376g., G = 288.4mm./0.0044g., H = 99.5%, I = 1.7mm.

T	0.0	0.25	0.50	1.0	1.5
D	192.9	151.1	114.4	67.9	40.3

k = 2910 x 10^{-7}

c) A = 24.84°, B = 2.5, C = 8.1569g., E = 0.0431g.,
F = 1.0611g., G = 266.8mm./0.0052g., H = 99.1%, I = 3.5mm.

T	0.0	5.95	21.0	30.35	44.85
D	248.5	226.0	177.0	152.5	121.7

k = 44.8 x 10^{-7}

d) A = 24.84°, B = 2.5, C = 7.8470g., E = 0.0303g.,
F = 0.6011g., G = 266.8mm./0.0052g., H = 99.4%, I = 1.7mm.

T	0.0	8.55	25.65	55.85	80.35
D	200.3	174.5	133.5	82.3	55.0

k = 44.4 x 10^{-7}

Run 43 [2-^{3}H]diphenyl sulphide

a) A = 70.11°, C = 10.8307g., E = 0.0308g., F = 1.8839g., (6 samples). The equilibrium deflection, determined experimentally, was found to be 36.0mm.

T	0.0	3.5	8.1	10.7	23.75
D	122.3	81.7	47.5	35.3	8.3

$k = 323 \times 10^{-7}$

b) A = 70.11°, C = 12.8736g., E = 0.0253g., F = 2.4459g., (6 samples). The equilibrium deflection, determined experimentally, was found to be 32.5mm.

T	0.0	2.05	6.2	8.1	10.5
D	90.3	71.6	43.9	38.3	29.2

$k = 309 \times 10^{-7}$

Run 44 [4-^{3}H]diphenyl sulphide

a) A = 70.11°, C = 7.5981g., B = 2.5, E = 0.0402g., F = 0.1697g., G = 283.2mm./0.0075g., H = 99.3%, I = 2.1mm.

T	0.0	1.15	2.85	5.15	7.0
D	298.7	200.9	111.9	55.4	31.1

$k = 935 \times 10^{-7}$

b) A = 70.11°, B = 2.5, C = 7.6021g., E = 0.0269g., F = 0.1062g., G = 283.2mm./0.0075g., H = 99.4%, I = 1.2mm.

T	0.0	1.0	2.0	4.0	6.15
D	244.8	173.8	124.8	64.2	32.3

$k = 933 \times 10^{-7}$

Run 45 [2-^{3}H]benzothiophen

a) A = 70.11°, B = 2, C = 7.6217g., E = 0.0191g.,

F = 0.1217g., G = 256.4mm./0.0039g., H = 99.6%, I = 1.0mm.

T	0.0	0.05	0.10	0.15	0.20
D	69.2	47.8	32.4	23.0	16.6

k = 20,300 x 10^{-7}

b) A = 24.84°, B = 2, C = 8.1978g., E = 0.0174g.,

F = 0.8078g., G = 256.4mm./0.0039g., H = 99.7%, I = 0.6mm.

T	0.0	1.1	3.45	6.05	9.45
D	127.4	107.0	76.0	50.9	31.2

k = 422 x 10^{-7}

c) A = 24.84°, B = 2, C = 7.7354g., E = 0.0175g.,

F = 0.2454g., G = 256.4mm./0.0039g., H = 99.6%, I = 0.9mm.

T	0.0	2.0	4.0	7.5	10.0
D	162.0	119.6	88.3	53.0	35.2

k = 420 x 10^{-7}

d) A = 40.0°, B = 2, C = 8.271g., E = 0.0361g.,

F = 0.5160g., G = 200.0mm./0.0043g., H = 99.3%, I = 2.2mm.

T	0.0	0.25	0.50	1.05	1.5
D	216.0	184.0	155.8	109.9	81.5

k = 1800 x 10^{-7}

e) A = 40.0°, B = 2, C = 8.0240g., E = 0.0316g.,

F = 0.2720g., G = 200.0mm./0.0043g., H = 97.4%, I = 1.7mm.

T	0.0	0.5	1.0	1.6	2.25
D	172.5	126.0	90.6	61.1	39.9

k = 1820 x 10^{-7}

Run 46 $[3\text{-}^{3}H]$benzothiophen

a) A = 24.84°, B = 2, C = 7.6852g., E = 0.0192g.,
F = 0.2912g., G = 389.5mm./0.0058g., H = 99.6%, I = 1.0mm.

T	0.0	0.75	2.05	3.75	6.05
D	162.6	136.9	103.1	71.3	42.4

$k = 610 \times 10^{-7}$

b) A = 24.84°, B = 2, C = 7.7151g., E = 0.0152g.,
F = 0.3136g., G = 389.5mm./0.0058g., H = 99.7%, I = 0.6mm.

T	0.0	1.0	2.0	4.1	6.45
D	119.9	98.0	77.5	50.7	30.8

$k = 590 \times 10^{-7}$

c) A = 40.0°, B = 2, C = 8.2400g., E = 0.0210g.,
F = 0.5194g., G = 389.5mm./0.0058g., H = 99.6%, I = 1.1mm.

T	0.0	0.25	0.50	1.0	1.55
D	117.6	95.8	77.3	49.8	29.0

$k = 2526 \times 10^{-7}$

d) A = 40.0°, B = 2, C = 8.2640g., E = 0.0212g.,
F = 0.4927g., G = 194.0mm./0.0058g., H = 99.6%, I = 0.5mm.

T	0.0	0.3	0.5	1.0	1.5
D	116.5	88.1	74.4	47.8	30.6

$k = 2500 \times 10^{-7}$

e) A = 70.11°, B = 2, C = 7.7065g., E = 0.0180g.,
F = 0.3049g., G = 389.5mm./0.0058g., H = 99.6%, I = 0.9mm.

T	0.0	0.05	0.1	0.15	0.2
D	61.3	39.0	25.1	17.25	10.64

$k = 24{,}500 \times 10^{-7}$

f) A = 70.11°, B = 2, C = 7.6658g., E = 0.0111g.,
F = 0.1692g., G = 389.5mm./0.0058g., H = 99.8%, I = 0.3mm.

T	0.0	0.05	0.1	0.15	0.35
D	39.7	26.2	17.05	11.17	2.87

$k = 23,500 \times 10^{-7}$

Run 47 $[1\text{-}^{3}\mathrm{H}]$dibenzothiophen

a) A = 70.11°, B = 8, C = 7.8366g., E = 0.0149g.,
F = 0.4289g., G = 111.2mm./0.0041g., H = 99.1%, I = 0.7mm.

T	0.0	30.2	70.7	95.4	142.8
D	55.2	41.8	28.5	22.6	14.6

$k = 25.8 \times 10^{-7}$

b) A = 70.11°, B = 8, C = 8.1897g., E = 0.0120g.,
F = 0.8287g., G = 111.2mm./0.0041g., H = 99.3%, I = 0.4mm.

T	0.0	20.7	45.0	71.1	104.3
D	48.9	40.8	32.0	25.2	19.1

$k = 25.8 \times 10^{-7}$

Run 48 $[3\text{-}^{3}\mathrm{H}]$dibenzothiophen

a) A = 70.11°, B = 7, C = 10.2997g., E = 0.0187g.,
F = 2.9774g., G = 194.5mm./0.0058g., H = 99.3%, I = 0.6mm.

T	0.0	28.5	55.4	105.2	169.4
D	77.2	50.2	33.6	17.0	6.98

$k = 41.0 \times 10^{-7}$

b) A = 70.11°, B = 7, C = 10.3060g., E = 0.0142g.,
F = 2.9860g., G = 194.5mm./0.0058g., H = 99.4%, I = 0.3mm.

T	0.0	14.85	48.0	68.9	90.9
D	66.0	53.0	32.9	24.5	19.0

$k = 40.6 \times 10^{-7}$

Run 49 $[1\text{-}^{3}\text{H}]$dibenzofuran

a) A = 70.11°, B = 8, C = 7.9300g., E = 0.0235g.,

F = 0.6084g., G = 170.7mm./0.0034g., H = 98.4%, I = 3.5mm.

T	0.0	48.4	96.7	208.3	328.6
D	129.4	102.7	82.1	50.3	29.8

k = 12.8 x 10^{-7}

b) A = 70.11°, B = 8, C = 7.8488g., E = 0.0259g.,

F = 0.5056g., G = 170.7mm./0.0034g., H = 98.2%, I = 4.3mm.

T	0.0	47.20	116.3	294.0
D	147.2	118.4	84.6	37.5

k = 12.8 x 10^{-7}

Run 50 $[3\text{-}^{3}\text{H}]$dibenzofuran

a) A = 70.11°, B = 8, C = 7.9234g., E = 0.0195g.,

F = 0.5116g., G = 224.5mm./0.0041g., H = 98.8%, I = 1.4mm.

T	0.0	28.3	68.75	93.75	145.3
D	143.1	106.4	67.6	51.5	30.6

k = 29.7 x 10^{-7}

b) A = 70.11°, B = 8, C = 7.9043g., E = 0.0210g.,

F = 0.5727g., G = 224.5mm./0.0041g., H = 98.7%, I = 1.8mm.

T	0.0	21.95	46.85	87.7	135.4
D	153.2	121.2	92.7	57.7	36.1

k = 29.7 x 10^{-7}

Run 51 $[9\text{-}^{3}\text{H}]$phenanthrene

a) A = 70.11°, B = 4, C = 8.2676g., E = 0.0132g.,

F = 0.9476g., the equilibrium deflection was negligeable.

T	0.0	3.95	8.05	22.15	29.05
D	40.5	32.6	25.6	11.9	8.45

k = 153 x 10^{-7}

b) A = 70.11°, B = 4, C = 10.2848g., E = 0.0178g.,

F = 1.8394g., the equilibrium deflection was negligeable

T	0.0	4.4	8.25	22.15	31.85
D	44.2	34.5	27.8	13.1	8.0

$k = 153 \times 10^{-7}$

Run 52 $[4\text{-}^{3}H]$ diphenylmethane

a) A = 70.11°, B = 3, C = 7.7788g., E = 0.0314g.,

F = 0.4501g., G = 119.1mm./0.0025g., H = 99.2%, I = 2.3mm.

T	0.0	49.85	114.0	192.5	282.0
D	158.0	130.6	101.6	74.3	51.6

$k = 10.9 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 7.8669g., E = 0.0312g.,

F = 0.5022g., G = 119.1mm./0.0025g., H = 99.3%, I = 2.0mm.

T	0.0	54.45	102.0	150.2	214.7
D	161.6	130.2	105.6	87.0	68.4

$k = 11.2 \times 10^{-7}$

Run 53 $[2\text{-}^{3}H]$ fluorene

a) A = 70.11°, B = 3, C = 7.8586g., E = 0.0196g.,

F = 0.4693g., G = 301.2mm./0.0061g., H = 99.5%, I = 0.9mm.

T	0.0	0.5	1.1	1.85	2.7
D	84.1	63.1	44.7	29.0	17.85

$k = 1596 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 7.8954g., E = 0.0197g.,

F = 0.5454g., G = 301.2mm./0.0061g., H = 99.5%, I = 0.7mm.

T	0.0	0.6	1.0	1.75	2.5
D	89.8	63.8	50.7	32.1	21.4

$k = 1600 \times 10^{-7}$

Run 54 9-methyl-$[2-{}^{3}H]$fluorene

a) A = 70.11°, B = 3, C = 7.8223g., E = 0.0224g.,

F = 0.4548g., G = 310.4mm./0.0109g., H = 99.5%, I = 0.6mm.

T	0.0	0.5	1.1	2.0	2.75
D	82.0	61.4	43.2	25.6	16.2

$k = 1645 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 7.9520g., E = 0.0249g.,

F = 0.5943g., G = 310.4mm./0.0109g., H = 99.5%, I = 0.8mm.

T	0.0	0.5	1.2	1.9	2.75
D	98.2	66.1	44.1	28.0	16.8

$k = 1685 \times 10^{-7}$

Run 55 9,9-dimethyl-$[2-{}^{3}H]$fluorene

a) A = 70.11°, B = 3, C = 7.8226g., E = 0.0189g.,

F = 0.4976g., G = 301.2mm./0.0061g., H = 99.6%, I = 0.7mm.

T	0.0	0.5	1.0	1.5	2.7
D	79.9	57.2	40.7	29.0	12.7

$k = 1890 \times 10^{-7}$

b) A = 70.11°, B = 3, C = 7.8252g., E = 0.0206g.,

F = 0.4752g., G = 271.6mm./0.0082g., H = 99.5%, I = 1.2mm.

T	0.0	0.55	1.0	1.75	2.25
D	77.7	54.1	39.6	23.4	16.2

$k = 1904 \times 10^{-7}$

Run 56 $[2-{}^{3}H]$benzofuran

a) A = 70.11°, B = 2, C = 7.9216g., E = 0.0230g.,

F = 0.7754g., G = 360.6mm./0.0060g., H = 99.4%, I = 1.5mm.

T	0.0	0.50	1.25	2.0	3.0
D	197.3	152.3	120.0	97.9	94.4

$k = 1600 \times 10^{-7}$

b) A = 70.11°, B = 2, C = 7.6526g., E = 0.02460g.,
F = 0.5993g., G = 360.6mm./0.0060g., H = 99.4%, I = 1.6mm.

T	0.0	0.50	1.4	2.55	3.95
D	200.9	161.4	129.3	112.2	103.1

$k = 1630 \times 10^{-7}$

In both a) and b) of this run the results, when plotted, gave curves and not linear plots. The rate constants (k) were obtained by drawing tangents to the curves at zero time.

Run 57 $[2\text{-}^{3}H]$ thiophen

a) A = 24.84°, B = 2, C = 7.8470g., E = 0.0650g.,
F = 0.4820g., G = 345.3mm./0.0054g., H = 98.4%, I = 9.3mm.

T	0.0	0.0167	0.0334	0.05	0.0667
D	89.0	58.3	36.0	24.2	15.6

$k = 73{,}000 \times 10^{-7}$

b) A = 24.84°, B = 2, C = 7.8151g., E = 0.0444g.,
F = 0.7551g., G = 345.3mm./0.0054g., H = 98.8%, I = 7.6mm.

T	0.0	0.0167	0.0334	0.05	0.0667
D	48.3	31.0	20.0	12.9	9.0

$k = 73{,}400 \times 10^{-7}$

c) A = -10.0°, B = 2, C = 8.5724g., E = 0.0736g.,
F = 1.3724g., G = 345.3mm./0.0054g., H = 98.6%, I = 3.3mm.

T	0.0	0.2	0.45	0.85	1.7
D	408.9	344.0	280.2	196.9	96.0

$k = 2380 \times 10^{-7}$

d) A = -10.0°, B = 2, C = 8.520g., E = 0.0745g.,
F = 1.3200g., G = 345.3mm./0.0054g., H = 98.6%, I = 3.3mm.

T	0.0	0.45	0.8	1.1	1.65
D	409.9	282.0	208.9	157.2	102.3

$\underline{k = 2340 \times 10^{-7}}$

<u>Run 58</u> $[3\text{-}^3H]$ thiophen

a) A = 24.84°, B = 4, C = 7.8770g., E = 0.0221g.,
F = 0.7882g., G = 178.6mm./0.0061g., H = 98.5%, I = 1.7mm.

T	0.0	17.85	27.3	60.0	80.0
D	27.4	23.0	21.0	15.3	12.5

$\underline{k = 27.2 \times 10^{-7}}$

b) A = 24.84°, B = 4, C = 7.8800g., E = 0.0230g.,
F = 0.7800g., G = 178.6mm./0.0061g., H = 98.5%, I = 1.7mm.

T	0.0	16.0	40.0	62.0	88.0
D	34.0	29.6	23.3	18.6	14.5

$\underline{k = 27.0 \times 10^{-7}}$

<u>Run 59</u> 5-ethyl-$[1\text{-}^3H]$carbazole

a) A = -10.0°, B = 8, C = 8.0491g., E = 0.0200g.,
F = 0.9691g., G = 64.9mm./0.0040g., H = 98.8%, I = 0.5mm.

T	0.0	0.25	0.50	1.0	1.2
D	29.8	20.7	14.46	7.97	5.25

$\underline{k = 4020 \times 10^{-7}}$

b) A = -10.0°, B = 8, C = 8.9074g., E = 0.0307g.,
F = 0.4114g.,(6 samples). The equilibrium deflection was determined experimentally and found to be 0.4mm.

T	0.0	0.3	0.5	1.0	1.5
D	39.6	24.8	19.3	8.9	4.76

$\underline{k = 3980 \times 10^{-7}}$

Run 60 5-ethyl-$[3\text{-}^{3}\text{H}]$carbazole

a) A = -10.0°, B = 2.5, C = 8.0246g., E = 0.0117g.,

F = 0.9446g., G = 118.6mm./0.0032g., H = 99.8%, I = 0.2mm.

T	0.0	0.0167	0.0334	0.0667	0.0834
D	34.5	28.1	23.3	15.65	12.9

k = 32,800 x 10^{-7}

b) A = -10.0°, B = 2.5, C = 8.4673g., E = 0.0168g.,

F = 1.3873g., G = 118.6mm./0.0032g., H = 99.7%, I = 0.3mm.

T	0.0	0.0167	0.05	0.1	0.15
D	29.2	23.6	16.1	8.96	4.96

k = 33,000 x 10^{-7}

Run 61 $[4\text{-}^{3}\text{H}]$-1,3,5,-trimethoxybenzene

a) A = 24.84°, B = 3, C = 8.3820g., E = 0.0510g.,

F = 1.3020g., G = 156.6mm./0.0062g., H = 98.3%, I = 3.7mm.

T	0.0	0.05	0.10	0.15	0.20
D	103.9	64.5	38.9	24.0	13.75

k = 27,200 x 10^{-7}

b) A = 24.84°, B = 3, C = 8.1976g., E = 0.0434g.,

F = 1.1176g., G = 156.6mm./0.0062g., H = 98.5%, I = 2.8mm.

T	0.0	0.05	0.10	0.15	0.20
D	101.8	60.8	35.7	23.3	13.55

k = 27,300 x 10^{-7}

c) A = -10.0°, B = 3, C = 8.2427g., E = 0.0655g.,

F = 1.1627g., G = 156.6mm./0.0062g., H = 97.8%, I = 6.2mm.

T	0.0	1.0	2.2	3.2	4.6
D	222.3	166.2	115.0	85.2	56.2

k = 826 x 10^{-7}

d) A = -10.0°, B = 3, C = 8.2802g., E = 0.0689g.,
F = 1.2002g., G = 156.6mm./0.0062g., H = 97.7%, I = 6.8mm.

T	0.0	1.05	1.75	3.45	5.0
D	225.4	164.6	132.7	82.1	50.5

k = 830 x 10^{-7}

Run 62 $[\alpha\text{-}^{3}\text{H}]$ naphthalene

a) A = 70.11°, B = 5, C = 7.9289g., E = 0.0422g.,
F = 0.1459g., G = 41.0mm./0.0093g., H = 98.8%, I = 0.4mm.

T	0.0	6.25	12.0	20.45	30.45
D	29.0	22.7	18.0	13.05	8.8

k = 108.8 x 10^{-7}

b) A = 70.11°, B = 5, C = 8.2060g., E = 0.0519g.,
F = 0.4230g., G = 41.0mm./0.0093g., H = 97.3%, I = 1.2mm.

T	0.0	5.85	12.1	24.9	32.95
D	33.8	26.75	20.7	12.35	9.03

k = 112.0 x 10^{-7}

Run 63 $[\beta\text{-}^{3}\text{H}]$ naphthalene

a) A = 70.11°, B = 8, C = 8.1860g., E = 0.0516g.,
F = 0.4360g., G = 23.0mm./0.0042g., H = 95.7%, I = 2.3mm.

T	0.0	72.0	125.9	173	245
D	33.95	23.25	17.85	13.85	9.3

k = 14.5 x 10^{-7}

b) A = 70.11°, B = 8, C = 8.0788g., E = 0.0457g.,
F = 0.3138g., G = 23.0mm./0.0042g., H = 96.1%, I = 1.9mm.

T	0.0	67.1	111.0	190.0	250.0
D	31.55	22.3	17.8	11.95	8.7

k = 14.3 x 10^{-7}

Run 64 [$\underline{p}$-^{3}H]biphenyl

a) A = 70.11°, B = 6, C = 8.2560g., E = 0.0545g.,

F = 0.5060g., G = 215.7mm./0.0068g., H = 97.2%, I = 9.0mm.

T	0.0	46.65	113.1	165.8	220.2
D	357.3	276.0	190.0	142.4	104.5

$\underline{k = 15.4 \times 10^{-7}}$

b) A = 70.11°, B = 6, C = 8.1848g., E = 0.0464g.,

F = 0.3720g., G = 190.3mm./0.0093g., H = 97.6%, I = 4.1mm.

T	0.0	46.75	102.7	169.7	213.9
D	137.2	105.2	76.0	53.2	41.4

$\underline{k = 15.5 \times 10^{-7}}$

Run 65 [$\underline{o}$-^{3}H]biphenyl

a) A = 70.11°, B = 6, C = 8.0500g., E = 0.0404g.,

F = 0.2850g.. G = 97.6mm./0.0076g., H = 97.9%, I = 2.1mm.

T	0.0	46.15	90.05	169.4	213.2
D	95.6	82.0	70.3	54.0	46.8

$\underline{k = 9.33 \times 10^{-7}}$

b) A = 70.11°, B = 6, C = 8.2703g., E = 0.0442g.,

F = 0.5359g., G = 159.0mm./0.0076g., H = 97.6%, I = 4.1mm.

T	0.0	70.65	142.7	209.5
D	219.7	173.4	134.1	109.2

$\underline{k = 9.29 \times 10^{-7}}$

Run 66 4-methyl-[4'-^{3}H]biphenyl

a) A = 70.11°, B = 4, C = 7.9323g., E = 0.0197g.,

F = 0.6834g., G = 489.6mm./0.0074g., H = 99.3%, I = 1.7mm.

T	0.0	12.35	24.0	40.7	62.75
D	277.3	210.0	160.3	112.5	69.3

$\underline{k = 61.3 \times 10^{-7}}$

b) A = 70.11°, B = 4, C = 7.9179g., E = 0.0203g.,

F = 0.3899g., G = 489.6mm./0.0074g., H = 99.3%, I = 2.8mm.

T	0.0	16.1	27.45	44.8	73.45
D	270.0	187.8	145.6	96.9	51.4

$k = 62.9 \times 10^{-7}$

Run 67 4-methoxy-$[4'-{}^{3}H]$biphenyl

a) A = 70.11°, B = 4, C = 7.9252g., E = 0.0197g.,

F = 0.4502g., G = 121.6mm./0.0027g., H = 99.4%, I = 1.0mm.

T	0.0	12.3	23.95	40.85	69.7
D	201.8	160.3	130.1	95.0	55.7

$k = 51.1 \times 10^{-7}$

b) A = 70.11°, B = 4, C = 7.9760g., E = 0.0225g.,

F = 0.7060g., G = 121.6mm./0.0027g., H = 99.3%, I = 1.7mm.

T	0.0	7.9	23.2	51.8	78.4
D	194.5	172.6	128.3	78.6	46.9

$k = 50.9 \times 10^{-7}$

Run 68 4-bromo-$[4'-{}^{3}H]$biphenyl

a) A = 70.11°, B = 4, C = 8.419g., E = 0.0160g.,

F = 0.9690g., G = 245.0mm./0.0044g., H = 99.6%, I = 0.6mm.

T	0.0	175.6	344.1	512.2	677.5
D	142.6	112.0	88.7	70.4	55.4

$k = 3.84 \times 10^{-7}$

b) A = 70.11°, B = 4, C = 8.7700g., E = 0.0140g.,

F = 1.2700g., G = 245.0mm./0.0044g., H = 99.8%, I = 0.3mm.

T	0.0	168.7	337.0	497.8	740.2
D	128.7	102.1	79.6	63.3	45.1

$k = 3.94 \times 10^{-7}$

Run 69 4-chloro-$[4'-{}^{3}H]$biphenyl

a) A = 70.11°, B = 4, C = 8.270g., E = 0.0191g.,

F = 0.7700g., G = 130mm./0.0022g., H = 99.5%, I = 1.0mm.

T	0.0	166.5	332.4	501.7	757.4
D	185.5	141.0	105.7	80.8	51.9

$k = 4.62 \times 10^{-7}$

b) A = 70.11°, B = 4, C = 8.3470g., E = 0.0202g.,

F = 0.3270g., G = 175.0mm./0.0022g., H = 99.4%, I = 1.6mm.

T	0.0	169.6	337.7	503.0	671.9
D	253.4	192.9	146.5	111.9	85.2

$k = 4.52 \times 10^{-7}$

Run 70 3-chloro-$[4'-{}^{3}H]$biphenyl

a))A = 70.11°, B = 7, C = 8.1060g., E = 0.0240g.,

F = 0.3410g., G = 528mm./0.0062g., H = 98.7%, I = 5.2mm

T	0.0	339.0	677.0	1016	1340
D	390.0	309.0	246.4	193.2	155.0

$k = 1.91 \times 10^{-7}$

b) A = 70.11°, B = 7, C = 8.1433g., E = 0.0234g.,

F = 0.2783g., G = 528mm/0.0062g., H = 98.8%, I = 4.6mm.

T	0.0	339.0	677.0	1016	1340
D	372.9	295.8	234.6	185.6	148.9

$k = 1.91 \times 10^{-7}$

Run 71 4-nitro-$[4'-{}^{3}H]$biphenyl

a) A = 110.15°, B = 4, C = 9.5240g., E = 0.0208g.,

F = 1.2240g., G = 462.0mm./0.0020g., H = 99.4%, I = 5.0mm.

T	0.0	511.9	700.0	888.2	1176
D	857.0	770.0	742.0	714.0	672.0

$k = 0.573 \times 10^{-7}$

b) A = 110.15°, B = 4, C = 9.6173g., E = 0.0240g.,

F = 0.3173g., G = 404.0mm./0.0020g., H = 99.3%, I = 6.0mm.

T	0.0	512.0	888.0	1176
D	776.0	698.0	647.0	608.0

$k = 0.575 \times 10^{-7}$

Run 72 2-bromo-[7-^{3}H]fluorene

a) A = 70.11°, B = 4, C = 8.0125g., E = 0.0153g.,

F = 0.5625g., G = 72.0mm./0.0028g., H = 99.6%, I = 0.3mm.

T	0.0	3.2	5.25	8.25	10.3
D	37.4	25.2	19.15	14.1	10.6

$k = 347 \times 10^{-7}$

b) A = 70.11°, B = 4, C = 8.2769g., E = 0.0127g.,

F = 0.7749g., G = 72.0mm./0.0028g., H = 99.7%, I = 0.2mm.

T	0.0	3.0	6.75	8.35	10.9
D	40.5	28.2	18.0	14.85	10.5

$k = 337 \times 10^{-7}$

Run 73 2-methyl-[7-^{3}H]fluorene

a) A = 70.11°, C = 10.5230g., E = 0.0623g., F = 0.5630g., the experimentally determined equilibrium deflection was 13.0mm

T	0.0	0.253	0.50	0.75	1.1
D	24.3	14.0	8.2	4.8	2.2

$k = 6050 \times 10^{-7}$

b) A = 70.11°, C = 9.9610g., E = 0.0540g., F = 0.2390g., the experimentally determined equilibrium deflection was 13.9mm.

T	0.0	0.10	0.30	0.60	1.0
D	26.6	21.3	13.9	6.9	2.95

$k = 6180 \times 10^{-7}$

<u>Run 74</u> 2-methoxy-$[7\text{-}^{3}H]$fluorene

a) $A = 70.11^{\circ}$, $C = 9.6920$g., $E = 0.0131$g., $F = 0.2420$g., the experimentally determined equilibrium deflection was 1.8mm.

T	0.0	0.20	0.40	0.90	1.4
D	269.0	191.3	136.3	57.0	24.3

$k = 4780 \times 10^{-7}$

b) $A = 70.11^{\circ}$, $C = 10.1740$g., $E = 0.0208$g., $F = 0.4240$g., the experimentally determined equilibrium deflection was 4.5mm.

T	0.0	0.20	0.45	0.80	1.2
D	223.7	159.2	101.3	54.8	27.2

$k = 4860 \times 10^{-7}$

<u>Run 75</u> 2-carboxy-$[7\text{-}^{3}H]$fluorene

a) $A = 70.11^{\circ}$, $B = 5$, $C = 8.2230$g., $E = 0.0053$g., $F = 0.7230$g., $G = 118.4$mm./0.0045g., $H = 99.8\%$, $I = 0.2$mm.

T	0.0	113.7	375.0	612.0	824.0
D	90.2	78.9	57.7	43.7	34.0

$k = 3.29 \times 10^{-7}$

b) $A = 70.11^{\circ}$, $B = 5$, $C = 8.2200$g., $E = 0.0052$g., $F = 0.7200$g., $G = 118.4$mm./0.0045g., $H = 99.8\%$, $I - 0.2$mm.

T	0.0	337.6	160.0	556.0	803.0
D	102.9	69.7	85.1	53.5	40.1

$k = 3.26 \times 10^{-7}$

<u>Run 76</u> 2-nitro-$[7\text{-}^{3}H]$fluorene

a) $A = 110.15^{\circ}$, $B = 5$, $C = 9.961$g., $E = 0.0324$g., $F = 2.1610$g., $G = 121.9$mm./0.0036g., $H = 99.1\%$, $I = 1.4$mm.

T	0.0	49.0	88.2	121.2	192.7
D	134.8	90.3	65.0	49.2	27.6

$k = 23.0 \times 10^{-7}$

b) A = 110.15°, B = 5, C = 10.3000g., E = 0.0380g., F = 2.0000g., G = 121.9mm./0.0037g., H = 99.1%, I = 1.4mm.

T	0.0	38.0	68.0	119.0	209.5
D	152.3	110.5	86.8	57.2	26.9

<u>k = 23.0 x 10^{-7}</u>

<u>Run 77</u> 2-chloro-[7-^{3}H]fluorene

a) A = 70.11°, C = 10.7360g., E = 0.0188g., F = 2.4360g., the experimentally determined equilibrium deflection was 12.0mm.

T	0.0	2.05	3.6	5.75	7.75
D	1090	796.0	628.0	450.0	332.0

<u>k = 425 x 10^{-7}</u>

b) A = 70.11°, C = 10.3530g., E = 0.0147g., F = 2.0530g., the experimentally dtermined equilibrium deflection was 9.5mm.

T	0.0	2.05	4.0	5.85	9.3
D	787.5	576.0	422.5	328.3	189.6

<u>k = 425 x 10^{-7}</u>

<u>Run 78</u> [^{3}H]benzene

a) A = 70.11°, C = 7.4020g., E = 0.0418g.,

T	0.0	2830	
D	48.7	44.2	<u>k = 0.096 x 10^{-7}</u>
T	0.0	2820	
D	47.7	43.4	<u>k = 0.093 x 10^{-7}</u>

b) A = 70.11°, C = 7.9110g., E = 0.0429g.,

T	0.0	2530	
D	46.7	42.8	<u>k = 0.0945 x 10^{-7}</u>
T	0.0	2580	
D	46.7	42.8	<u>k = 0.0945 x 10^{-7}</u>

In a) and b), only 10% of the reaction occurred over 3 months but the results are probably not in error by more than ±5%. Since the initial and final deflections differed by only 10% the equilibrium deflections were neglected.

c) A = 110.15°, B = 6, C = 10.3180g., E = 0.0472g.,
F = 1.0770g., (6 samples), G = 412.0mm./0.0052g.,
H = 97.2%, I = 15.8mm

T	0.0	173.0	339.8	533.0	862.6	1297
D	540.2	434.2	345.2	276.4	178.3	110.5

$\underline{k = 3.61 \times 10^{-7}}$

d) A = 110.15°, B = 6, C = 10.5410g., E = 0.04910g.,
F = 0.1410g., (6 samples), G = 398.0mm./0.0045g.,
H = 96.1%, I = 29.0mm.

T	0.0	171.0	338.0	531.0	863.0	1195
D	678.0	543.0	432.0	316.0	225.0	138.0

$\underline{k = 3.67 \times 10^{-7}}$

<u>Run 79</u> [*p*-^{3}H] anisole

a) A = 24.84°, B = 2, C = 7.7705g., E = 0.0438g.,
F = 0.4460g., G = 163.7mm./0.0051g., H = 98.9%, I = 2.9mm.

T	0.0	1.45	4.15	7.55	10.8
D	172.5	150.7	117.9	84.3	62.8

$\underline{k = 262 \times 10^{-7}}$

b) A = 24.84°, B = 2, C = 8.2007g., E = 0.0385g.,
F = 0.4671g., G = 163.7mm./0.0051g., H = 99.0%, I = 2.3mm.

T	0.0	1.30	3.45	5.75	8.3
D	160.0	139.7	113.1	91.7	69.0

$\underline{k = 277 \times 10^{-7}}$

c) A = 40.0°, B = 2, C = 8.2165g., E = 0.0438g.,

F = 0.4460g., G = 163.7mm./0.0051g., H = 98.9%, I = 2.9mm.

T	0.0	0.85	1.8	3.1	4.65
D	155.5	106.3	70.1	39.6	20.5

$k = 1224 \times 10^{-7}$

d) A = 40.0°, B = 2, C = 8.0628g., E = 0.0308g.,

F = 0.2612g., G = 163.7mm./0.0051g., H = 99.2%, I = 1.5mm.

T	0.0	0.8	1.55	2.3	4.25
D	117.6	82.0	58.3	41.4	18.0

$k = 1260 \times 10^{-7}$

Run 80 $[p\text{-}^{3}H]$ thioanisole

a) A = 24.84°, B = 2, C = 8.1128g., E = 0.0353g.,

F = 0.3481g., G = 170.0mm./0.060g., H = 99.2%, I = 1.2mm.

T	0.0	5.0	10.45	23.1	33.15
D	166.8	133.9	104.7	58.0	34.3

$k = 122.8 \times 10^{-7}$

b) A = 24.84°, B = 2, C = 8.2232g., E = 0.0341g.,

F = 0.4610g., G = 170.0mm./0.0060g., H = 99.3%, I = 2.0mm.

T	0.0	4.65	8.45	22.75	31.1
D	163.5	132.2	110.2	54.1	33.8

$k = 125.0 \times 10^{-7}$

c) A = 40.0°, B = 2, C = 8.0663G., E = 0.0542g.,

F = 0.0542g., G = 170.0mm./0.0060g., H = 98.9%, I = 3.2mm.

T	0.0	1.4	4.0	7.2	11.5
D	262.8	199.6	122.1	57.1	21.2

$k = 538 \times 10^{-7}$

b) A = 40.0°, B = 2, C = 8.2810g., E = 0.0489g.,

F = 0.5050g., G = 170mm./0.0060g., H = 98.8%, I = 3.1mm.

T	0.0	2.25	4.55	7.25	9.45
D	228.0	155.1	98.7	53.8	32.2

k = 538 x 10^{-7}

Run 81 [m-^{3}H]diphenyl ether

a) A=110.15°, B = 10, C = 10.3781g., E = 0.0170g., (6 samples),

F = 0.3506g., G = 401.0mm./0.0008g., H = 98.2%, I = 25.0mm.

T	0.0	324.0	667.3	1384	1865	2369
D	1356	1294	1230	1107	1025	957.0

k = 0.422 x 10^{-7}

b) A = 110.15°, B = 10, C = 10.3696g., E = 0.0072g.,

F = 0.4696g., G = 415.9mm./0.0006g., H = 99.5%, I = 4.0mm.

(6 samples)

T	0.0	667.3	1191	1384	1865	2369
D	785.0	709.2	653.0	534.0	590.2	545.3

k = 0.428 x 10^{-7}

Run 82 [2-^{3}H]-1,3-dimethylbenzene

a) A = 24.84°, B = 2.5, B = 8.0736g., E = 0.0381g.,

F = 0.9944g., G = 115.1mm./0.0060g., H = 99.1%, I = 1.1mm.

T	0.0	1.78	9.95	22.65	47.3
D	106.6	102.6	85.9	66.3	39.3

k = 59.2 x 10^{-7}

b) A = 24.84°, B = 2.5, B = 7.9440g., E = 0.0481g.,

F = 0.8736g., G = 115.1mm./0.0060g., H = 98.4%, I = 2.6mm.

T	0.0	9.35	22.35	31.9	40.0
D	118.2	96.8	73.9	59.6	50.1

$k = 59.6 \times 10^{-7}$

In the next three runs the effects of salts were examined. The weight of the salt in a given volume of anhydrous trifluoroacetic acid is given, followed by the details as given for the previous runs in anhydrous trifluoroacetic acid.

Run 83 $[2\text{-}^{3}\text{H}]$-1,3-dimethylbenzene

0.2137g.,of sodium trifluoroacetate in 15ml. of anhydrous trifluoroacetic acid.

a) A = 24.84°, B = 2.5, C = 8.1174g., E = 0.0342g., F = 1.0054g., G = 118.1mm./0.0060g., H = 98.9%, I = 1.3mm.

T	0.0	7.4	21.45	31.05	45.0
D	85.3	70.6	49.2	38.4	27.0

$k = 71.0 \times 10^{-7}$

b) A = 24.84°, B = 2.5, C = 8.2016g., E = 0.0538g., F = 1.0953g., G = 115.1mm./0.0060g., H = 98.1%, I = 3.5mm.

T	0.0	6.85	22.15	31.85	47.0
D	134.0	112.5	76.7	60.0	41.0

$k = 70.2 \times 10^{-7}$

Run 84 $[2\text{-}^{3}\text{H}]$-1,3-dimethylbenzene

0.1597g. of lithium perchlorate in 15ml. of anhydrous trifluoroacetic acid.

a) A = 24.84°, B = 2.5, C = 7.8088g., E = 0.0393g., F = 0.6167g., G = 115.1mm./0.0060g., H = 98.7%, I = 1.8mm.

T	0.0	0.25	0.50	0.75	1.5
D	65.8	47.3	34.5	25.1	9.65

$k = 3580 \times 10^{-7}$

Run 85 [2-^{3}H]-1,3-dimethylbenzene

0.1789g. of lithium trifluoroacetate in 15ml. of anhydrous trifluoroacetic acid.

a) A = 24.84°, B = 2.5, C = 8.2353g., E = 0.0350g.,
F = 0.4548g., G = 115.1mm./0.0060g., H = 98.9%, I = 1.4mm.

T	0.0	6.15	20.85	29.6	54.0
D	94.7	81.3	56.5	46.0	25.5

$k = 67.7 \times 10^{-7}$

b) A = 24.84°, B = 2.5, C = 8.2770g., E = 0.0385g.,
F = 0.5090g., G = 115.1mm./0.0060g., H = 98.8%, I = 1.7mm.

T	0.0	8.2	72.9	34.2	47.25
D	104.6	86.3	60.0	45.4	32.4

$k = 69.7 \times 10^{-7}$

Trifluoroacetic acid - acetic acid

Media of different compositions were prepared by accurate weighing of the two components, anhydrous trifluoroacetic acid and acetic acid (99.2%).

The composition of the media is given as wt.-% of acetic acid (99.2%).

Run 86 [2-^{3}H] fluorene

Acetic acid - 13.2wt.-%

A = 70.11°, B = 3, C = 8.3327g., E = 0.0071g., F = 0.5827g.,
G = 469.6mm./0.0001g., H = 99.8%, I = 1.2mm.

T	0.0	2.25	3.8	8.2	11.6
D	614.0	451.0	368.0	199.0	124.0

$k = 382 \times 10^{-7}$

<u>Run 87</u> 2-methyl-[7-^{3}H]fluorene

Acetic acid - 13.2wt.-%

A = 70.11°, C = 10.2184g., E = 0.9184g., the equilibrium deflection was determined experimentally and was 11.4mm.

T	0.0	0.35	0.85	2.0	3.45
D	28.1	22.4	16.2	7.7	2.9

$k = 1800 \times 10^{-7}$

<u>Run 88</u> 2-methoxy-[7-^{3}H]fluorene

Acetic acid - 13.2wt.-%.

A = 70.11°, C = 8.4856g., E = 0.0211g., the equilibrium deflection was determined experimentally and was 9.8mm.

T	0.0	1.05	1.75	2.35	3.2
D	646.0	267.7	148.4	88.6	41.1

$k = 2370 \times 10^{-7}$

<u>Run 89</u> [4-^{3}H]diphenyl ether

Acetic acid - 13.2wt.-%.

A = 70.11°, B = 2.5, C = 8.1535g., E = 0.0436g.,

F = 0.1463g., G = 489.0mm./0.0008g., H = 99.1%, I = 46.8mm.

T	0.0	1.0	3.25	6.65	9.4
D	4983	3388	1527	448.0	175.0

$k = 1015 \times 10^{-7}$

<u>Run 90</u> 4-methyl-[4'-^{3}H]biphenyl

Acetic acid - 13.2wt.-%.

A = 70.11°, B = 4, C = 8.2428g., E = 0.0201g.,

F = 0.4928g., G = 445.7mm./0.0005g., H = 99.4%, I = 13.0mm.

T	0.0	49.3	94.0	159.7	206.2
D	2012	1330	917.0	536.0	377.0

<u>$k = 23.1 \times 10^{-7}$</u>

<u>Run 91</u> 4-methoxy-[4'-^{3}H]biphenyl

Acetic acid - 13.2wt.-%,

A = 70.11°, B = 4, C = 8.3462g., E = 0.01560g.,

F = 0.5962g., G = 398.0mm./0.0010g., H = 99.5%, I = 5.7mm.

T	0.0	51.25	95.9	161.5	208.0
D	1122	632.3	402.3	201.8	118.2

<u>$k = 29.8 \times 10^{-7}$</u>

<u>Run 92</u> [4-^{3}H]diphenyl ether

Acetic acid - 22.8wt.-%

A = 70.11°, B = 2.5, C = 8.1304g., E = 0.0180g.,

F = 0.3804g., G = 474.5mm./0.0005g., H = 99.6%, I = 13.0mm.

T	0.0	0.6	2.3	4.75	7.75
D	3222	3010	2467	1862	1308

<u>$k = 323 \times 10^{-7}$</u>

<u>Run 93</u> [2-^{3}H]fluorene

Acetic acid - 22.8wt.-%

A = 70.11°, B = 3, C = 8.1824g., E = 0.0072g.,

F = 0.3354g., G = 461.9mm/0.0020g., H = 98.2%, I = 10.3mm.

T	0.0	3.9	5.9	23.6	23.6
D	555.7	475.3	439.6	224.1	223.2

<u>$k = 109.0 \times 10^{-7}$</u>

<u>Run 94</u> 2-methyl-[7-^{3}H] fluorene

Acetic acid - 22.8wt.-%

A = 70.11°, C = 10.3154g., E = 0.520g., the equilibrium deflection was determined experimentally and was 14.6mm.

T	0.0	0.8	2.25	3.65	4.85
D	31.3	26.2	21.0	16.1	13.5

$k = 494 \times 10^{-7}$

Run 95 2-methoxy-$[7\text{-}^{3}H]$fluorene

Acetic acid - 22.8wt.-%

A = 70.11°, C = 8.0775g., E = 0.0181g., the equilibrium deflection was determined experimentally and was 9.8mm.

T	0.0	0.75	3.0	6.4	9.15
D	1342	1087	596.2	223.0	106.5

$k = 780 \times 10^{-7}$

Run 96 4-methyl-$[4'\text{-}^{3}H]$biphenyl

Acetic acid - 22.8wt.-%

A = 70.11°, B = 4, C = 8.3138g., E = 0.218g.,

F = 0.5765g., G = 426.7mm./0.0008g., H = 99.3%, I = 15.2mm.

T	0.0	78.0	165.3	197.9	309.8
D	2127	1853	1585	1505	1324

$k = 4.90 \times 10^{-7}$

Run 97 4-methoxy-$[4'\text{-}^{3}H]$biphenyl

Acetic acid - 22.8wt.-%

A = 70.11°, B = 4, C = 8.0029g., E = 0.0222g.,

F = 0.2667g., G = 364.5mm./0.0010g., H = 99.3%, I = 11.0mm.

T	0.0	78.25	143.9	198.2	358.0
D	1533	1218	1008	860.2	533.3

$k = 8.15 \times 10^{-7}$

Run 98 4-methoxy-[4'-^{3}H]biphenyl

Acetic acid - 1.68wt.-%

A = 70.11°, B = 4, C = 8.8619g., E = 0.0139g.,

F = 0.5730g., G = 342.9mm./0.0010g., H = 99.6%, I = 3.6mm.

T	0.0	17.85	27.1	47.1	72.45
D	878.4	669.3	576.7	410.7	274.9

k = 43.5 x 10^{-7}

Run 99 4-methyl-[4'-^{3}H]biphenyl

Acetic acid - 1.68wt.-%

A = 70.11°, B = 4, C = 8.6015g., E = 0.0230g.,

F = 0.3126g., G = 415.9mm./0.0008g., H = 99.5%, I = 11.5mm.

T	0.0	15.9	25.2	45.2	70.45
D	2220	1660	1406	979.5	632.5

k = 50.3 x 10^{-7}

Run 100 [2-^{3}H]dibenzofuran

Acetic acid - 19.3wt.-%

A = 70.11°, B = 2.5, C = 8.4350g., E = 0.0184g.,

F = 0.1400g., G = 360.2mm./0.0010g., H = 99.6%, I = 5.2mm..

T	0.0	11.55	23.0	32.6	47.7
D	1278	1098	953.8	844.8	695.8

k = 35.3 x 10^{-7}

Run 101 [4-^{3}H]diphenyl sulphide

Acetic acid - 19.3wt.-%

A = 70.11°, B = 3, C = 8.3047g., E = 0.0177g.,

F = 0.4341g., G = 255.2mm./0.0005g., H = 99.7%, I = 5.0mm.

T	0.0	11.0	22.4	31.75	47.0
D	1705	1346	1044	848.1	614.3

k = 60.6 x 10^{-7}

Run 102 2-bromo-[7-^{3}H]fluorene

Acetic acid - 19.3wt.-%

A = 70.11°, B = 4, C = 8.2594g., E = 0.0107g.,

F = 0.5094g., G = 320.0mm./0.0020g., H = 99.8%, I = 0.6mm.

T	0.0	9.1	21.0	68.5	119.0
D	315.4	281.3	239.4	130.3	69.3

k = 35.8 x 10^{-7}

Run 103 [2-^{3}H]dibenzothiophen

Acetic acid - 19.3wt.-%

A = 70.11°, B = 2.5, C = 8.3645g., E = 0.0108g.,

F = 0.6145g., G = 480.4mm./0.0010g., H = 99.8%, I = 1.9mm.

T	0.0	9.2	21.0	68.5	120.0
D	948.3	903.1	853.6	666.1	512.7

k = 14.3 x 10^{-7}

The results are summarised, classified under types of media, in the next few pages.

AQUEOUS SULPHURIC ACID. Temperature: 24.84°

Composition (wt.-%)	Compound	Position	Run no.	10^7k (sec.$^{-1}$)	$\frac{f_o}{f_p}$
74.85	toluene	o	11	5185	1.055
		p	10	4915	
73.25	toluene	o	4	2800	1.04
		p	3	2710	
70.70	toluene	o	1	753	1.00
		p	2	753	
69.00	toluene	o	6	316	0.99
		p	5	320	
64.50	toluene	o	13	49.6	0.98
		p	12	50.7	
71.41	t-butylbenzene	o	8	768	0.955
		p	7	805	
71.41	toluene	p	9	1095	-

ACETIC ACID - SULPHURIC ACID - WATER. Temperature: 25.0°

The molar composition of the medium was: acetic acid (20.83%) - sulphuric acid (44.74%) - water (34.43%).

Compound	Run no.	10^7k(sec.$^{-1}$)	Partial rate factor
[2-^{3}H] fluorene	14	3900	2100
9-methyl-[2-^{3}H] fluorene	15	3795	2040
9,9-dimethyl-[2-^{3}H] fluorene	16	3585	1930
[9-^{3}H] fluorene	17	102	54.9
[p-^{3}H] toluene	18	581	313^a

a- this figure was obtained by Eaborn and Taylor.[40]

TRIFLUOROACETIC ACID - SULPHURIC ACID - WATER. Temp.: 24.84°

The molar composition of the medium was: trifluoroacetic acid (93.00%) - sulphuric acid (1.88%) - water (5.12%).

Compound	Position	Run no.	$10^7k(\text{sec}^{-1})$	$\frac{f_o}{f_p}$
t-butylbenzene	*o*	19	1565	0.72
	p	20	2185	
toluene	*o*	22	1295	0.73
	p	21	1770	

TRIFLUOROACETIC ACID - PERCHLORIC ACID - WATER. Temp.: 25.0°

The molar composition of the medium was: trifluoroacetic acid (99.962%) - perchloric acid (0.0102%) - water (0.0278%)

Compound	Run no.	$10^7k(\text{sec}^{-1})$	Partial rate factor
$[2\text{-}^3H]$ fluorene	23	2950	3610
9-methyl-$[2\text{-}^3H]$ fluorene	24	3115	3810
9,9-dimethyl-$[2\text{-}^3H]$ fluorene	25	3975	4860
$[p\text{-}^3H]$ toluene	26	256	313 [a]

a- Value obtained in a slightly different medium by Eaborn and Taylor[40].

ANHYDROUS HEPTAFLUOROBUTYRIC ACID. Temperature: 70.11°

Compound	Position	Run no.	10^7k(sec.$^{-1}$)	$\frac{f_o}{f_p}$
toluene	*o*	29	2.79	0.39
	p	27	7.08	
t-butylbenzene	*o*	30	3.34	0.37
	p	28	8.94	
biphenyl	*o*	32	1.82	0.43
	p	31	4.26	

ANHYDROUS TRIFLUOROACETIC ACID. Temperature: 70.11°

Compound	Position	Run no.	10^7k (sec.$^{-1}$)	$\frac{f_o}{f_p}$	Partial rate factor
Benzene	1	78	0.095	-	1
toluene	*o*	36	20.8	0.49	219
	p	33	42.7		450
t-butylbenzene	*o*	35	23.0	0.45	242
	p	34	50.9		535
biphenyl	*o*	65	9.31	0.60	163
	p	64	15.45		98.0

medium: anhydrous trifluoroacetic acid, temperature: 70.11°,

Compound	Position	Run no.	10^7k (sec.$^{-1}$)	Partial rate factor
Dibenzofuran	1	49	12.8	135
	2	39	349	3670
	3	50	29.7	313
	4	40	15.2	160
Dibenzothiophen	1	47	25.8	272
	2	37	174	1830
	3	48	40.8	430
	4	38	34.4	362
Diphenyl ether	2	41	658	6930
	4	42	2930	30,800
Diphenyl sulphide	2	43	316	3330
	4	44	934	9830
Phenanthrene	9	51	153	1620
Diphenylmethane	4	52	11.05	117
Fluorene	2	53	1598	16,800
9-Methylfluorene	2	54	1665	17,500
9,9-Dimethylfluorene	2	55	1897	20,000
Benzofuran	2	56	1615	17,100
Thiophen	3	58	1780	18,700
Naphthalene	α	62	110.4	1160
	β	63	14.4	151
4-Methylbiphenyl	4'	66	62.1	654
4-Methoxybiphenyl	4'	67	51.0	537
4-Bromobiphenyl	4'	68	3.89	41.0

medium: anhydrous trifluoroacetic acid, temperature: 70.11°

Compound	Position	Run no.	10^7k (sec.$^{-1}$)	Partial rate factor
4-Chlorobiphenyl	4'	69	4.57	48.1
3-Chlorobiphenyl	4'	70	1.91	20.1
2-Bromofluorene	7	72	342	3600
2-Methylfluorene	7	73	6115	64,400
2-Methoxyfluorene	7	74	4820	50,700
2-Carboxyfluorene	7	75	3.275	34.5
2-Chlorofluorene	7	77	425	4470

medium: anhydrous trifluoroacetic acid, temperature: 110.15°

Compound	Position	Run no.	10^7k (sec.$^{-1}$)	Partial rate factor
Benzene	1	78	3.64	1
4-Nitrobiphenyl	4'	71	0.573	0.157
2-Nitrofluorene	7	76	23.0	6.32
Diphenyl ether	3	81	0.425	0.117

medium: anhydrous trifluoroacetic acid, temperature: 24.84° and 40.0°

Compound	Position	Run no,	10^7k(sec.$^{-1}$)		Partial rate factor
			24.84°	40.0°	
Benzothiophen	2	45	421	1810	2.58×10^5
Benzothiophen	3	46	600	2513	3.41×10^5
Anisole	*p*	79	270	1242	1.87×10^5
Thioanisole	*p*	80	123.9	538	8.19×10^4

The exchange reactions were followed at 24.84° and 40.0°, and extrapolated to give the rate of exchange at 70.11°. The partial rate factor for detritiation of the compound was then obtained by comparison of the rate of exchange and the detritiation rate of a single position of benzene at 70.11°.

medium: anhydrous trifluoroacetic acid, temperature: -10.0° and 24.84°.

Compound	Position	Run no.	10^7k(sec.$^{-1}$)		Partial rate factor
			-10.0°	24.84°	
Thiophen	2	57	2360	73,200	2.31×10^7
1,3,5-Trimethoxybenzene	2	61	828	27,250	9.49×10^6

The partial rate factors were obtained by comparison of the rate of exchange of the compounds at 70.11° (obtained by extrapolation from the temperatures -10.0° and 24.84°) with the rate of exchange of a single position of benzene at 70.11°.

medium: anhydrous trifluoroacetic acid, temperature: -10.0°

Compound	Position	Run no.	10^7k(sec.$^{-1}$)	Partial rate factor
5-Ethylcarbazole	1	59	4000	9.13×10^7
	3	60	32,900	7.51×10^8

The partial factors were obtained by comparison of the rates of exchange of the compounds with that of 1,3,5-trimethoxybenzene (the partial rate factor of this compound was found as described above).

medium: approximately 0.1N solutions of salts in anhydrous trifluoroacetic acid (the exact composition of the media has been given in the details of the runs), temperature: 24.84°.

Compound	Salt added	Run no.	$10^7k(\text{sec}^{-1})$
1,3-Dimethylbenzene	none	82	59.4
	lithium trifluoroacetate	85	68.7
	sodium trifluoroacetate	83	70.6
	lithium perchlorate	84	3580

TRIFLUOROACETIC ACID - ACETIC ACID . Temperature: 70.11°

Acetic acid wt.-%	Compound	Position	Run no.	$10^7k(\text{sec}^{-1})$
13.2	Fluorene	2	86	382
	2-Methylfluorene	7	87	1800
	2-Methoxyfluorene	7	88	2370
	Diphenyl ether	4	89	1015
	4-Methylbiphenyl	4'	90	23.1
	4-Methoxybiphenyl	4'	91	29.8
22.8	Diphenyl ether	4	92	323
	Fluorene	2	93	109
	2-Methylfluorene	7	94	494
	2-Methoxyfluorene	7	95	780
	4-Methylbiphenyl	4'	96	4.90
	4-Methoxybiphenyl	4'	97	8.15
1.68	4-Methoxybiphenyl	4'	98	43.5
	4-Methylbiphenyl	4'	99	50.3

medium: trifluoroacetic acid - acetic acid, temperature: 70.11°

Acetic acid wt.-%	Compound	Position	Run no.	$10^7k(\mathrm{sec.}^{-1})$
19.3	Dibenzofuran	2	100	35.3
	Diphenyl sulphide	4	101	60.6
	2-Bromofluorene	7	102	35.8
	Dibenzothiophen	2	103	14.3

DISCUSSION

1. Diphenyl ether, diphenyl sulphide, dibenzofuran and dibenzothiophen.

The rates of detritiation of [2- and 4-^{3}H]- diphenyl ether and -diphenyl sulphide and [1-, 2-, 3- and 4-^{3}H]-dibenzofuran and -dibenzothiophen were measured in anhydrous trifluoro-acetic acid at 70.11°, and the results are shown in Table 1.

Table 1

Rates of detritiation in anhydrous trifluoroacetic acid at 70.11°.

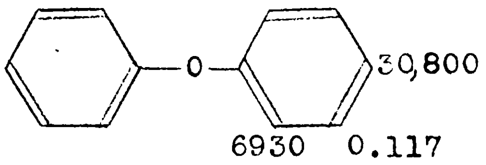
Compound	Position	$10^6k(\text{sec.}^{-1})$	k_{rel}
Diphenyl ether	2	65.8	30,800
	3	0.0425[a]	0.117[a]
	4	293	6930
Diphenyl sulphide	2	31.6	9830
	4	93.4	3330
Dibenzofuran	1	1.28	135
	2	3.49	3670
	3	2.97	313
	4	1.52	160
Dibenzothiophen	1	2.58	272
	2	17.4	1830
	3	4.08	430
	4	3.44	362
Benzene	1	0.0095	1

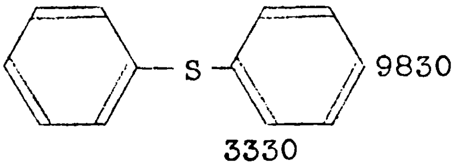
a- measured and compared with the rate of exchange of a single position of benzene at 110.15°

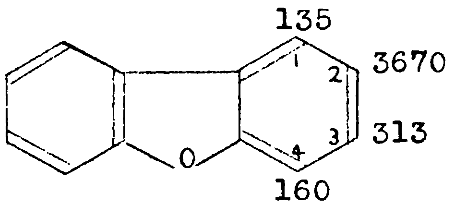
For benzene at 110.15°, $k = 3.64 \times 10^{-7} \text{sec.}^{-1}$

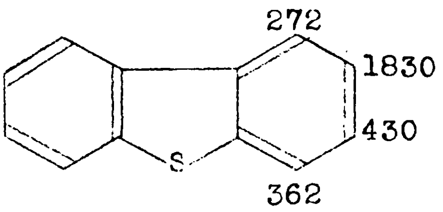
In both dibenzofuran and dibenzothiophen the order of reactivity of the positions in detritiation is $2 > 3 > 4 > 1$. The 1-, 3-, and 4-positions are more reactive in dibenzothiophen than in dibenzofuran but the 2-position of the oxygen compound is twice as reactive as that of the sulphur compound. The 2- and 4-positions of diphenyl ether are more reactive than the corresponding positions of diphenyl sulphide, in agreement with the smaller $+\underline{T}$ effect of a sulphur than an oxygen atom. The rate of exchange of the 3-position of diphenyl ether was measured at 110.15°, since the reaction was too slow to follow at 70.11°. Closure of the five-membered rings on going from diphenyl ether to dibenzofuran, and diphenyl sulphide to dibenzothiophen is associated with a large reduction in reactivity of the positions *ortho-* and *para-* to the heteroatoms: the reduction being greater for the oxygen than for the sulphur compounds. The effect is so large in the case of the atom *ortho-* to the oxygen, that the 4-position of dibenzofuran is less than half as reactive as the 4-position of dibenzothiophen, even though the corresponding 2-position of diphenyl ether is more than twice as reactive as that in diphenyl sulphide. The reduction of the reactivity on ring-closure is to be attributed mainly to the engagement of the lone-pair of the oxygen and sulphur atoms in giving aromatic character to the five-membered rings; the $+\underline{T}$ effect of these atoms can only be made available to the 2- and 4-positions of the heterocyclic compounds at the expense of aromatic character.

The partial rate factors obtained are summarised in the following diagrams:





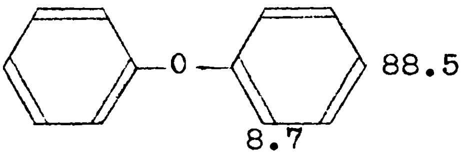


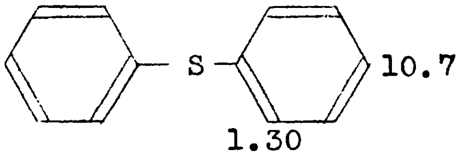


The positions *meta*- to the hetero-atoms are greatly increased in reactivity by the ring closure. The value for the 3-position of diphenyl ether is 0.117 (that of diphenyl sulphide is probably similar). The values for the 3-positions of dibenzo- furan and -thiophen are 313 and 430, respectively, and for the 1-position are 135 and 272. The activation of the 1- and 3-positions can probably be attributed to the +T effect of the substituted phenyl group *ortho*- and *para*- to these positions, respectively. (As will be described below the 2- and 4-positions of biphenyl are activated 98 and 163 times in detritiation in anhydrous trifluoroacetic acid.)

Dewar[110] studied the nitration, with nitric acid in acetic anhydride, of diphenyl ether and dibenzofuran and found that closure of the five-membered ring lowered the overall reactivity. He reported partial rate factors of 117 and 234 for the 2- and 4- positions of diphenyl ether and 47, 94, 94, and 0 for the 1-, 2-, 3-, and 4-positions of dibenzofuran. A much greater spread of rates in detritiation is evident, and this can be attributed to a larger demand on polarizability effects in hydrogen exchange than in nitration.

The partial rate factors obtained for the protodesilylation of some diphenyl ether and diphenyl sulphide compounds in methanol-aqueous perchloric acid [113] are shown in the following diagrams:-



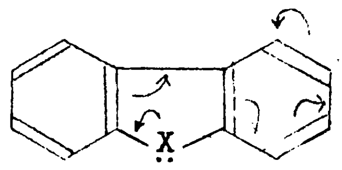


The greater reactivity of diphenyl ether than of diphenyl sulphide is again evident. The spread of rates is usually much smaller in protodesilylation than in detritiation but diphenyl ether is 8 times faster than diphenyl sulphide in protodesilylation, but only 3 times in detritiation. The reactivity of the 4-relative to that of the 2-position of diphenyl ether in detritiation $\left(\frac{\log f_4}{\log f_2}\right) = 1.17$, agrees with that in nitration $\left(\frac{\log f_4}{\log f_2}\right) = 1.14$, but is smaller than that in protodesilylation $\left(\frac{\log f_4}{\log f_2}\right) = 2.07$[113], and the difference between detritiation and protodesilylation in this respect is even more marked for diphenyl sulphide. It is unlikely that the differences can be ascribed to steric influences at the 2-position, since primary steric effects have been shown to be unimportant in hydrogen-exchange,[114] and steric interference from ortho- substituents normally results in acceleration of protodesilylation reactions.

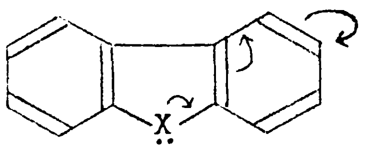
From evidence of ultra-violet spectra and kinetic data of methoxy-fluorene and -diphenyl (page 172), it is suggested that some hydrogen-bonding occurs between the oxygen atom of the methoxy group and trifluoroacetic acid. The rate of detritiation of $[4\text{-}^{3}\text{H}]$diphenyl ether was compared with that of $[2\text{-}^{3}\text{H}]$fluorene in a mixture of trifluoroacetic acid and acetic acid. In a medium containing 22.8wt.-% of acetic acid the rate of exchange of $[4\text{-}^{3}\text{H}]$diphenyl ether decreased by a factor of 9 from that in anhydrous trifluoroacetic acid, compared with that of 15 for $[2\text{-}^{3}\text{H}]$fluorene and 6 for 2-methoxy-$[7\text{-}^{3}\text{H}]$fluorene. Some interaction of trifluoroacetic acid with the lone pair of electrons on the oxygen of the diphenyl ether could, therefore, possibly occur.

No evidence for any interaction, of the solvent, with the hetero-atom was found with diphenyl sulphide, dibenzofuran and dibenzothiophen. The solvent interaction with diphenyl ether could explain the smaller difference in the reactivity of diphenyl ether and diphenyl sulphide, in detritiation, than in protodesilylation.

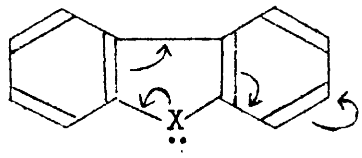
In dibenzothiophen and dibenzofuran, the tautomeric release of the hetero-atoms can be conveyed to the ring positions in the following ways:-



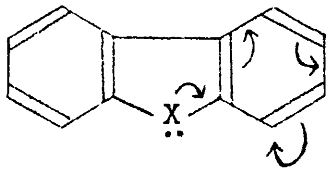
l



ll

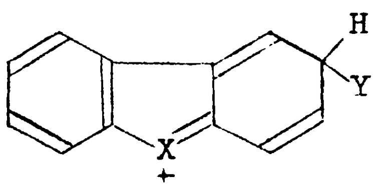


lll

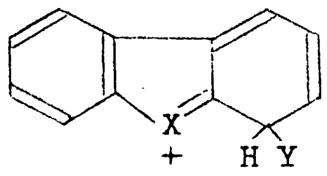


lV

l and lll involve resonance interactions with both benzene rings, while in ll and lV one benzene ring remains unchanged, and there is a smaller loss of resonance energy. On this basis, electrophilic substitution would be expected to be either in the 2- or 4-position. A possible reason for prefered 2-substitution is the greater stability of a p-quinoid system (llA), than an o-quinoid system (lVA), which are formed as intermediates in the reactions.[115]



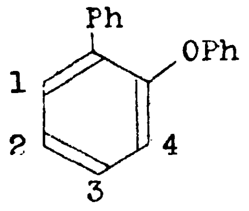
(llA)



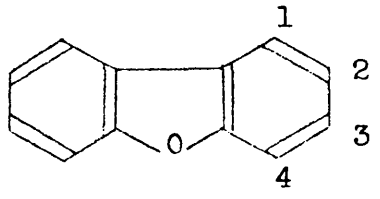
(lVA)

Y^{+} - electrophilic group

Dibenzofuran contains both a biphenyl and a diphenyl ether system, and it is of interest to attempt to calculate the reactivities of the positions in dibenzofuran, assuming the systems activate independently.



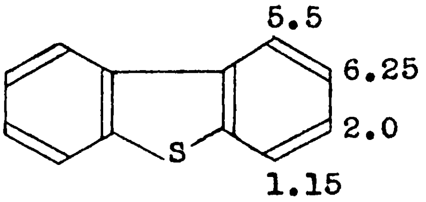
cf.



A position <u>para</u>- to a phenoxy group is activated by a factor of 31,000; a position <u>meta</u>- to a phenyl group is deactivated, in a slightly different medium, by a factor of 0.68.[54] The overall figure for the activity, if there was no interaction, would be 21,000, compared with the figure of 3670 found. The deactivating effect of a <u>meta</u>-phenoxy is 0.117. The <u>para</u>-phenyl group activates by a factor of 163; the rate factor for the 3-position would be expected to be 19. Similarly, the <u>ortho</u>-phenyl group activates by a factor of 98 and the rate factor for the 1-position would be expected to be 11.5. Both these are much less than the figures obtained, but the higher reactivity can be explained by the greater activation of a phenyl group held in a planar configuration, as in dibenzofuran, and not one ring at 45° to the other as in biphenyl itself. The 4-position, of dibenzofuran, is formally <u>ortho</u>- to the phenoxy group and <u>meta</u>- to the phenyl group; <u>ortho</u>-phenoxy activates by a factor of 6930 and the position should be activated by a factor of about 4700. The figure obtained for the 4-position of dibenzofuran is 160, so that it appears that the activating effect of a phenoxy group is modified in the dibenzofuran system. It was suggested by Baker and Eaborn[116] that the lone pairs of electrons on the oxygen in dibenzofuran are engaged in giving aromatic character to the five-membered ring, and are thus less available to activate the benzene rings.

Dibenzothiophen can be treated in the same way. The *para*-thiophenoxy group activates the *para*-position by a factor of 9830, the deactivating effect of a *meta*-phenyl group should bring the reactivity of the 2-position to about 6350, compared with the factor of 1830 found. The *ortho*-thiophenoxy group activates 3330 times so that a rate factor of 2260 is to be expected for the 4-position of dibenzothiophen which, again, is considerably higher than the factor of 362 obtained. The lower reactivity, observed for the 2- and 4-positions of dibenzothiophen, can be explained by the lone pairs of electrons on the sulphur being engaged in giving aromatic character to the five-membered ring, and are thus less available to activate the benzene rings.[116] The factor for the *meta*-thiophenoxy is not known but if it is assumed to be the same as for *meta*-phenoxy, factors of 11.5 and 19 are obtained for the 1- and 3-positions respectively. The higher reactivity observed can, again, be explained by the effect of a phenyl group held in a planar configuration and not as in biphenyl.

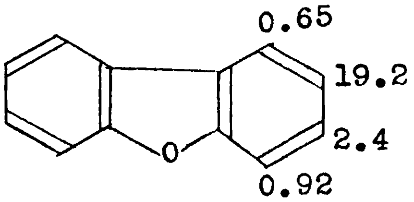
The reactivity of the 2-position of dibenzothiophen represents 64% of the total reactivity of the 1-, 2-, 3-, and 4-positions. From nitration in acetic acid,[77] 40% of the 2-nitro derivative was obtained along with an equal amount of dibenzothiophen-5-oxide, but Gilman and Nobis[117] could obtain the 2-nitro derivative in only 28% yield. A yield of 80% of 2-bromodibenzothiophen has been reported[77] from bromination in carbon disulphide or chloroform. Sulphonation is reported to give 2-substitution[118]; and Gilman and Nobis[117] obtained 41% of the 2-acetyl derivative in acetylation. None of these experimental results excludes the formation of other isomers in the above reactions. Indeed, from the results in detritiation, other isomers are almost certainly formed, but in some cases in such small amounts that separation is virtually impossible. It is wrong, therefore, to say that only 2-substitution occurs in electrophilic aromatic substitution of dibenzothiophen, although, in a highly selective reaction such as molecular bromination this situation is probably approached. Burger, Wartman and Lutz[119] reported a mixture is formed in acetylation and isolated only 25% of the 2-, along with a very small amount of the 4-acetyl derivative.



Eaborn and Sperry[113] report the above partial rate factors, for dibenzothiophen, in protodesilylation. The high value obtained for the 1-position was considered to be due to steric acceleration, and otherwise the figures agree with those obtained in detritiation.

The reactivity of the 2-position, in dibenzofuran, represents about 86% of the total reactivity of the 1-, 2-, 3-, and 4-positions, and a greater predominance of 2-substitution, in other reactions, than for dibenzothiophen is expected. Molecular bromination[120] yields 80% of the 2-bromo derivative, and more than 76% of the 2-derivative is formed in sulphonation.[121] In benzoylation, the 2-derivative was isolated exclusively, but only in 40% yield.[122]

Results of mercuration[123] and nitration of dibenzofuran are anomalous. Initial attachment of the acetoxymercuric group to the oxygen atom, followed by migration, probably explains why only 4-substitution is obtained in mercuration. In nitration in acetic acid,[80] 80% of the 3-nitrodibenzofuran has been obtained. Nitration, in acetic anhydride,[124] is reported to give 40% of the 2- and 3- and 20% of 1--nitration.

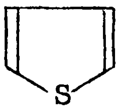


Good agreement is found between the results in detritiation and those shown in the above figure for the protodesilylation of dibenzofuran compounds.[113]

Recently, Brown and Coller[125] have calculated the π-electron density of dibenzofuran and related heterocyclic compounds, by a molecular orbital treatment. They regarded the nitration results, in acetic anhydride, as general for electrophilic substitution, whereas, they are clearly anomalous. Their calculations, therefore, cannot apply to other electrophilic reactions and it is difficult to see how calculations of π-electron densities, in the ground state of the aromatic molecule, can apply to various reactions with different electron demand of reagents and differing polarizations of the molecule.

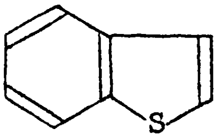
2. Thiophen, benzothiophen and benzofuran

The partial rate factors for detritiation of some positions of thiophen, benzothiophen and benzofuran were measured, in anhydrous trifluoroacetic acid at 70.11°, and the values obtained are shown in the following diagrams:-



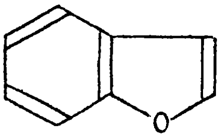
1.87×10^4

2.31×10^7



3.41×10^5

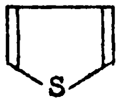
2.58×10^5



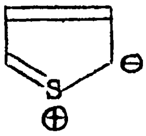
1.7×10^4

[2-^{3}H]furan was prepared but a rate-factor could not be obtained because the compound polymerised rapidly on contact with anhydrous trifluoroacetic acid.

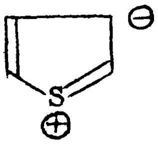
The rate of detritiation of the 2-position of thiophen was too fast to measure at 70.1°, and the exchange reaction was followed at -10.0° and 24.84°. The rate of exchange at 70.1° was then obtained by extrapolation from the lower two temperatures and the partial rate factor for the 2-position, of thiophen, was obtained by the direct comparison of this rate with the rate of exchange of a single position in benzene. Pauling and Schomaker[133] considered that the structure of thiophen was a resonance hybrid, consisting of the following classical and polar stuctures



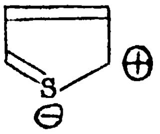
V



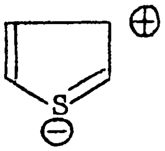
VI



V11



V111



1X

In structures V1 and V11, the 2p electrons of the sulphur atom conjugate with the π-electrons of the ring, but since sulphur is a second row element the "d" orbitals play a part in forming three pd^2 hybrid orbitals with the sulphur atom, two of which have the correct symmetry and energy to conjugate with the carbon atoms (Figures V111 and 1X). The overall effect is to make the sulphur atom a less effective donor than the oxygen atom. A result of these contributions is that the resonance energy of thiophen is increased, the stabilization as measured by heats of combustion is for furan 16.2Kcal./mole, and for thiophen 29.1Kcal./mole (which could explain the breakdown of the furan molecule in anhydrous trifluoroacetic acid).

The results indicate that, in hydrogen exchange, the reactivity of the 2-position of thiophen is 1240 times that of the 3-position. This is in good agreement with the figures of Halvarson and Melander,[66] who found that the 2-position is 955±140 as reactive as the 3-position of thiophen in detritiation in 59.4% aqueous sulphuric acid. In protodesilylation, Deans and Eaborn[64] showed that the 2-thienyltrimethylsilane is cleaved 43.5 times faster than the 3-isomer.

This quantitative data shows clearly that the 2-position of thiophen is much more reactive, towards electrophilic substitution, than the 3-position. The 2-position is activated by the tautomeric effect of the sulphur atom, as shown in Figure X.

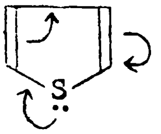
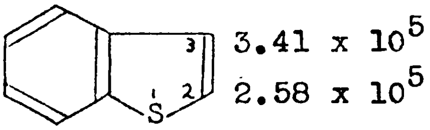


Figure X

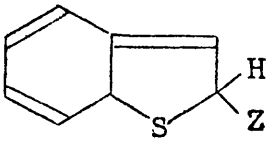
The bromination of thiophen in carbon tetrachloride gives 2-bromothiophen in 55% yield and some 2,5-dibromothiophen.[134] Coonradt, Hartough and Johnson[135] studied the chlorination of thiophen in detail and found, in monochlorosubstitution, that 99.7% of 2-chlorothiophen and 0.3% of 3-chlorothiophen was produced. Further chlorination of the 2-chloro isomer gave 99% of 2,5-dichlorothiophen and 1% of 2,3-dichlorothiophen. Addition products can also be obtained in the chlorination of thiophen.[136] In acylation and amino-alkylation, substitution has been reported to be exclusively in the 2-position. In nitration,[137] the product consisted of 97% 2- and 3% of the 3-substituent, and in sulphonation[137] although the major product was the 2-isomer, a trace of the 3-isomer was formed. With alkylation,[138] however, almost equal proportions of the two isomers are reported to be formed.

The rate factors obtained for benzothiophen are shown in the following figure:-

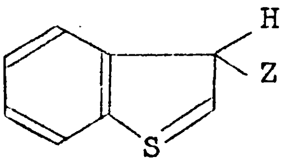


Anhydrous trifluoroacetic acid was the medium used for the detritiations but the rates of exchange could not be measured at 70.1° (which would be desirable in order to compare the rates directly with that for a single position in benzene) as the compounds were too reactive. The exchange reactions were followed at 24.84° and 40.0°, and extrapolated to give the rate of exchange at 70.1°. It was shown in the case of the $[2-{}^{3}H]$ benzothiophen, that agreement between the extrapolated and measured values at 70.1° was satisfactory (the measured value of 2.15×10^{5} being within 10% of the extrapolated figure).

The fusion of a benzene to a thiophen ring to give benzothiophen results in a large decrease in reactivity of the 2-position, but an increase in that of the 3-position. The large change, in reactivity of the 2-position of the thiophen ring, can be associated with the fact that the +*T* effect of a sulphur atom can only reach this position in benzothiophen by disturbing the conjugation within the benzene ring, as shown in structure X1 for the Wheland intermediate.



X1



X11

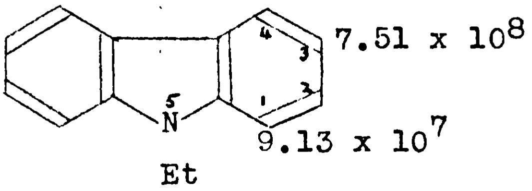
This is not so with the 3-position (structure X11).

Eaborn and Sperry[113] report, in protodesilylation that the reactivities of the 2- and 3-positions are almost equal, i.e. 39.6 and 40.7 repectively. The results indicate that, in the electrophilic substitution of benzothiophen, although substitution should occur mainly at the 3-position, large amounts of the 2-substituted products should be formed.

Farrar and Levine[139] found that in the acylation of benzothiophen, in the presence of seven different acidic catalysts, a mixture of the 2- and 3-isomers was always formed. In nitration[140], only the 3-nitro product has been isolated, but a recent preliminary communication[141] indicates that at least 10-15% of the 2-substitution occurs. Other reactions such as molecular bromination,[90,142] chloromethylation[143] and mercuration[144] seem to result in 3-substitution only.

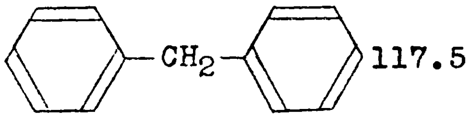
The reactivity of the 2-position of benzofuran appears to be less than that of the 2-position of benzothiophen. The figure for benzofuran, however, can only be regarded as approximate since a side-reaction occurred in the anhydrous trifluoroacetic acid, and first order kinetics could not be obtained. The rate was obtained by drawing a tangent at zero time. Other electrophilic substitutions of benzofuran, occur at the 2- rather than the 3-position.

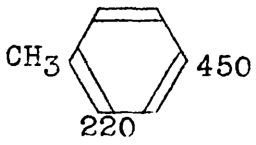
3. 5-Ethylcabazole



The partial rate factors, obtained for detritiation in trifluoroacetic acid, are shown in the above figure. Hydrogen exchange in this compound was so fast that the kinetics had to be studied at -10.0°. The rates of exchange of the 1- and 3-positions of 5-ethylcarbazole was compared with the rate of detritiation of $[2\text{-}^{3}\text{H}]$mesitylene at -10.0°. The rate of exchange of $[2\text{-}^{3}\text{H}]$mesitylene was measured at 24.84° and the rate of exchange, of this compound, was found at 70.1° by extrapolation from the lower two temperatures; the partial rate factor for $[2\text{-}^{3}\text{H}]$mesitylene was then found by comparison of its rate of exchange with that of a single position of benzene. The partial rate factors of the 1- and 3-positions of 5-ethylcarbazole were then found by comparison with that deduced for $[2\text{-}^{3}\text{H}]$mesitylene. Eaborn and Sperry[113] have previously shown that 5-ethylcarbazole is not protonated, to a detectable extent, in a stronger acidic medium than anhydrous trifluoroacetic acid. The results indicate the much greater reactivity of 5-ethylcarbazole over dibenzo-furan and -thiophen; Eaborn and Sperry[113] obtained a rate factor of 50,000 for the protodesilylation of the 3-position in 5-ethylcarbazole, which was again much more reactive than the corresponding position on dibenzo-furan and thiophen. Dewar and Urch[110] have reported partial rate factors for the 1- and 3-positions of carbazole of 32,000 and 77,600 respectively, for nitration by nitric acid in acetic anhydride, the 3-position is slightly more than twice as reactive as the 1-position. The results for detritiation show that the 3-position is about 7 times more reactive than the 1-position, in agreement with the larger spread of rates in hydrogen exchange than in nitration.

4. Diphenylmethane, phenanthrene and naphthalene

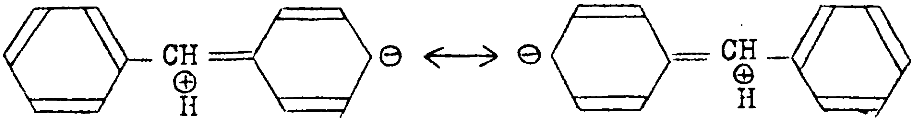




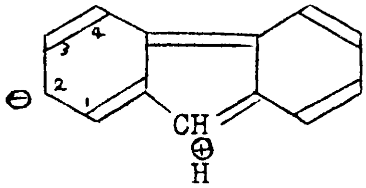
The partial rate factor obtained for detritiation of $[4\text{-}{}^{3}H]$diphenylmethane, in anhydrous trifluoroacetic acid at 70.1°, is shown above and compared with the values obtained for the <u>ortho</u>- and <u>para</u>- positions of toluene. The reactivity of the 4-position of diphenylmethane is less than that of the 4-position of toluene because of the electron-withdrawing inductive effect of the phenyl group. In nitration, with nitric acid in acetic anhydride, Dewar and Urch[110] obtained partial rate factors of 32 and

58 for the 4-position of diphenylmethane and toluene respectively. Sperry[147] reported partial rate factors of 7.84 and 21.1, respectively, for the 4-position of diphenylmethane and toluene in protodesilylation.

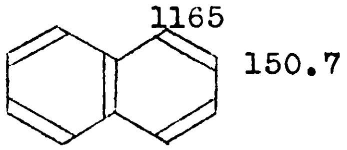
The activation of the *para*-position of diphenylmethane arises partly from hyperconjugation, there being contributions to the resonance hybrid by the structures:

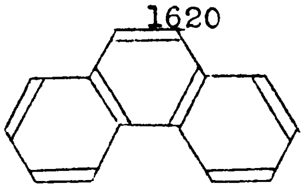


In fluorene, the 2-position is formally *meta*- to the bridging alkyl group, but de la Mare *et. al.*[148] considered that the alkyl group could conjugate through the second ring, as shown:



Hyperconjugation in fluorene is discussed on page 180 but if hyperconjugation of the electron-pair of a C-H bond is analogous to the conjugation by a lone pair of electrons, it should be much greater in fluorene where the C-H bond, in the alkyl group, is held in a plane at right angles to the plane of the rings, than in diphenylmethane, where the C-H bond is in the plane of the unsaturated system.





The rates of detritiation of [α- and β-^{3}H] naphthalene, in anhydrous trifluoroacetic acid at 70.1° relative to a single position in benzene, are 1165 and 151. The partial rate factor obtained for the detritiation for the 9-position of phenanthrene, under the same conditions is shown in the above diagram. The figures for naphthalene, agree with those of Eaborn and Taylor,[54] who report partial rate factors for [α- and β-^{3}H] naphthalene of 1079 and 127 for detritiation in trifluoroacetic acid - aqueous sulphuric acid, and 370 and 62 in trifluoroacetic acid - aqueous perchloric acid. Dallinga, Stuart, Smit and Mackor[55] obtained a similar difference in reactivity for the α- and β-positions of naphthalene in deuteration; they report partial rate factors for the α- and β-positions, in trifluoroacetic acid - carbon tetrachloride - deuterated sulphuric acid , of 178 and 23.4, respectively.

The α-position of naphthalene is considerable more activated than the β-position, in agreement with calculations.[55,56] The β-position is slightly less reactive than the 4-position in biphenyl, again agreeing with calculations.[55, 56]

The value of the ratio $\left(\frac{\log f_p^{Me}}{\log f_{3,4}^{C_4H_4}}\right)$ is lower than for other reactions for which it is known, with the exception of nitration, which appears to be anomalous. Apart from this, the value of the ratio tends generally to fall as f_p^{Me} rises, indicating that electron-release by the activating ring is called forth more strongly as the general electron-demand rises.[54]

Reaction	Reference	f_p^{Me}	$\frac{\log f_p^{Me}}{\log f_{3,4}^{C_4H_4}}$
Protodegermylation	145	14	4.54
Protodesilylation	146	21	3.96
Mercuridesilylation	146	17.5	2.69
Detritiation	54	313	1.39
Detritiation	54	702	1.32
Detritiation	present work	450	1.22
Nitration	56b)	58	1.02

The results confirm the observation[146] that no single substituent constant can satisfactorily represent the effect of the 3,4-C_4H_4 system in electrophilic aromatic substitution.

5. The Ortho/Para-Ratio.

The rates of detritiation of ortho- and para-tritiotoluene and ortho- and para-tritio-t-butylbenzene have been measured in a number of media: aqueous sulphuric acid, trifluoroacetic acid - aqueous sulphuric acid, anhydrous trifluoroacetic acid and heptafluorobutyric acid. The results are recorded in Table 11.

Table 11

Detritiation of $X.C_6H_4.[^3H]$ compounds.

i) Medium: $H_2SO_4 - H_2O$. Temperature: 24.84°.

H_2SO_4 a)	$10^7k(\text{sec.}^{-1})$ b) X = o-Me	p-Me	$\frac{f_o}{f_p}$
74.85	5185	4915	1.055
73.25	2800	2710	1.04
70.70	753	753	1.00
69.00	316	320	0.99
64.50	49.6	50.7	0.98
71.41	-	1090	-
	X = o-Bu^t	p-Bu^t	
71.41	768	805	0.955

a) wt.-% , b) No corrections for sulphonation have been applied since they would be small, and identical for the ortho- and para- isomers.

ii) Temperature: 70.11°

Medium	$10^7k(\text{sec.}^{-1})$ X = o-Me	p-Me	o-Bu	p-Bu	$\frac{f_o}{f_f}$	$\frac{f_o}{f_p}$
anhydrous CF_3CO_2H	20.8	42.7	23.0	50.9	0.49	0.45
anhydrous $C_3F_7CO_2H$	2.79	7.08	3.34	8.94	0.39	0.37

iii) Temperature: 24.84°

Medium	X = o-Me	p-Me	o-Bu	p-Bu	$\frac{f_o}{f_p}$	$\frac{f_o}{f_p}$
CF_3CO_2H - H_2O - H_2SO_4 (93.00)-(5.12)-(1.80)[c]	1295	1770	1565	2180	0.73	0.72

c) Figures in parentheses denote mole-%

In the medium $CF_3CO_2H(92.04)$ - $H_2O(5.45)$ - $HClO_4(2.51)$, Eaborn and Taylor[40] obtained a $\frac{f_o}{f_p}$ ratio for toluene of 1.05 and t-butylbenzene of 1.02.

The $\frac{f_o}{f_p}$ ratio for toluene and for t-butylbenzene varies markedly, but in precisely the same way, with the change in medium; the $\frac{f_o}{f_p}$ ratio for t-butylbenzene being always slightly less than the $\frac{f_o}{f_p}$ ratio for toluene.

The small increase in the $\frac{f_o}{f_p}$ ratio for toluene, with increasing concentration of aqueous sulphuric acid, is probably real, and this would agree with the few results previously reported separately for particular concentrations.[12,19,21,23]

Lauer *et al.*[23] measured the rates of deuteration of benzene and toluene in deuterium oxide and trifluoroacetic acid mixtures. They obtained a ratio, $\frac{f_o}{f_p}$, for toluene of 0.60 and (taking into account Gold and Satchell's[19] $\frac{f_o}{f_p}$ ratio of 1.0 for the dedeuteration of toluene in 68wt.-% sulphuric acid) suggested that the steric hindrance to solvation for reaction at the ortho-position relative to the para-position might be smaller in sulphuric acid than in trifluoroacetic acid or heptafluorobutyric acid. Other ratios, $\frac{f_o}{f_p}$, for hydrogen-exchange in toluene have been reported: 1.11 for tritiation in 80.8% aqueous sulphuric acid,[12] 1.09 for dedeuteration in 70.8% aqueous perchloric acid,[21] 0.70 for dedeuteration in trifluoroacetic acid containing a little sulphuric acid,[20] 0.60 for dedeuteration in *ca.* 95vol.-% aqueous trifluoroacetic acid,[23] 0.41 for dedeuteration in anhydrous heptafluorobutyric acid,[21] 0.25 for dedeuteration in liquid hydrogen bromide[51] and 0.5 for dedeuteration in liquid hydrogen iodide.[51]

The rates of detritiation of ortho- and para-tritiobiphenyl have also been measured in anhydrous trifluoroacetic acid and anhydrous heptafluorobutyric acid. The results are shown in Table 111.

Table 111

Detritiation of o- and p-tritiobiphenyl.

Temperature: 70.11°.

Medium	10^7k(sec.$^{-1}$)		f_o	f_p	$\frac{f_o}{f_p}$
	o	p			
anhydrous CF_3CO_2H	9.31	15.5	98.0[a]	163[a]	0.60
anhydrous $C_3F_7CO_2H$	1.82	4.28	-	-	0.43

a) for benzene at 70.11°, $k = 0.095 \times 10^{-7}$sec.$^{-1}$

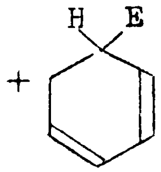
When these results are compared with other reported values for the $\frac{f_o}{f_p}$ ratio of biphenyl in hydrogen-exchange reactions, the variation of the reactivity of the ortho- relative to the para-position, with the medium, is again evident. Eaborn and Taylor[54] obtained a $\frac{f_o}{f_p}$ ratio of 1.0 for the detritiation of biphenyl in a trifluoroacetic acid - aqueous perchloric acid medium, and 0.93 in a trifluoroacetic acid - aqueous sulphuric acid medium. Other values of the $\frac{f_o}{f_p}$ ratio for these positions, in hydrogen-exchange, have been reported: 0.63 for dedeuteration in aqueous trifluoroacetic acid,[59] 0.33 for dedeuteration in liquid hydrogen bromide and 0.25 for dedeuteration in liquid hydrogen iodide.[51]

Considering first the results for toluene and t-butylbenzene. Tiers[21] suggested that the smallness of the $\frac{f_o}{f_p}$ ratio in heptafluorobutyric acid is a consequence of the large steric requirement of the proton donor. However, if the variation of the $\frac{f_o}{f_p}$ ratio in toluene arises from steric hindrance, either by compression between the methyl groups and the incoming and outgoing groups at the reaction centre, or by interference with solvation, then the effect should be much greater with t-butylbenzene. Since the $\frac{f_o}{f_p}$ ratio of the two compounds varies in almost identical ways with the change in media, a steric explanation is unsatisfactory. The evidence suggests, in fact, that the steric requirement of the attacking entities in detritiation are small; this is in agreement with the conclusion reached by Lauer *et. al.*,[24] after studying the deuteration of toluene and t-butylbenzene in trifluoroacetic acid - deuterium oxide mixtures.

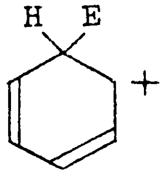
In the present work, the fall in the $\frac{f_o}{f_p}$ ratio parallels the fall in the dielectric constant of the medium. Baker, Eaborn and Taylor[114] put forward an explanation of the variations of the *ortho/para*- ratio for toluene and for t-butylbenzene in different media; they considered that the polar effects, of the *ortho*- relative to that of a *para*-alkyl group, varied with the electron demand of the attacking species. It was assumed that the inductive effects of the alkyl groups reach the *ortho*- more effectively than the *para*- positions, but the tautomeric effects reach the *para*-positions more easily. They noted that high $\frac{f_o}{f_p}$ ratios could be associated with positively charged, and low ratios with neutral attacking species (e.g., the un-ionised acids, trifluoroacetic acid, heptafluorobutyric acid and liquid hydrogen halides). A decrease in the reactivity of the attacking acid is accompanied by increasing polarizability effects and Baker, Eaborn and Taylor considered that the $\frac{f_o}{f_p}$ ratio was expected to fall.

Following their work on the isomer distribution for the chlorination and nitration of monosubstituted benzenes, Norman and Radda[149] put forward an explanation for the variation of the <u>ortho/para</u> - ratios in terms of electronic effects. Earlier work by Knowles, Norman and Radda[150] had indicated that the principle suggested by Hammond[151] was applicable to aromatic substitution; this was, that the transition state resembles the reactants when these are of high reactivity, and the Wheland intermediate when they are of low reactivity.

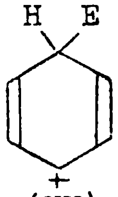
For a reactant of low reactivity, the transition state was assumed to have the same structure as the Wheland intermediate.



(XIII)

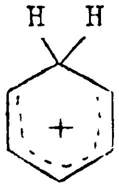


(XIV)



(XV)

The structure being a resonance hybrid of the canonical structures (XIII),(XIV), and (XV). Evidence has recently been obtained,[152,153] that the positive charge in a benzonium ion:-



is more heavily concentrated on the para- than on the ortho-position. Principles of electron correlation lead to a deeper understanding of this, since the four π-electrons in the resonance hybrid tend to be distributed in pairs, lying as far as possible from each other on opposite sides of the nucleus.[154]

Norman and Radda pointed out that any substituent group will exert a more powerful effect on the stability of the hybrid ion when it is in the para- rather than the ortho-position to the entering reagent. Thus, for the electron-releasing methyl group, the hybrid ion will be stabilised in the order of the para- greater than the ortho- position. Therefore, when the transition state resembles the intermediate, electron-releasing substituents will activate the para- more than the ortho-position.

For reactants of high reactivity Norman and Radda assumed the Hammond postulate to apply, so that the transition state in the reactions should involve only minor deformations of the aromatic system. The relative reactivities of the ortho- and para-positions should then be determined by the relative electron densities, at these positions, in the ground state of the molecule. From evidence on the σ-values for the _m_- and _p_-NMe_3^+ groups,[155] which indicated a more powerful operation of the inductive effect on the _meta_- than the _para_-position, and also the small contribution of the resonance polar effect,[154,156] they concluded that a methyl group induces a higher electron density at the _ortho_- than at the _para_-position. The _ortho_- position, should therefore, be more reactive towards reagents of high reactivity when the transition state involves little deformation of the aromatic system.

The present results, for the detritiation of toluene and t-butylbenzene, can be explained in terms of these electronic factors suggested by Norman and Radda. The highest _ortho/para_- ratios are obtained with acids involving positively charged attacking species; quoting results for toluene: aqueous sulphuric acid (1.11),[12] aqueous perchloric acid (1.09),[21] trifluoroacetic acid containing perchloric acid (1.02),[40] trifluoroacetic acid containing sulphuric acid (0.73),[40] Low _ortho/para_- ratios have been obtained with the neutral, attacking species; liquid hydrogen iodide (0.5),[51] anhydrous trifluoroacetic acid (0.49), anhydrous heptafluorobutyric acid (0.39) and liquid hydrogen bromide (0.25).[51]

Chlorination reactions show the same effect, in that, higher _ortho/para_- ratios are obtained for the attack by the chlorinium ion or related species ($\frac{f_o}{f_p} = 1.63$)[157] than for attack by molecular chlorine ($\frac{f_o}{f_p} = 0.75$). Steric factors probably also play a part in molecular chlorination, but this is possibly small in the case of toluene, since the $\frac{f_o^{Bu^t}}{f_p^{Bu^t}}$[157] ratio is only five times smaller than the $\frac{f_o^{Me}}{f_p^{Me}}$ ratio.

The Norman and Radda application of the Hammond postulates, can also be applied to an explanation of the results for the detritiation of the ortho- and para-tritiobiphenyls in acidic media. Again, as with the alkylbenzenes, high ortho/para- ratios are obtained in reactive media involving charged ions (media containing perchloric acid and sulphuric acid) and low ratios with the neutral, undissociated molecules (trifluoroacetic acid and heptafluorobutyric acid). With the acids of high reactivity, the transition state, in these reactions, would involve only minor deformations of the aromatic systems, so that, the relative reactivities of the ortho- and para- positions should be determined by the relative electron densities, at these positions, in the ground state of the molecule. The transition state in the less reactive acids may be taken to have a structure similar to the Wheland intermediate. In this structure, there is probably a greater positive charge on the para- than the ortho- position, as indicated by the evidence,[152,153,154] previously discussed. The phenyl group, will therefore, exert a greater +E effect on the para- than on the ortho-position; this will give rise to a larger amount of para- orientation. This effect is shown in that the detritiation results for biphenyl, in anhydrous heptafluorobutyric acid (0.43), has a smaller ortho/para- ratio than in anhydrous trifluoroacetic acid (0.60). High ortho/para- ratios have been obtained, in hydrogen-exchange reactions, in more reactive media containing perchloric acid and sulphuric acid (1.0 and 0.93, respectively).[54]

Evidence from other reactions shows that, as with alkylbenzenes, high ortho/para- ratios are found in attack by positively charged ions, and low ratios with neutral, unionised species. De la Mare and Hassan[58] showed in bromination by the brominium ion, biphenyl has a $\frac{f_o}{f_p}$ ratio of 0.68, whilst bromination by molecular bromine yields only a small amount of the ortho- derivative. This cannot be explained on wholly steric grounds, since in nitration by nitric acid in acetic anhydride,[158] biphenyl has a $\frac{f_o}{f_p}$ ratio of 1.8, and it has been shown that the nitronium ion is effectively larger than the brominium ion.[159]

Recent work by Weingarten,[160] on the chlorination of biphenyl, shows a striking change of the ortho/para- ratio under different conditions; the results are shown in Table lV.

Table 1V

The chlorination of biphenyl.

Chlorinating system	$\frac{1}{2}$o/p-ratio
$AlCl_3$, Cl_2, benzene	0.73
$GaCl_3$, Cl_2, *o*-dichlorobenzene	0.93
$AlBr_3$, Cl_2, *o*-dichlorobenzene	0.89
$FeCl_3$, Cl_2, benzene	0.69
$SbCl_5$, Cl_2, benzene	0.88
$SnCl_4$, Cl_2, benzene	0.83
H_2SO_4, Ag_2SO_4, Cl_2, CCl_4	0.73
$BF_3O(C_2H_5)_2$, Cl_2, CCl_4	0.37
HOAc, Cl_2	0.26
HOAc, Cl_2, CCl_4	0.2

Weingarten proposed that, for the more selective chlorinating agents, the transition state would be similar to the Wheland intermediate. He suggested that as the reagent increases in reactivity the carbon-chlorine bond would become longer and be much less effected by steric interactions; the *ortho/para*- ratio would therefore rise. He found that the increase in *ortho/para*- ratio parallelled the increase in Lewis-acid strength of the chlorinating medium. However, the results can be explained by the Norman and Radda treatment, without the need to consider steric effects. The decrease in the *ortho/para*-

ratio would then be a consequence of the transition state resembling, more closely, the structure of the Wheland intermediate with decrease in reactivity of the chlorinating medium.

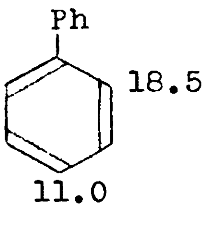
6. The Reactivity of Biphenyl

The rates of detritiation of 2- and 4-tritiobiphenyl have been measured in anhydrous trifluoroacetic acid. The partial rate factors were 98 and 163 for the 2- and 4-position respectively. The decrease in the *ortho/para*-ratio on changing the medium to heptafluorobutyric acid has already been discussed.

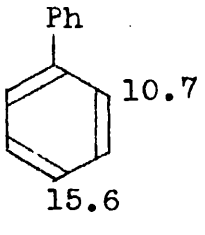
The results indicate that the *ortho*-phenyl and the *para*-phenyl groups have an activating effect. Partial rate factors have been reported[54,55,161] for the 3-position of biphenyl and these show that the *meta*-phenyl group has a deactivating effect. The facts are in accord with the representation of the phenyl group as withdrawing electrons by an inductive effect, but returning electrons directly to the 2- and 4-positions by an electromeric effect, at the demand of the reagent.

Primary steric effects have been shown to be unimportant in detritiation,[114] and the partial rate factors are probably a true reflection of the relative electronic activation at these positions. This is in agreement with Dewar's simple estimates of localisation energies,[56a),56b)] but not with more complicated calculations of localisation,[56c)] with calculations by the self-consistent-field method of the energies required to convert the hydrocarbon, ArH, into the ion ArH_2^+,[55] or with the free-valence numbers,[56d)] all of which assign a higher reactivity to the *ortho*-position.

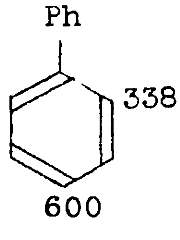
Preparative chemistry has shown biphenyl to be chemically more reactive than benzene towards electrophilic reagents. It can be acetylated in benzene,[162] benzoylation takes place several times faster than benzene,[163] and halogenation many times faster.[164] Biphenyl is 12.6 times as reactive as benzene in bromination by Br^+ and it was concluded that the *ortho*- and *para*-positions are activated while the *meta*-position is deactivated.[58] Partial rate factors have been determined for nitration,[56b)] chlorination by Cl_2,[148,166] bromination by Br_2,[166] and for bromination by Br^+,[58] these are shown in the following diagrams.



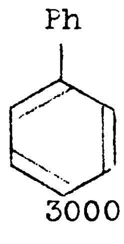
HNO_3 in Ac_2O



Br^+ or $BrOH_2^+$



Cl_2



Br_2

Nitric acid in acetic anhydride was reported by Simamura and Mizuno[165] to give the *ortho-* and *para-*nitro derivatives in a ratio of 68:32. Billings and Norman[193] studied the nitration of biphenyl under five sets of conditions. Their values, for nitration in acetic anhydride, were close to those obtained by Simamura and Mizuno, but in heterogeneous conditions they found that a larger proportion of the *para-* isomer was formed (57:43).

Weingarten[160] studied the chlorination of biphenyl under different conditions; the variation in the *o/p-* ratio has been discussed (page 165).

Partial rate factors reported in hydrogen-exchange work are given in Table V.

Table V

Hydrogen - exchange in biphenyl.

Medium	f_o	f_m	f_p	Reference
anhydrous CF_3CO_2H	98.0	-	162.6	present work
CF_3COOD - CCl_4 - D_2SO_4	37.2	0.3	143	55
CF_3CO_2H - H_2O - H_2SO_4	133	0.34	142	54
CF_3CO_2H - H_2O - $HClO_4$	52	-	52	54
aqueous CF_3CO_2H	82	0.49	149	59
liquid HBr	$3\text{x}10^{-5}$[a]	-	$1\text{x}10^{-4}$[a]	161
liquid HI	$1\text{x}10^{-6}$[a]	-	$4\text{x}10^{-6}$[a]	51

a - rate constants.

The spread of rates varies with the medium used, as found with the detritiation of alkylbenzenes.[40,25,27] The values of $\frac{\log f_p^{Me}}{\log f_p^{Ph}}$ are in line with the observation that the ratio shows a tendency to fall as f_p^{Me} rises, probably as the electron demand rises and calls forth increasingly the +E effect of the *para*-phenyl group.[57,58] This is illustrated in Table V1.

Table V1

Reaction	Reference	f_p^{Me}	$\frac{\log f_p^{Me}}{\log f_p^{Ph}}$
protodestannylation	168	5.6	3.0
protodegermylation	145	14	2.66
protodesilylation	57	18	2.40
mercuridesilylation	146	17.5	1.70
nitration	56b,	58	1.48
ionic bromination	58	59	1.45
detritiation	present work	450	1.2
molecular chlorination	148,166	820	1.05

The results confirm the observation that no single substituent constant can satisfactorily represent the effect of the *para*-phenyl group in electrophilic aromatic substitution.

It was suggested[58] that the high reactivity of the *ortho*-position, relative to that of the *para*-position in the nitration of biphenyl, depended on the fact that in the transition state for *ortho*-substitution, tetrahedral disposition of bonds at the *ortho*-carbon atom allows the two benzene rings to be coplanar. The maximum amount of delocalisation of the positive charge in the aromatic system, in this state, can then occur.

The variation in the percentage of the *ortho*- to the *para*-isomer can now be understood in the light of the postulates proposed by Norman and Radda;[149] these have already been discussed (page 160). It was shown that attack of the aromatic compound by reactive reactants would yield high *ortho/para*- ratios, and low ratios would be expected with reactants of lower reactivity.

7. The transmission of substituent effects in biphenyl.

Biphenyl in the gas phase, and also in solution, is known to exist in a non-planar form;[169] the angle between the planes of the rings being about 45°. The barrier restricting rotation through a planar conformation is not known. Bulky substituents in the 2-position increase this barrier and force the rings still further away from coplanarity.[170] Conjugation between the two rings must fall from a maximum when these are coplanar to a minimum when they are at right angles to one another.

The values of $k_{rel.}$ which were obtained in the detritiation of substituted $[4\text{-}^3H]$ biphenyl compounds in anhydrous trifluoroacetic acid are shown in Table Vll.

Table Vll

Detritiation of substituted [4-^{3}H] biphenyl compounds in anhydrous trifluoroacetic acid at 70.11°.

Substituent	10^7k(sec.$^{-1}$)	$k_{rel.}$ a)	log $k_{rel.}$
4'-Me	62.1	654	2.815
4'-MeO	51.0	537	2.730
4'-H	15.45	162.6	2.211
4'-Cl	4.57	48.1	1.682
4'-Br	3.89	41.0	1.613
3'-Cl	1.91	21.0	1.303
4'-NO_2	0.615 b)	0.169 b)	-0.772

a) -for benzene at 70.11°, k = 0.095 x 10^{-7}(sec.$^{-1}$)

b)- measured and compared with benzene at 110.15°, for benzene at 110.15°, k = 3.64 x 10^{-7}(sec.$^{-1}$).

The increased reactivity of biphenyl is reflected in the fact that only when there is a nitro-group in the 4'-position does the reactivity fall below that of a single position in benzene, $k_{rel.}$ for 4'-NO_2-[4-^{3}H] biphenyl being 0.169. The nitro-group deactivates the compound to such an extent that the rate of exchange had to be measured at 110.15°, the partial rate factor of the compound was obtained by direct comparison of this rate of exchange with that of a single position in benzene at 110.15°. Halogens deactivate the molecule with respect to biphenyl, but 4'-Cl-$\left[4\text{-}^3H\right]$biphenyl and 4'-Br-$\left[4\text{-}^3H\right]$biphenyl are still 48 and 41 times respectively more reactive than benzene. The greater reactivity of 4'-Me-$\left[4\text{-}^3H\right]$biphenyl than that of 4'-MeO-$\left[4\text{-}^3H\right]$biphenyl ($k_{rel.}$ being 654 and 537) appeared to be anomalous. The value of $k_{rel.}$ for 3-Cl-$\left[4\text{-}^3H\right]$biphenyl is 20.1 (i.e., about half the value of $k_{rel.}$ for the 4'-chloro- compound). The small difference in reactivity, of the two compounds, is indicative of a less effective transmission of substituent effects in biphenyl than in benzene (in which a chloro- substituent deactivates the <u>meta</u>- position 100 times more than the <u>para</u>- position).

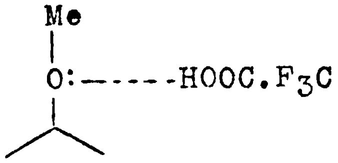
A series of measurements of the detritiation of 4'-Me-$\left[4\text{-}^3H\right]$- and 4'-MeO-$\left[4\text{-}^3H\right]$-biphenyl were made in mixtures of anhydrous trifluoroacetic acid and acetic acid. Three media were prepared of different compositions and, therefore, different acidities. The results are summarised in Table V111.

The decrease in the rate of exchange (with decrease in acidity of the media) of the 4'-MeO-$\left[4\text{-}^3H\right]$biphenyl was much less than that of the 4'-Me-$\left[4\text{-}^3H\right]$biphenyl, so that, in the weaker acidic media, the rate of detritiation of the methoxy- compound was greater than that of the methyl- compound. It is evident that some interaction occurs

Table V111

Wt.-% of CH_3CO_2H (99.2%) in anhydrous CF_3CO_2H	10^7k(sec.$^{-1}$) 4'-MeO	10^7k(sec.$^{-1}$) 4'-Me
0%	51.0	62.1
1.68%	43.5	50.3
13.2%	29.8	23.1
22.8%	8.15	4.90

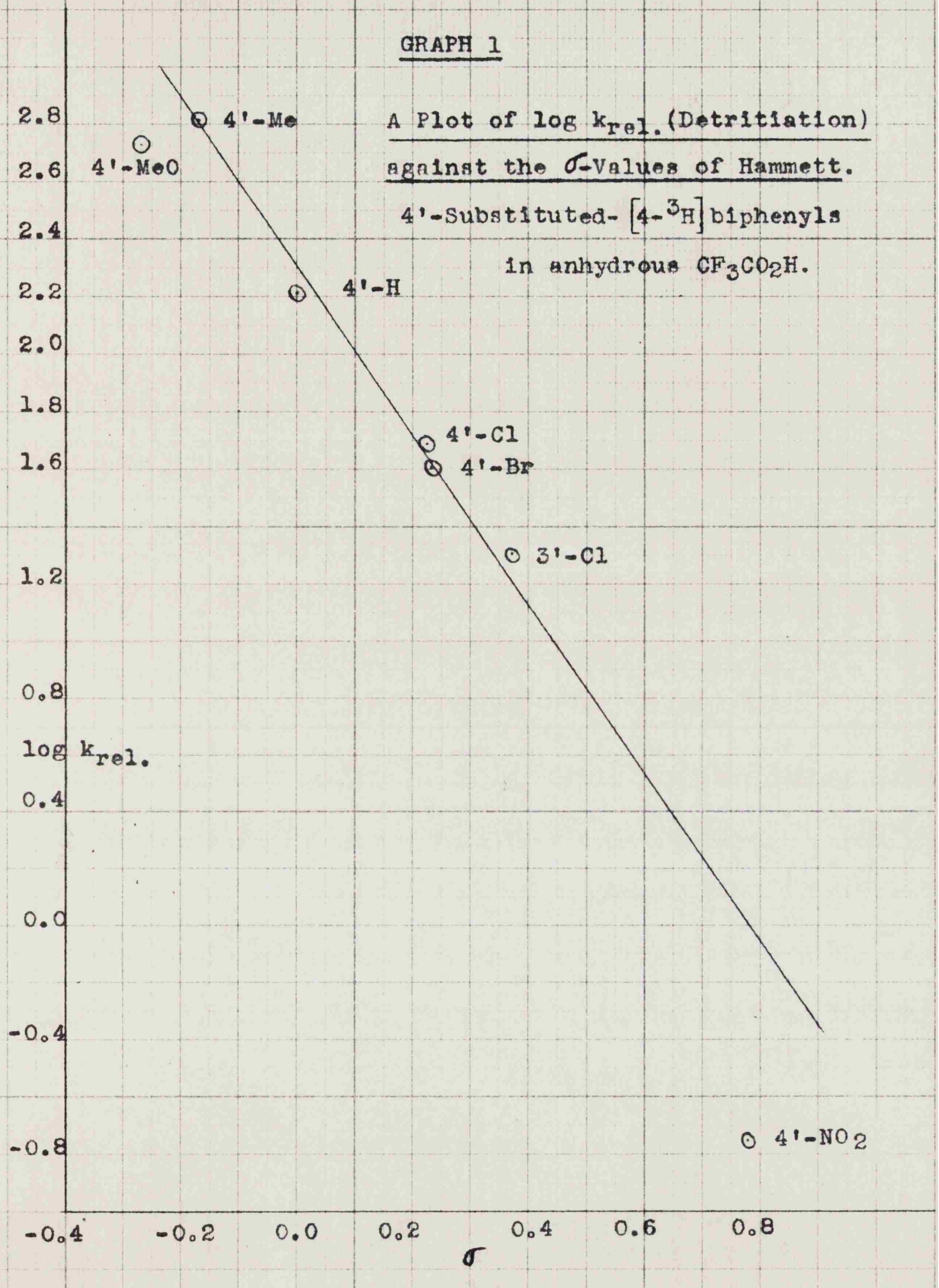
between a methoxy-group and the acidic media used. This is consistent with studies of the base strength of aromatic ethers in aqueous sulphuric acid , which have shown that some phenolic ethers (methyl, ethyl, n-propyl, n-butyl, sec.-butyl and n-amyl) are protonated on the oxygen atom.[171] Ultra-violet spectra of the methoxy-compound were studied in both a methanol and a trifluoroacetic acid medium, but no difference in spectra could be detected; a detectable amount of protonation of the methoxy- group in trifluoroacetic acid is, therefore, unlikely. It is possible that some hydrogen-bonding occurs between the oxygen atom, of the methoxy- group, and the trifluoroacetic acid.



The effect of this is to suppress the electron-supplying ability of the methoxy- group, though apparently not sufficient to change the ultra-violet spectrum appreciably. The fact that the 4'-MeO-$[4-{}^{3}H]$biphenyl was more reactive than 4'-Me-$[4-{}^{3}H]$biphenyl, in the weaker acidic media, indicated that some conjugation effects are transmitted between the two rings in biphenyl.

The results for the detritiation of substituted biphenyl compounds are consistent with those obtained by Greasley[172] of the cleavage of 4,4'-trimethylsilyl-substituted biphenyls in sulphuric acid - acetic acid - water mixtures, and also the results of Benkeser et. al.[173] of similar reactions in glacial acetic acid. Rice[59] obtained a partial rate factor of 490 for the dedeuteration of 4'-Me-$[4-{}^{2}H]$biphenyl in aqueous trifluoroacetic acid.

Graph 1 shows a plot of log $k_{rel.}$ for the detritiation of the biphenyl compounds against the Hammett σ-constants, and Graph 11 a plot of log $k_{rel.}$ against the Brown σ^{+}-constants. There is a somewhat better correlation with σ-constants than with σ^{+}-constants, which would be consistent with relative unimportance of the transmission of electromeric effects between the rings. The point for the *para*-methoxy substituent lies off the line on both graphs (though it is much nearer the line on the σ-plot). This is to be expected if the solvent interaction with the methoxy-group decreases the electromeric influences of the group.

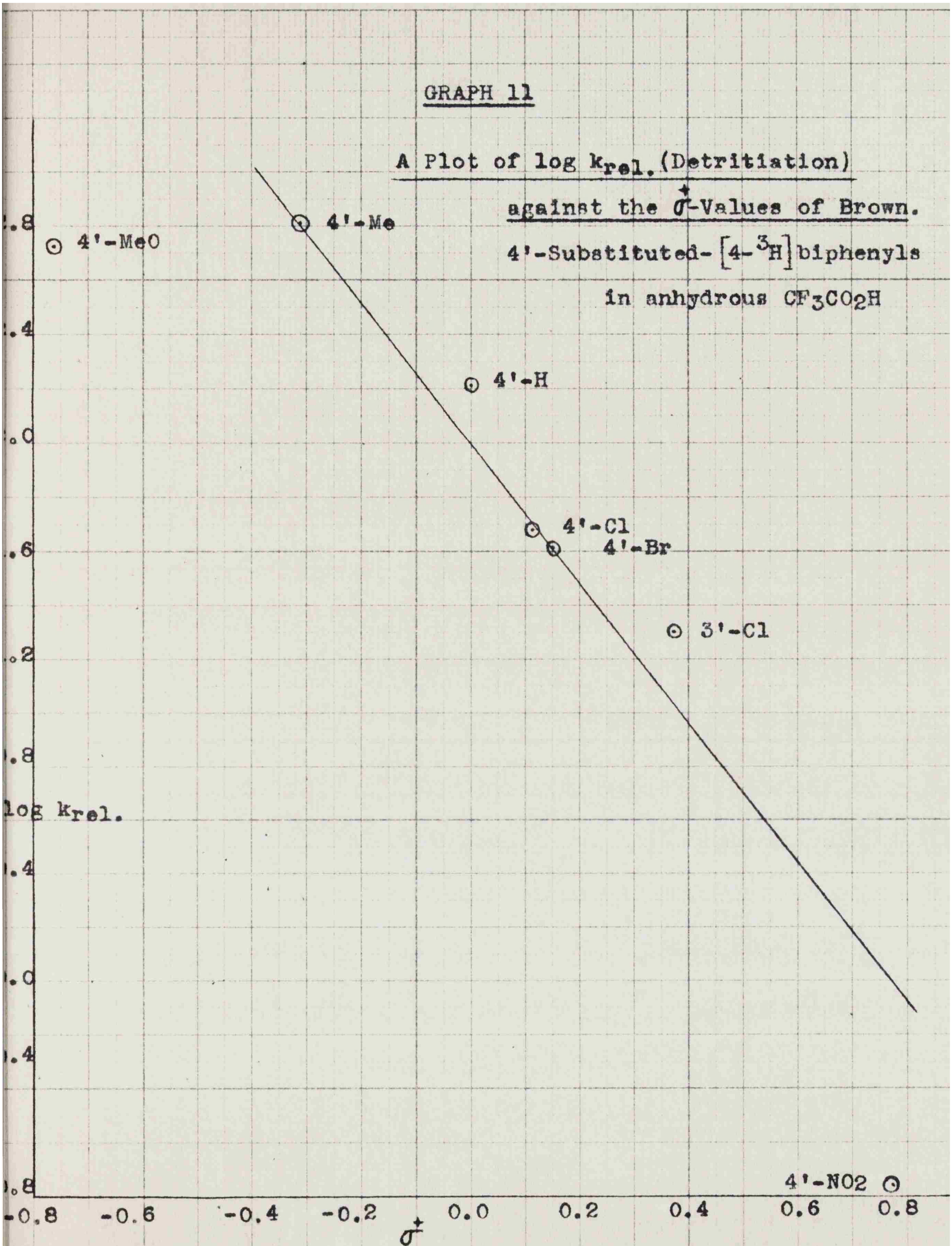


GRAPH 1

A Plot of log $k_{rel.}$ (Detritiation) against the σ-Values of Hammett.

4'-Substituted-[4-^{3}H]biphenyls in anhydrous CF_3CO_2H.

GRAPH 11



A Plot of log $k_{rel.}$ (Detritiation) against the σ^+-Values of Brown. 4'-Substituted-[4-^{3}H]biphenyls in anhydrous CF_3CO_2H

On the basis of the absence of 3'-substitution in the nitration of 2- and 4- nitrobiphenyl and the non-activation of halogen atoms in one ring by the presence of nitro-groups in the second ring, Le Fevre and Turner[174] suggested that "the two nuclei in biphenyl should be regarded as two independent, mobile, cyclohexatrienoid systems, united at the 1-1' position by an invariable single bond, which is not a link in a true conjugated system". The higher reactivity of biphenyl than benzene, however, implies some conjugation between the rings. Later physical data can best be explained by interaction between the rings. For example, Le Fevre and Le Fevre's[175] determinations of dipole moments indicate that "the lack of conjugation between the rings is not as complete as previously stated". Thermochemical data, X-ray, quantum mechanical calculations, and particularly absorption spectra indicate conjugation across the Ar-Ar bond in biphenyl.

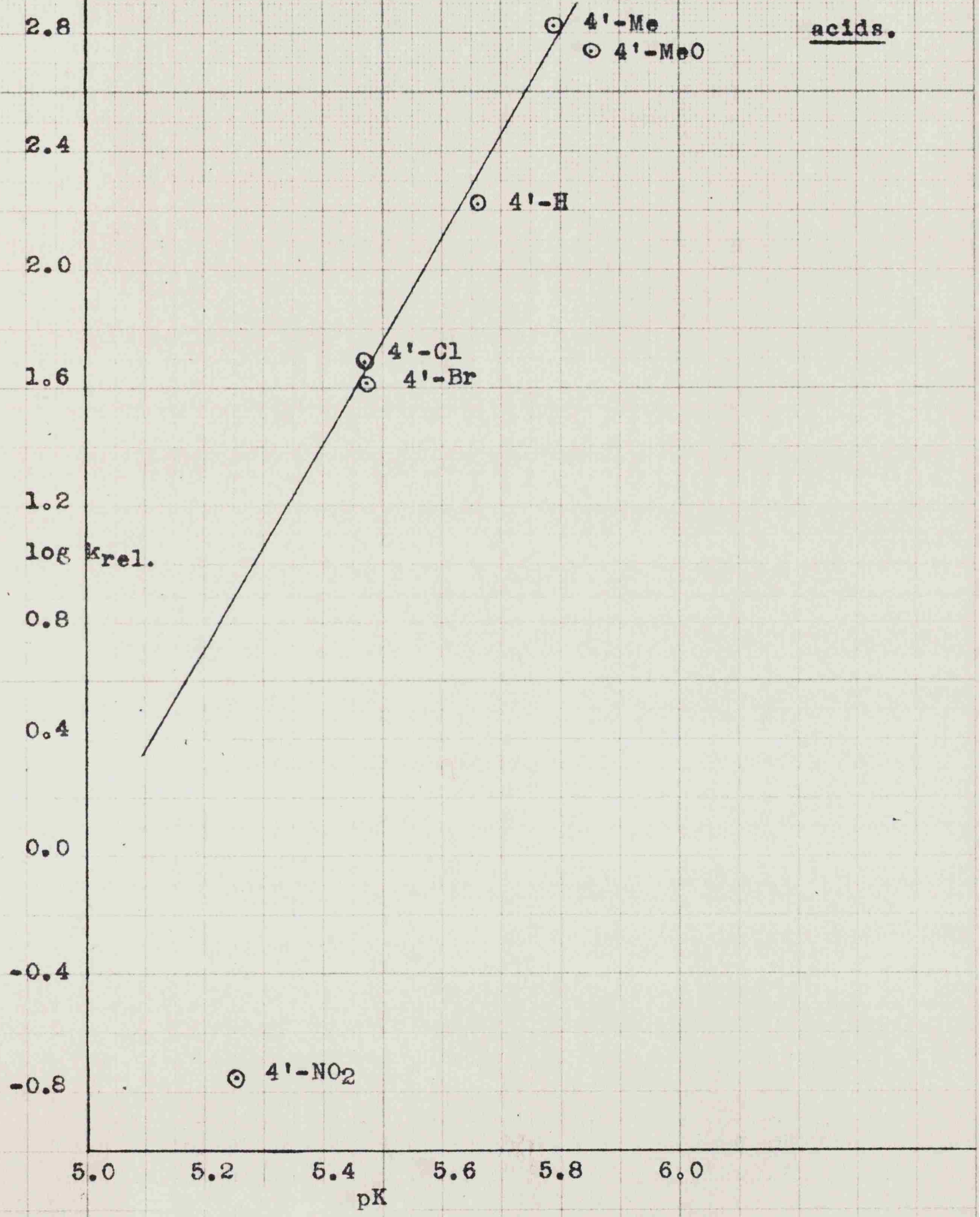
Berliner and Blommers[176] determined, potentiometrically, the dissociation constants of ten substituted biphenyl-4-carboxylic acids, and compared them with the dissociation constants of similarly benzoic acids. The dissociation constants of the biphenyl compounds were satisfactorily related to σ-constants, and the rho value was +0.37 (benzoic acids +1). The results indicated that substituent effects are transmitted through the biphenyl system as through the benzene system but that the effects are smaller in the biphenyl system. Graph 111 shows a plot of log $k_{rel.}$ for detritiation against their pK values; the points for the nitro- and methoxy- substituents deviate from the straight line. A possible explanation for the deviation in the case of the nitro- substituent, could be that some hydrogen-bond interaction occurs between the nitro- group and the trifluoroacetic acid; this would make the group more electron-withdrawing. A point against this explanation is , however, that rate measurements were made on the detritiation of 2-NO_2-$[7-^3H]$ fluorene and only a small deviation, with this compound, is noticed in the correlation between the log(rate of exchange) of the substituted fluorenes compounds and the Hammett and Brown substituent constants.

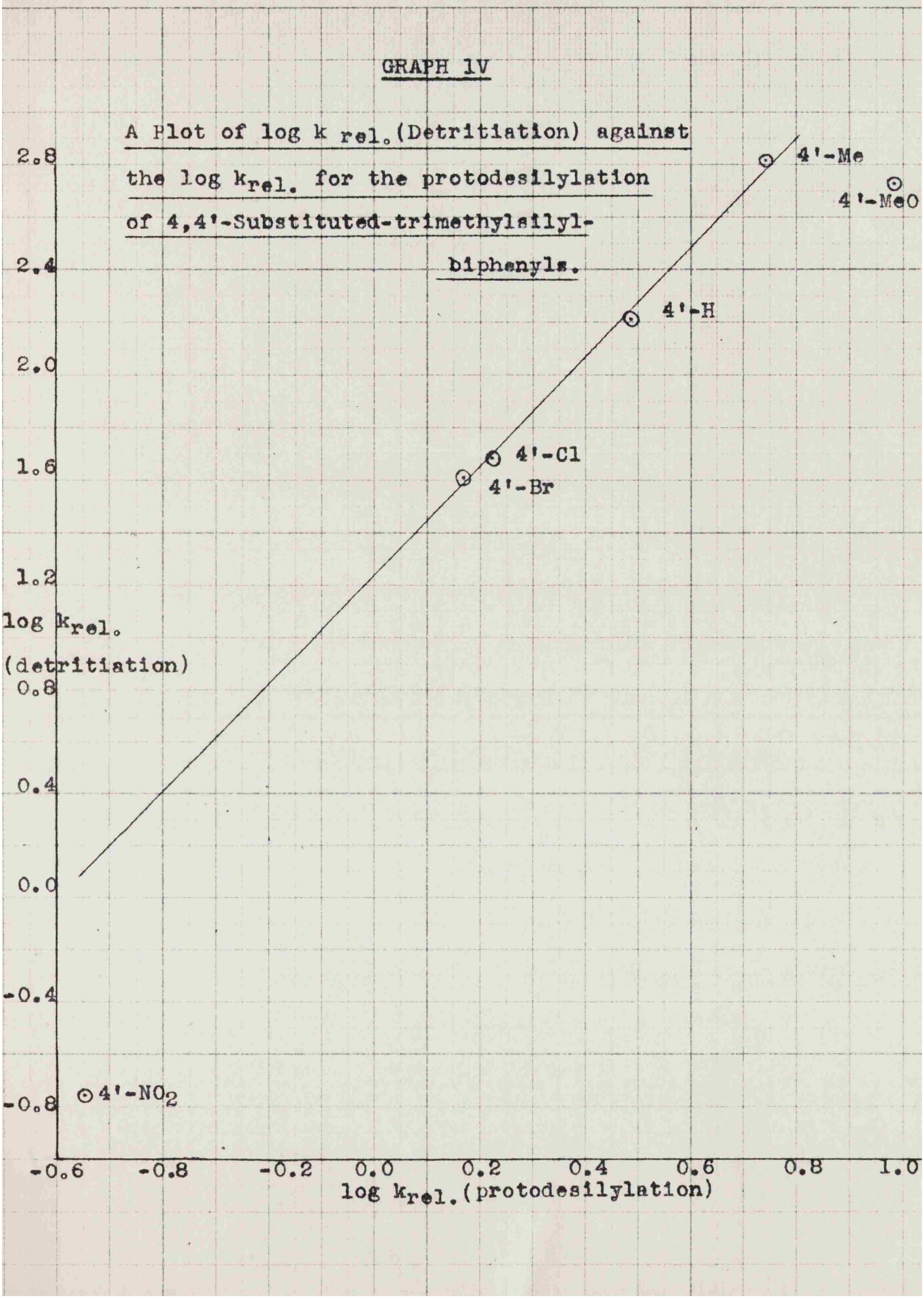
Berliner and Liu[177] examined the rates of alkaline hydrolysis of ethyl-*p*-carboxylates in 88.7%. A plot of log $k_{rel.}$ for this reaction against log $k_{rel.}$ for the detritiation of 4'-substituted biphenyl compounds gives a straight line (Graph V); deviations from linearity for the methoxy- and nitro- substituents are again obtained. A similar situation is obtained when log $k_{rel.}$ for the detritiation of 4'-substituted biphenyl compounds are plotted against the log $k_{rel.}$ for the protodesilylation of 4'-substituted biphenyl compounds (Graph 1V).

From a consideration of the chemical evidence of the reactions of biphenyl compounds, it is evident that biphenyl

GRAPH 111

Plot of log $k_{rel.}$ (Detritiation) against the pK values for 4,4'-Substituted Biphenylcarboxylic acids.



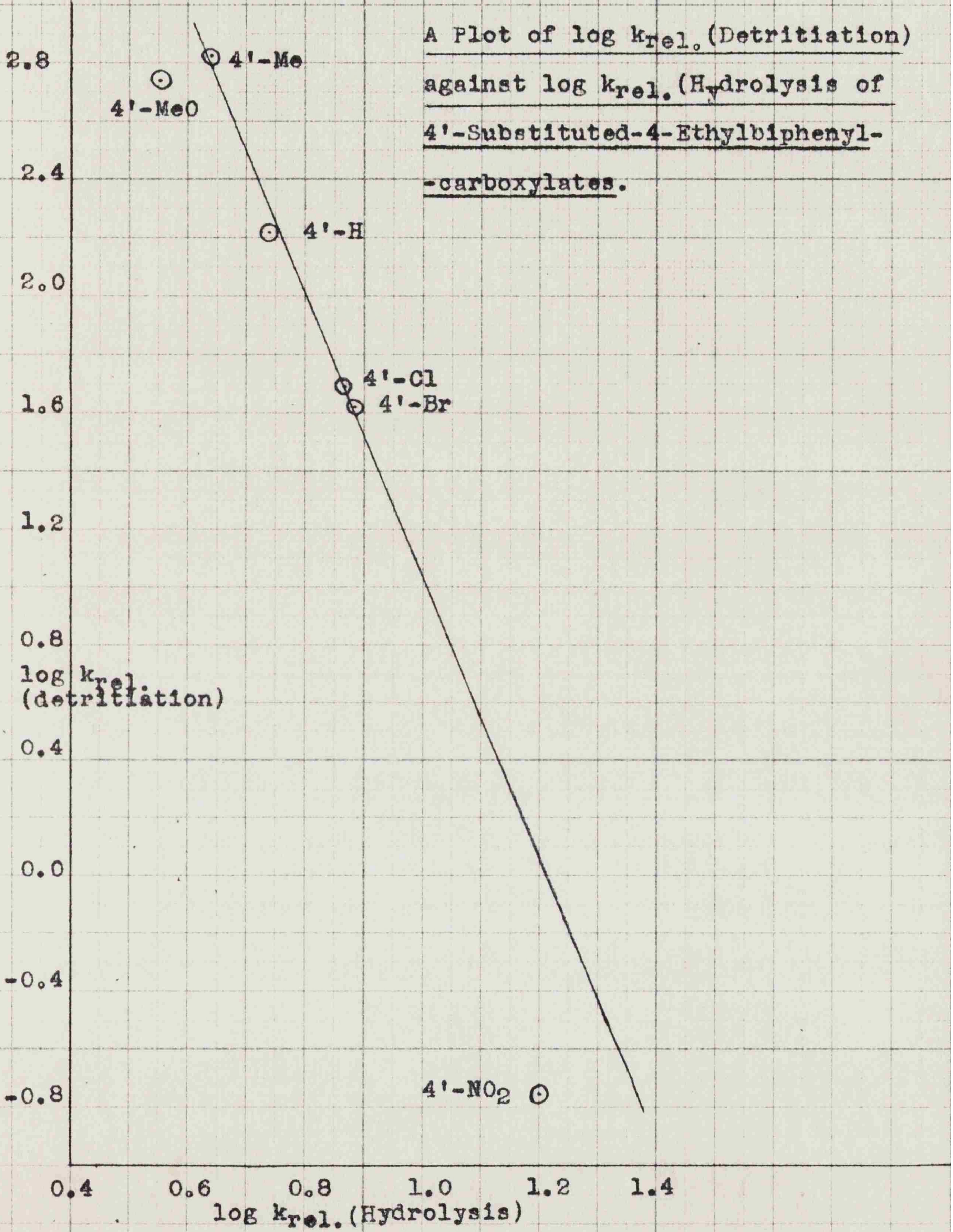


GRAPH 1V

A Plot of log $k_{rel.}$(Detritiation) against the log $k_{rel.}$ for the protodesilylation of 4,4'-Substituted-trimethylsilyl-biphenyls.

GRAPH V

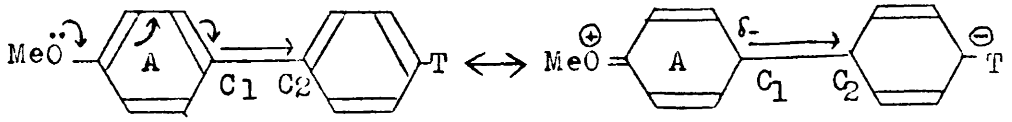
A Plot of log $k_{rel.}$ (Detritiation) against log $k_{rel.}$ (Hydrolysis of 4'-Substituted-4-Ethylbiphenyl--carboxylates.



is not as effective a conductor of substituent effects as benzene, and that only diminished electronic effects are transmitted through the Ar-Ar bond. The nitro- group is much more effective in reducing the reactivity within its own nucleus than in an attached ring. Powerful electron-releasing substituents (e.g., MeO, OH, NHAc, NH_2, NMe_2) usually direct substitution into their own ring.[178] A combination of electrostatic and resonance effects is still operating, as shown by Graphs 1 and 11. The extent of weakening in the biphenyl system may be a measure of both the long distance of the substituents from the reaction centre, which will decrease the electrostatic effects, and the lack of complete coplanarity of the two rings.

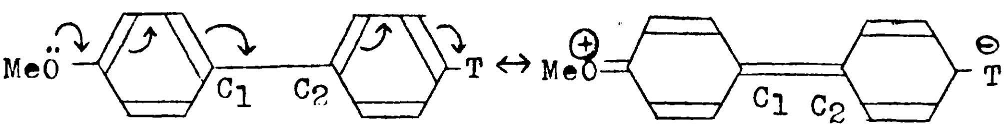
There are two ways by which electronic effects in one ring can be transmitted to the other.

1) by an inductive mechanism-

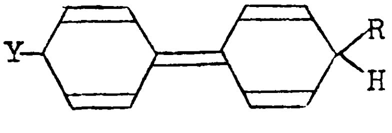


that is the substituent in the ring A, induces a charge at C_1 which is relayed through to C_2, from where it is transmitted by the normal processes.

ii) by a resonance mechanism,



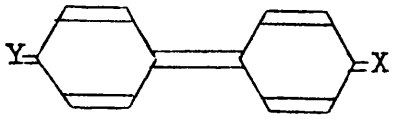
That this mechanism is operating to a certain extent was shown by de la Mare and Ridd,[179] by the additive properties of methyl derivatives in the molecular chlorination of substituted biphenyls. 2,2'-Dimethylbiphenyl was found to be much less reactive than biphenyl with the methyl- groups in the 3- and 4-positions. This is due to the steric hindrance of the groups in the 2-positions obstructing the approach of the rings to coplanarity. The resonance mechanism (ii) can also explain the lack of meta- substitution in one ring even if a meta- directing group is present in the other ring,



where Y is a meta- directing group and R is an electrophile.

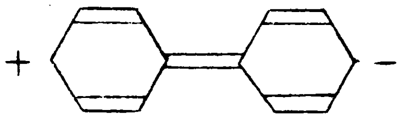
If substitution ortho- or para- to the second ring occurs, the induced positive charge can be stabilized by spreading over both rings, and the molecule will tend to a planar configuration in the transition state, i.e., C_1-C_2 becomes a partial double bond. It is necessary to conclude, from the data, that resonance stabilization of the transition state overcomes the electronic effects of deactivating groups. Thus, in the bromination of biphenyl, although a nitro- group cannot prevent _ortho_- and _para_- substitution in the second ring, it can deactivate the whole molecule such that bromination occurs 300 times slower in 4-nitrobiphenyl than in biphenyl.[180] In protodesilylation a 4-nitro- substituent deactivates the 4'- position by a factor of 10,[172] and in detritiation by a factor of 1000.

The results for the detritiation of substituted fluorene compounds, in anhydrous trifluoroacetic acid, resemble closely those obtained with 4'-substituted biphenyl compounds. A possible explanation, of the weaker transmission of substituent effects through biphenyl than in benzene, could be that first proposed by Kreiter, Bonner and Eastman.[181] They compared, spectrophotometrically, the dissociation constants of similarly substituted fluorene and biphenyl compounds. From their data, they could find no evidence of a relationship between co-planarity and the dissociation constants. It was suggested that the failure of biphenyl to transmit substituent effects fully, is due to the high energy of the quinonoid structure (XVl), occasioned by the sacrifice of the resonance energy of two aromatic sextets in reaching it.



(XVI)

In benzene derivatives, an analogous quinonoid structure is achieved at the expense of only a single aromatic sextet. But once again, the fact that biphenyl is more reactive than benzene indicates that the structure XVII must be important in determining the reactivity of biphenyl.

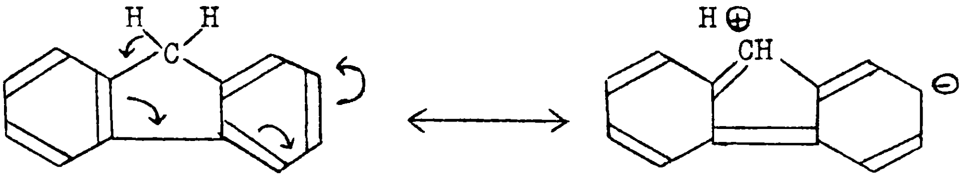


(XVII)

In conclusion, the results appear to show that diminished substituent effects are transmitted from one ring to the other in biphenyl but the results do not show whether tautomeric effects are transmitted across the bond connecting the two rings.

8. The reactivity of the 2-position of fluorene and its 9-methyl- derivatives.

De la Mare, Hall, Harris, and Hassan[148] found that fluorene undergoes molecular chlorination 1.6 times faster than 9,9'-dimethylfluorene, and suggested the existence of hyperconjugation involving the methylene group as shown:-



(XV111)

The hyperconjugation would increase the electron supply at the 2-position so that the methylene group would influence this position in the same way as the methyl-group of toluene influences the para- position. The para- position of toluene is more reactive than that of t-butylbenzene in molecular chlorination, and an analogy could be drawn between the relative activation of the 2-position of fluorene or 9,9-dimethylfluorene on the one hand, and of the para- position of toluene or t-butylbenzene on the other.

The rates of detritiation of $[2\text{-}^3H]$fluorene and its 9-methyl- and 9,9-dimethyl- derivatives have been measured in a) acetic acid containing aqueous sulphuric acid at 25.0° (molar composition: CH_3CO_2H - 20.83%, H_2O - 34.43%, H_2SO_4 - 44.74%), b) trifluoroacetic acid containing aqueous perchloric acid at 25.0° (molar composition: CF_3CO_2H - 99.962%, H_2O - 0.0278%, $HClO_4$ - 0.102%), and c) anhydrous trifluoroacetic acid at 70.11°. The results are given in Table 1X as observed first-order rate constants, k, and as rates, $k_{rel.}$, relative to tritiobenzene.

Table 1X

Compound	$CH_3CO_2H-H_2O-H_2SO_4$ (25.0°)	
	10^7k (sec.$^{-1}$)	$k_{rel.}$
[2-^{3}H] fluorene	3900	2100
9-methyl-[2-^{3}H] fluorene	3795	2040
9,9-dimethyl-[2-^{3}H] fluorene	3585	1930
[p-^{3}H] toluene	581	313[a]
[^{3}H] benzene	-	1

Compound	$CF_3CO_2H-H_2O-HClO_4$ (25.0°)	
	10^7k (sec.$^{-1}$)	$k_{rel.}$
[2-^{3}H] fluorene	2950	3610
9-methyl-[2-^{3}H] fluorene	3115	3810
9,9-dimethyl-[2-^{3}H] fluorene	3975	4860
[p-^{3}H] toluene	256	313[b]
[^{3}H] benzene	-	1

Compound	CF_3CO_2H (70.11°)	
	10^7k (sec.$^{-1}$)	$k_{rel.}$
[2-^{3}H] fluorene	1598	16,800
9-methyl-[2-^{3}H] fluorene	1665	17,500
9,9-dimethyl-[2-^{3}H] fluorene	1897	20,000
[p-^{3}H] toluene	42.7	450
[^{3}H] benzene	0.095	1

a-value previously obtained[40] in a slightly different medium

b -value obtained in medium $CF_3CO_2H(99.79)-H_2O(0.065)-HClO_4$ - (0.145)

In detritiation in acetic acid - aqueous sulphuric acid, in which the *para*- position of toluene is more reactive than the *para*- position of t-butylbenzene,[40] the 2- position of fluorene is more reactive than that of 9,9-dimethylfluorene (with that of 9-methylfluorene intermediate in reactivity). An analogous order of reactivity is found in desilylation in methanol - aqueous perchloric acid.[182,183] Detritiation in trifluoroacetic acid - aqueous perchloric acid or anhydrous trifluoroacetic acid, in which the relative reactivities of the *para*- position of toluene and t-butylbenzene are reversed,[40] so also those of the 2- position of fluorene and 9,9-dimethylfluorene are reversed (with the 9-methyl- derivative again intermediate in reactivity). The 2- position of fluorene is normally regarded as *meta*- to the methylene group, but detritiation of the *meta*- position of toluene is markedly less reactive than that of t-butylbenzene in all the media used. The results confirm the analogy between the effect on the 2- position of fluorene and the effect on the *para*- position to the methyl- group of toluene.

The same difficulties in explaining the relative reactivities of the *para*- positions of toluene and of t-butylbenzene arise again[40] in explaining the results for the fluorene compounds in terms of hyperconjugation. A change from the hyperconjugative order to the inductive order of activation takes place when the medium is changed (*viz.* from acetic acid - aqueous sulphuric acid to trifluoroacetic acid) in such a way that the overall electron demand, as measured by the rate-factor for the *para-* position of toluene (*viz.* 313 and 450, respectively) is increased.

Recently Eaborn, Golesworthy and Lilly,[184] studying the SN1 hydrolysis of 9-chloro-2-methoxy-9-phenylfluorene, showed that there was insignificant conjugation between a 2-methoxy- group and a carbonium ion formed at the 9-position. This suggests that process (XV111) is unlikely to occur to any extent. There may, however, be a greater general hyperconjugative release from the methylene group into the five-membered ring of fluorene than from the methyl- group into the ring of toluene (the shorter length of the bond between the 9-carbon atom and the aromatic ring, *viz.* 1.52Å is consistent with this), and this would result in increased availability of electrons at all the aromatic positions of fluorene.

The fact that the t-butyl- group activates the *para-* position less than a methyl- group is often explained in terms of steric hindrance to solvation. Interpretation of the results for fluorene compounds in these terms is even more difficult, and even aids arguments against attributing the hyperconjugative order, in alkylbenzenes to steric hindrance to solvation by the t-butyl- group. With toluene or t-butylbenzene a large proportion of the excess of positive charge, in the transition state of an electrophilic substitution, at the para- position resides on the ring carbon bearing the alkyl- group. With fluorene this charge will be more dispersed, the charge residing on the 1-, 3-, 5- and 7- carbon atoms being at least as great as that on one of the ring carbon atoms joined to the methylene group (the other such carbon atom will carry a smaller amount of charge similar to that at the 4-position). Therefore, steric hindrance to solvation of charge by methyl- groups, in the 9- position, must be fairly unimportant.

The reactivity of the 2- position of fluorene, relative to that of the para- position of biphenyl, falls with increasing electron demand, as indicated by the partial rate factor, f_p^{Me}, for the para- position of toluene.

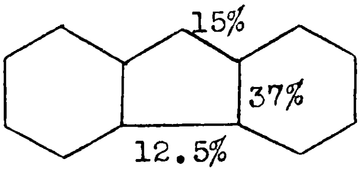
Reaction	$\frac{\log f^{2\text{-Fl.}}}{\log f_p^{Ph}}$	f_p^{Me}
protodetrimethylsilylation	3.02	20
detritiation (CF_3CO_2H)	1.91	450
molecular chlorination (CH_3CO_2H)	1.82	820

These data indicate that polarizability effects are less important, relative to polarization effects in fluorene than in biphenyl. This is probably because the methylene group in fluorene provides a substantial part of the activation, and is only weakly polarizable compared with the aromatic ring conjugated with the reaction centre.

9. The transmission of substituent effects through the fluorene molecule.

The molecular dimensions of fluorene have been conclusively established by X-ray studies of Brown and Bortner[185] and confirmed in later work by Burns and Iball.[186] The structure is planar and the axes do not coincide with the line of the bond joining them.

The resonance energy of fluorene has been calculated as 101Kcal. by Wheland.[187] This value, together with bond lengths, angles and absorption spectra data, has been used by Weisburger and Ray[188] to calculate the partial double bond character of the five-membered ring.



The detriation of a number of 2-substituted (X) - [7-^{3}H] fluorenes (XIX) have been studied in anhydrous trifluoroacetic acid at 70.11°, the values of the rate constant, k, and the partial rate factor, $k_{rel.}$, are recorded in the Table X.

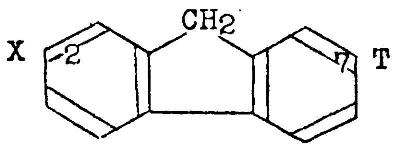


Table X

The detritiation of 2-X- [7-^{3}H] fluorene compounds in anhydrous trifluoroacetic acid at 70.11°.

Substituent (X)	10^7k(sec.$^{-1}$)	$k_{rel.}$^{a}	log $k_{rel.}$
Me	6115	64,400	4.81
MeO	4820	50,700	4.705
H	1598	16,800	4.23
Cl	425	4470	3.65
Br	342	3600	3.56
CO_2H	3.26	34.3	1.54
NO_2	23.0^b	6.32^b	0.80

a) for benzene , k = 0.095 x 10^{-7}sec.$^{-1}$

b) measured at 110.15°, at which k for benzene is 3.64 x 10^{-7} (sec.$^{-1}$)

The rate of detritiation of 2-NO_2- [7-^{3}H] fluorene is very slow at 70.11° and accurate measurements are difficult. The exchange rate was more conveniently measured at 110.15°; the partial rate factor of the compound was obtained by comparison of this rate of exchange with that of a single position of benzene, again measured at 110.15°.

That fluorene compounds are more reactive than biphenyl compounds is immediately evident. Even with the deactivating carboxy- and nitro- groups in the 7- position the rates of detritiation of the 2- position in fluorene are still 34 and 7 times, respectively, faster than a single position in benzene. A methyl- and a methoxy- group, meanwhile, activates the 2-position of fluorene so that its rate of detritiation is 64,000 and 51,000 faster than a position in benzene. It is interesting that the methyl- and methoxy- groups activate the 2-position only 4 and 3 times respectively, while the chloro-, bromo-, carboxy-, and nitro-, substituents deactivate 3.5, 4.7, 490 and 2560 times respectively.

Again, as with the analogous biphenyl compounds, the methyl- group appears to have a greater activating effect than the methoxy- group. It was suggested on page 173 that this was due to hydrogen-bond interaction of the methoxy- group with the trifluoroacetic acid. An examination of the ultra-violet spectra of 2-methoxy-$[7-^3H]$fluorene in both a methanol and a trifluoroacetic acid solvent failed to yield any evidence for protonation of the oxygen atom. A series of measurements of the detritiation of 2-MeO-$[7-^3H]$- and 2-Me-$[7-^3H]$-fluorene were made in mixtures of anhydrous trifluoroacetic acid and acetic acid. Two media were prepared of different compositions and, therefore , different acidities. The results are summarised in Table X1.

Table X1

Wt.-% of CH_3CO_2H (99.2%) in anhydrous CF_3CO_2H	10^7k(sec.$^{-1}$) 2-MeO	10^7k(sec.$^{-1}$) 2-Me
0%	4820	6115
13.2%	2370	1800
22.8%	780	494

The decrease in the rate of exchange of the 2-methoxy-compound (with decrease in acidity of the media) was much less than that of the 2-methyl compound, so that, in the weaker acidic media, the rate of detritiation of the 2-methoxy compound was the greater. This is consistent with some hydrogen-bonding taking place between the methoxy- group and the trifluoroacetic acid.

In detritiation, in trifluoroacetic acid, the 2- position of fluorene is 100 times as reactive as the 4- position of biphenyl. The greater reactivity of the 2- position of fluorene over the 4- position of biphenyl, has been observed by a number of other workers. Partial rate factors of 2040 for the 2- position of fluorene and 11 for the 4- position of biphenyl have been obtained for nitration by nitric acid in acetic anhydride.[110] De la Mare, Hall, Harris and Hassan[148] found that, in molecular chlorination, fluorene is 290 times as reactive as biphenyl; they consider this to be due to enhanced conjugation between the two rings and partly to hyperconjugation of type

(XVIII, page 181). Berliner and Shieh[189] came to the same conclusion after studying the solvolysis of α-arylethylchlorides.

It is of interest to attempt to calculate the reactivity expected in detritiation, in anhydrous trifluoroacetic acid, for the 2- position of fluorene by the simple treatment used previously for the dibenzo- furan and -thiophen compounds. The 2- position of fluorene is formally para- to a Ph- group and meta- to a $PhCH_2$- group. The figure for the m-$PHCH_2$-group in detritiation, in anhydrous trifluoroacetic acid, is not available, but the activation by a m-CH_3 group, in similar media, is about 8[40]. The activation by a m-$PhCH_2$-group will then probably be about 5. The 2- position of fluorene would therefore, be expected to be about 5 times as reactive as the 4-position of biphenyl. This must be compared with the factor determined experimentally of 100. This greatly increased reactivity of the 2- position of fluorene from the calculated figure can be due to enhanced conjugation between the two rings and also to hyperconjugation (XVIII, page 181), as suggested by de la Mare et. al.[148] and also by Berliner and Shieh.[189] An alternative explanation could be that the $PhCH_2$- group acts on the 2- position of fluorene as if it had some para- character; if there was 100% para-character the 2- position of fluorene would be 118 times more reactive than the 4- position of biphenyl.

The effects of substituents on the detritiation of fluorene are interesting in that they reflect very closely the results obtained for substituted biphenyl compounds. The methoxy-, methyl-, bromo-, and chloro- substituents activate or deactivate biphenyl or fluorene, with respect to the unsubstituted compounds, by about the same amounts. The nitro- group in fluorene, however, deactivates 10 times more than in biphenyl. The rates of exchange of these compounds were measured at 110.15° and normally, rate differences decrease as the temperature is raised, so that the effect of the nitro- group might be even greater at 70.1°.

Kreiter, Bonner and Eastman[181] measured, spectrophotometrically, the ionisation constants of analogously-substituted fluorene and biphenyl compounds, the hydroxy-derivatives being mainly used. They could find no significant difference in the effects of substituents in biphenyl or fluorene, so that there was no evidence for a relationship between coplanarity and acid strength.

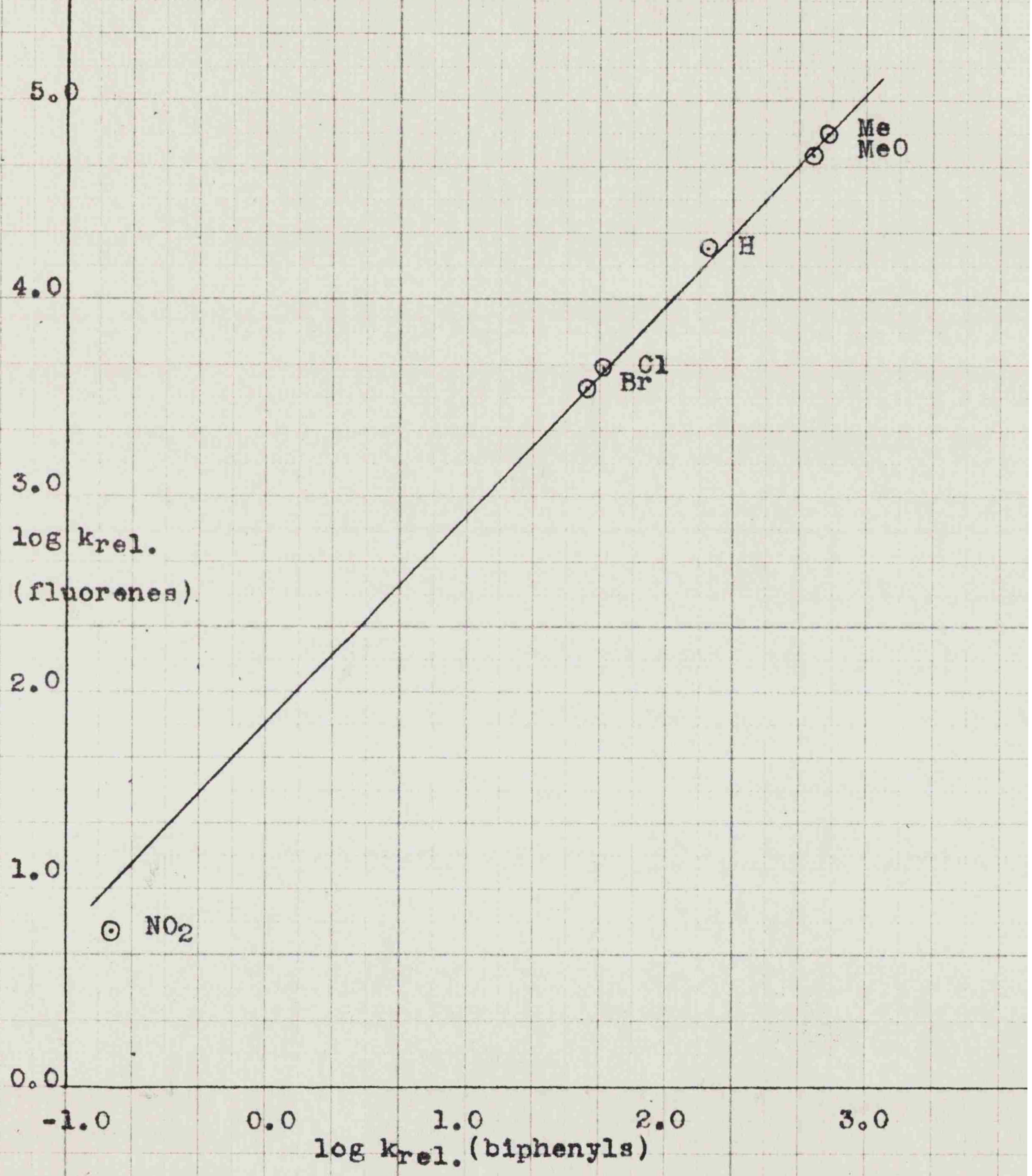
The present results for the methyl-, bromo-, and chloro-, substituents are not inconsistent with this conclusion, but the evidence from the nitro- substituent indicates that there is more conjugation between the rings in fluorene than in biphenyl. This would agree with the work of Weisburger and Weisburger and Grantham[190]; they found apparent ionization constants, in 70% ethanol, of a number of hydroxy-, carboxy-, and amino-, derivatives of fluorene and biphenyl. They concluded that inductive and resonance interactions of substituents in the two rings in biphenyl are rather weak, but exchanges are more pronounced in the planar and more rigid fluorene molecule.

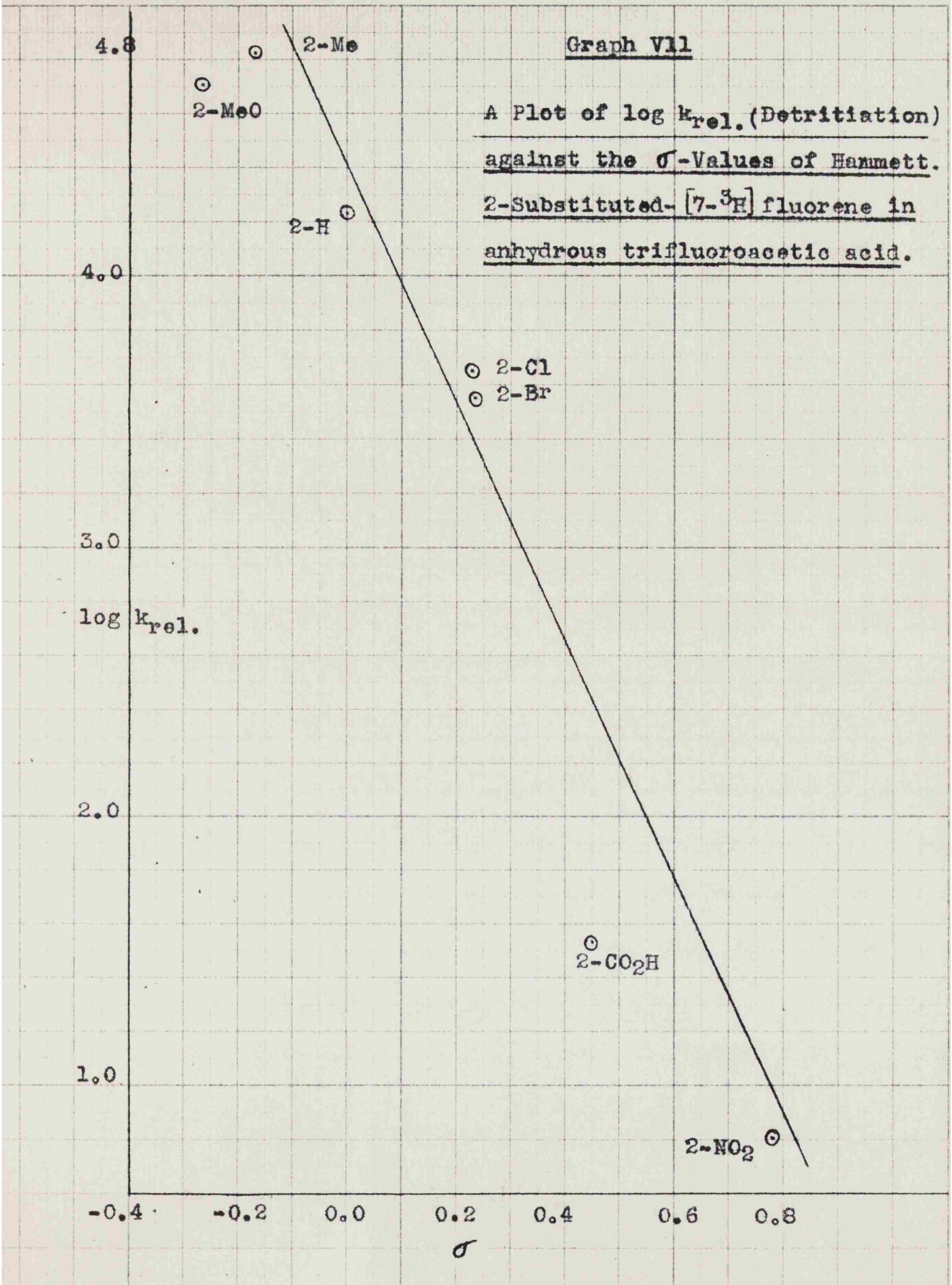
Chemical evidence indicates that a substituent in one ring only very inefficiently deactivates the other; further substitution, therefore, is not difficult . Upon further nitration, with a mixture of equal parts of fuming nitric acid and glacial acetic acid, the 2- nitro derivative gives a mixture of 2,5- and 2,7-dinitrofluorene, plus a small quantity of 2.4-dinitrofluorene.[110] This indicates that the deactivation of the 7- and 5- positions has been small compared with that of the 4-position, no 1- or 3- isomer being obtained because of the strong deactivation of the inductive mechanism. Bromination of 2-bromofluorene gives 2,7-dibromofluorene using only mild conditions. Substituents such as amino-, acetamido-, and alkoxy- are usually sufficiently activating to control the position of substitution, even when in competition with an aryl-group held in planar configuration. So, 2-acetamidofluorene gives on nitration[191] the 3-, together with the 7-nitro derivative, and chlorination[192] occurs mainly in the 3-position.

The log (rate of detritiation) of substituted fluorene

GRAPH V1

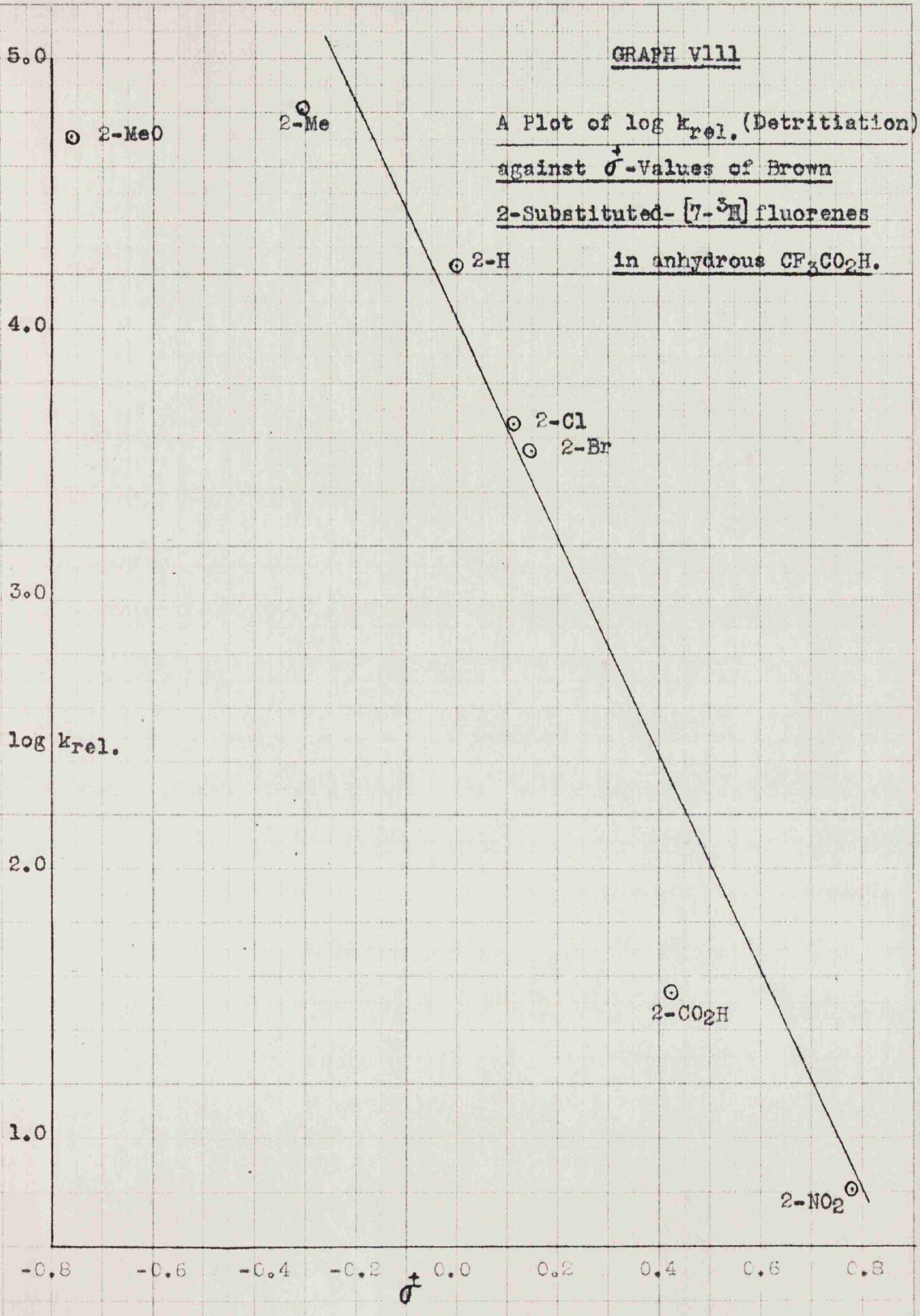
A plot of log $k_{rel.}$ (detritiation of 4'-substituted-[4-^{3}H] biphenyls) against log $k_{rel.}$ (detritiation of 2-substituted-[7-^{3}H] fluorenes) in anhydrous trifluoroacetic acid.





Graph VII

A Plot of log $k_{rel.}$ (Detritiation) against the σ-Values of Hammett. 2-Substituted-[7-^{3}H] fluorene in anhydrous trifluoroacetic acid.



GRAPH V111

A Plot of log $k_{rel.}$ (Detritiation) against σ^+-Values of Brown 2-Substituted-[7-^{3}H] fluorenes in anhydrous CF_3CO_2H.

compounds were plotted against the Hammett-σconstants and the Brown-σ^{+}constants, (Graphs V11 and V111). A marked deviation, from the linear plots is again noted with the point for the methoxy- substituent. This is probably due to hydrogen-bond interaction (page 189).

Graph V1 shows a plot of log $k_{rel.}$ for substituted fluorene compounds against the log $k_{rel.}$ for the substituted biphenyl compounds. A good linear correlation is obtained with only the point for the nitro- substitution showing a deviation.

The higher reactivity of fluorene over biphenyl compounds, is clearly shown in the results but the transmission of effects from the substituents methyl-, chloro-, and bromo-, are very similar in both compounds. The greater deactivation by a nitro- group in fluorene than in biphenyl, however, indicates more conjugation in fluorene than in biphenyl.

10. Salt Effects in detritiation in anhydrous trifluoroacetic acid

In order to throw further light on the mechanism of aromatic hydrogen-exchange in trifluoroacetic acid the effect of the addition of certain salts on the detritiation of 1,3-dimethyl-$[2\text{-}^{3}H]$benzene was studied. The results are given in Table X11.

Table X11

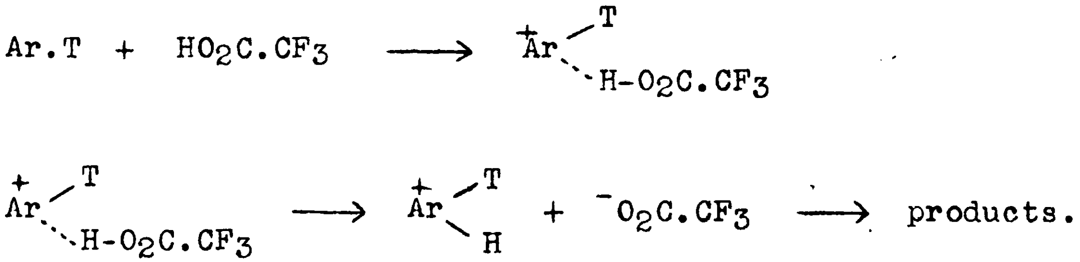
added salt	$10^7k(\text{sec.}^{-1})$
pure acid	59.4
N/10 lithium trifluoroacetate	68.7
N/10 sodium trifluoroacetate	70.6
N/10 lithium perchlorate	3580

The strengths of added salts are given as N/10 but these compositions are only approximations. The accurate compositions of the media are recorded in the details for the kinetic measurements.

The addition of salt to anhydrous trifluoroacetic acid caused the rate of exchange to increase in the order LiT.F.A. < NaT.F.A. < $LiClO_4$. Lithium and sodium trifluoroacetate cause only a small increase in the rate of exchange, whereas, with lithium perchlorate a marked acceleration in the rate of exchange is observed.

The greater acceleration by lithium perchlorate than lithium trifluoroacetate finds an analogy in the work of Winstein *et al.*[36]. They showed that lithium perchlorate was a more effective catalyst than lithium acetate in the acetolysis of some arylsulphonates. A weaker catalysis by acetate than perchlorate ions has also been observed in some halogen substitution and addition reactions in acetic acid.[194] It was suggested that the small catalysis by sodium acetate was related to the fact that the compound is a base in acetic acid, and indicated that the removal of a proton was not a rate-determining step.

The increase in the exchange rate of the detritiation of 1,3-dimethyl-$[2\text{-}^{3}H]$benzene with the addition of salts could be due to undissociated molecules:-

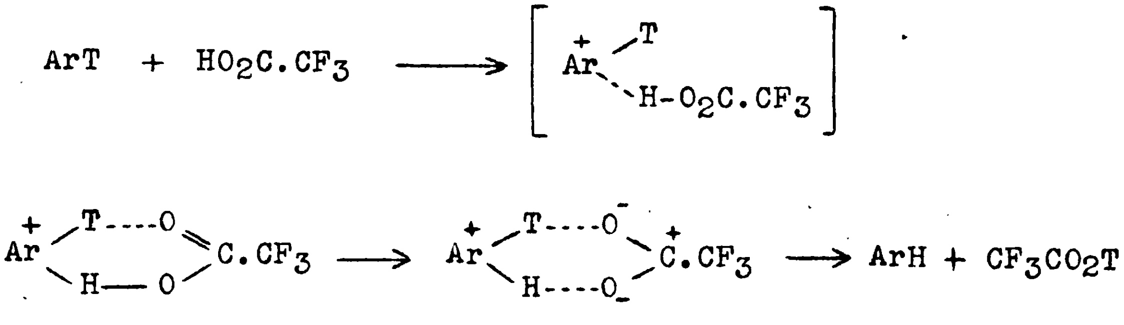


$$\mathrm{Ar.T} + \mathrm{HO_2C.CF_3} \longrightarrow \overset{+}{\mathrm{Ar}}\begin{smallmatrix} \diagup \mathrm{T} \\ \cdots \mathrm{H\text{-}O_2C.CF_3} \end{smallmatrix}$$

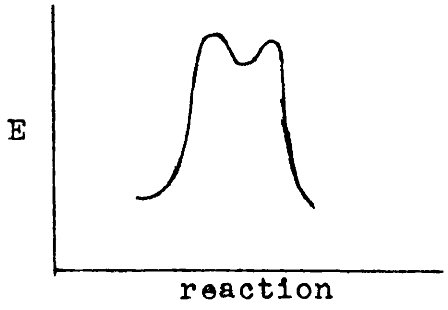
$$\overset{+}{\mathrm{Ar}}\begin{smallmatrix} \diagup \mathrm{T} \\ \cdots \mathrm{H\text{-}O_2C.CF_3} \end{smallmatrix} \longrightarrow \overset{+}{\mathrm{Ar}}\begin{smallmatrix} \diagup \mathrm{T} \\ \diagdown \mathrm{H} \end{smallmatrix} + {}^{-}\mathrm{O_2C.CF_3} \longrightarrow \text{products.}$$

However, if this is the mechanism, then a large decrease in the rate of exchange would be expected on the addition of trifluoroacetate ions; this has been shown not to occur.

Similar salt effects were observed by Greasley[172] in the cleavage of *p*-methoxyphenyltrimethylsilane in a mixture of trifluoroacetic acid and acetic acid. The absence of a retardation in the rate of detritiation on the addition of trifluoroacetate ions could be associated with a cyclic transition state in trifluoroacetic acid; a suggestion also put forward by Greasley[172] for the cleavage of the carbon-silicon bond.



This reaction would have the almost symmetrical energy profile:-



In the mechanism involving a cyclic intermediate, the trifluoroacetic acid molecule will remove tritium as the Ar.H bond is forming; the absence of any marked catalysis by the trifluoroacetate ion can then be understood.

Similar cyclic transition states have been proposed by de la Mare and co-workers for chlorination by chlorine acetate.[195]

An alternative explanation could be that even if there is not a cyclic transition state formed, proton transfers would give $\overset{+}{ArTH}\ \overset{-}{O}_2C.CF_3$, and these would remain together as an ion pair long enough for the same $\overset{-}{O}_2C.CF_3$ to take part in the tritium removal. In this way absence of catalysis by trifluoroacetate ions can be explained.

11. Anisole and thioanisole

Partial rate factors were determined for the para-positions of anisole and thioanisole in anhydrous trifluoroacetic acid. The rates had to be measured at 24.84° and 40.0° (and not at 70.1° which was desirable, in order to compare the rates of exchange with that of a single position in benzene for the same temperature). The rates of exchange of $[p\text{-}^3H]$-anisole and $[p\text{-}^3H]$-thioanisole at 70.1° were found by extrapolation (by plotting log k against 1/T) from the lower two temperatures. The partial rate factors were found to be 1.87×10^5 for the para- position of anisole and 8.19×10^4 for the para-position of thioanisole. For protodesilylation, in methanol - aqueous perchloric acid, partial rate factors of 1510 and 78.1 were obtained for the para- positions of anisole and thioanisole respectively.[172]

A much smaller difference in reactivity of the two compounds is observed in detritiation than in protodesilylation. A possible explanation could be that some hydrogen-bond interaction takes place between the oxygen atom in anisole (this has been suggested to occur with trifluoroacetic acid and the methoxy- group in biphenyl and fluorene), but no interaction takes place with thioanisole. The rate of detritiation of anisole would therefore be depressed.

REFERENCES

1. Horiuti, Polanyi and Ogden, Trans.Farad.Soc., 1934, 30, 663.

2.a) Ingold, Raisin and Wilson, Nature, 1934, 134, 734.

b) Ingold, Raisin and Wilson, J.C.S., 1936, 915.

3. Ingold, Raisin and Wilson, J.C.S., 1936, 1637.

4. Best and Wilson, J.C.S., 1938, 28.

5. Lauer and Day, J.A.C.S., 1955, 77, 1904.

6. Allen, Oxford, Robinson and Smith, J.C.S., 1926, 401.

7.a) Allen and Robinson, J.C.S., 1926, 376.

b) Robinson and Smith, J.C.S., 1926, 392.

c) Bradfield, Jones and Orton, J.C.S., 1929, 2810.

d) Bradfield, Jones and Spencer, J.C.S., 1931, 2907.

8. McKay, Nature, 1938, 142, 997.

9.a) Roginsky, Acta Physicochim., U.R.S S., 1941, 14, 1.

b) Duffield and Calvin, J.A.C.S., 1946, 68, 557.

c) Friedlander and Kennedy, "Introduction to Radiochemistry" Wiley and Sons, New York, 1949, chapt. 13.

d) Norris, J.Phys.Chem., 1950, 54, 777.

10. Harris, Trans.Farad.Soc., 1951, 47, 716.

11. Melander, Arkiv Kemi., 1954, 7, 287.

12. Olsson and Melander, Acta Chem. Scand., 1956, 10, 879.

13. Gold and Satchell, J.C.S., 1955, 3609.

14. Gold and Satchell, J.C.S., 1955, 3619.

15. Brown and Brady, J.A.C.S., 1952, 74, 3570

16. de la Mare, Hughes, Ingold and Pocker, J.C.S., 1954, 2930.

17. Gold and Satchell, J.C.S., 1955, 3622.

18. Satchell, J.C.S., 1956, 3911.

19. Gold and Satchell, J.C.S., 1956, 2743.

20. Mackor, Smit and Van der Waals, Trans.Farad.Soc., 1957, 53, 1309.

21. Tiers, J.A.C.S., 1956, 78, 4165.

22. Crawford, J.Chem.Soc., 1953, 2058.

23. Lauer, Matson and Stedman, J.A.C.S., 1958, 80, 6433.

24. Lauer, Matson and Stedman, J.A.C.S., 1958, 80, 6437.

25. Eaborn and Taylor, J.C.S., 1960, 3301.

26. Stock and Brown, J.A.C.S., 1959, 81, 3323.

27. Eaborn and Taylor, Chem. and Ind., 1959, 949.

28. Hammett and Deyrup, J.A.C.S., 1932, 54, 2721.

29. Long and Paul, Chem. Reviews, 1957, 57, 1.

30. Gold, Lambert and Satchell, Chem. and Ind., 1959, 1312.

31.a)Long and Paul, Chem. Reviews, 1957, 57, 935.

   b)Melander and Myhre, Arkiv Kemi., 1959, 13, 507.

   c)Deno and Perizzolo, J.A.C.S., 1957, 79, 1345.

32. Kresge and Chiang, J.A.C.S., 1959, 81, 5509.

33. R.D.Brown, J.C.S., 1959, 2224, 2232.

34. Kresge and Chiang, Proc.Chem.Soc., 1961, 81.

35. Deno, Groves and Saines, J.A.C.S., 1959, 81, 5790.

36. Winstein et al., J.A.C.S., 1956, 78, 2763, 2780.

37. Gold, Proc.Chem.Soc., 1961, 453.

38. Bell, Quart.Rev., 1959, 13, 169.

39. Eigen and DeMaeyer, "The Structure of Electrolytic Solutions", ed. W.J.Hamer, John Wiley and Sons, New York, 1959, chapt. 5.

40. Eaborn and Taylor, J.C.S., 1961, 247.

41. Schubert, Craven, Minton and Murphy, Tetrahedron, 1959, 5, 194.

42. Kosower and Skorcz, J.A.C.S., 1960, 82, 2195.

43. Eaborn and Taylor, J.C.S., 1961, 2388.

44. de la Mare and Ridd, "Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, pp. 138-139.

45. Illuminati and Marino, J.A.C.S., 1956,78, 4975.

46. Brown, Okamoto and Ham, J.A.C.S., 1957, 79, 1906.

47. Brown and Okamoto, J.A.C.S., 1957, 79, 1913.

48. Olsson, Arkiv Kemi., 1959, 14, 85.

49. Lauer and Stedman, J.A.C.S., 1958, 80, 6439.

50. Blackley, Univ. Microfilms, L.C.Card No. Mic 60-5592 Dissertation Abstr. 1961, 21, 1755-6.

51. Shatenshtein and Alikanov, Zhur. Obschei. Khim. 1960, 30, 992.

52. Shatenshtein, Kalinachenko and Varshavsky, Reports of the U.S.S.R. Academy of Science, 1953, 3, 577.

53. Shatenshtein, Vedeneev and Alikanov, Zhur. Obschei. Khimi., 1958, 28, 2638.

54. Eaborn and Taylor, J.C.S., 1961, 1012.

55. Dallinga, Verrijn Stuart, Smit and Mackor, z. Electrochem., 1957, 61, 1019.

56.a)Dewar, J.A.C.S., 1952, 74, 3341, 3345.

b)Dewar, Mole and Warford, J.C.S., 1956, 3581.

c)Burkitt, Coulson and Lonquet-Higgins, Trans.Farad.Soc., 1951, 47, 553.

56.d)Mason, J.C.S., 1959, 1233.

57. Deans, Eaborn and Webster, J.C.S., 1959, 3031.

58. de la Mare and Hassan, J.C.S., 1957, 3004.

59. Rice, Dissertation Abstract, 1960, 20, 3961.

60. Shatenshtein, Kalinachenko, Zhur.Fiz.Khim., 1956, 30, 2093.

61. Shatenshtein, Kalinachenko, Zhur.Fiz.Khim., 1956, 30, 2098.

62. Shatenshtein, Kalinachenko, Yurygina and Basmanova, Zhur.Obschei.Khimi., 1959, 29, 849.

63. Shatenshtein, Varshavskii, D.A.N., 1954, 95, 297.

64. Eaborn and Deans, J.C.S., 1959, 2299.

65. Colapietro and Long, Chem. and Ind., 1960, 1056.

66. Halvarson and Melander, Arkiv Kemi., 1955, 29.

67. Pearson, Cowan and Beckler, J.Org.Chem., 1959, 24, 504.

68. Fieser, "Experiments in Organic Chemistry", Heath, Boston, 1955, Third Ed., p.265.

69. Culvenor, Davies and Pausacker, J.C.S., 1946, 1050.

70. Huston, Fox and Binder, J.Org.Chem., 1938, 3, 251.

71. Shoesmith and Mackie, J.C.S., 1928, 2334.

72. Smith, "Organic Synthesis", Coll.Vol.11, Blatt, Wiley and Sons Inc., New York, p.95.

73. Gilman and Jacoby, J.Org,Chem., 1938, 3, 108.

74. Gilman and Nobis, J.A.C.S., 1950, 72, 2629.

75. Brown, Christiansen and Sandrin, J.A.C.S., 1948, 70, 1748

76. Brown, Illuminati and Nobis, J.A.C.S., 1951, 73, 5887.

77. Cullinane, Davies and Davies, J.C.S., 1936, 1435.

78. Gilman and Wilder, J.A.C.S., 1954, 76, 2906.

79. Meen and Gilman, J.Org.Chem., 1955, 20, 73.

80. Gilman, Bywaters and Parker, J.A.C.S., 57, 885.

81. Gilman and Avakian, J.A.C.S., 1946, 68, 580.

82. Yamasiro, Bull.Soc.Chem., 1941, 6.

83. Bui and Royer, Rec.Trav.Chim., 1948, 67, 175.

84. Gilman and Ingram, J.A.C.S., 1953, 75, 4843.

85. Gilman and Van Ess, J.A.C.S., 1939, 61, 1365.

86. Gilman and Gaj, J.Org.Chem., 1957, 1165.

87. de Visser, Rec.Trav.Chim., 1893, 12, 101.

88. Gilman and Struckwisch, J.A.C.S., 1943, 65, 1461.

89. Cook and Davies, J.C.S., 1937, 1697.

90. Kommpa, J.Prackt.Chem., 1929, 122, 319.

91. Smith, Doctoral Dissertation, Iowa College, 1936.

92. Greenhow, White and McNeil , J.C.S., 1951, 2848.

93. Kuhn, Org. Synthesis, 1933, X111, 447.

94. Miller and Bachman, J.A.C.S., 1935, 57, 2447.

95. Campbell and Temple, J.C.S., 1957, 207.

96. Gray and Hartley, J.C.S., 1955, 2686.

98. Cormack and Spielman, Organic Reactions, 1946, 3, 83.

97. Bachmann and Boatner, J.A.C.S., 1936, 58, 2194.

99. Bergmann et al., Bull.Soc.Chim., 1951, 18, 669.

100. Sawicki, J.A.C.S., 1954, 76, 2269.

101. Eaborn and Taylor, J.C.S., 1960, 1480.

102. Elks, Haworthand and Hey, J.C.S., 1940, 1284.

103. Gomberg and Pernert, J.A.C.S., 1926, 48, 1372.

104. Turner and Shaw, J.C.S., 1928, 253.

105. Abernethy and Pollock, J.A.C.S., 1951, 73, 1351.

106. Blakey and Scarborough, J.C.S., 1927, 3005.

107. Gilman and Bebb, J.A.C.S., 1939, 61, 109.

108. Org. Synth., Coll. Vol. 11, 1947, 242.

109. Orton and Bradfield, J.C.S., 1927, 963.

110. Dewar and Urch, J.C.S., 1958, 3079.

111. Pictet and Ramseyer, Ber., 1911, 44, 2491.

112. Bourgeois and Fouassin, Bull.Soc.Chim., 1911, 9, 941.

113. Eaborn and Sperry, J.C.S., 1961, 4921.

114. Baker, Eaborn and Taylor, J.C.S., 1961, 4927.

115. Hartough and Meisel, "The Chemistry of Heterocyclic Compounds, Condensed Thiophens", Interscience, New York, 1954, p.11.

116. Baker and Eaborn, J.C.S., 1961, 5077.

117. Gilman and Nobis, J.A.C.S., 1949, 71, 274.

118. Courtot, Compt. rend., 1934, 198, 2260.

119. Burger, Wartman and Lutz, J.A.C.S., 1938, 60, 2628.

120. Mayer and Krieger, Ber., 1922, 55, 1659.

121. Gilman, Smith and Oatfield, J.A.C.S., 1934, 56, 1412.

122. Gilman, Johnson and Willis, J.A.C.S., 1954, 76, 6407.

123. Gilman and Young, J.A.C.S., 1934, 56, 1415.

124. Dewar and Urch, J.C.S., 1957, 345.

125. Brown and Coller, Austral.J.Chem., 1959, 12, 152.

126. Eaborn and Matsukawa, Research Correspondence 1956, 9.

127. Eaborn, Matsukawa and Taylor, The Review of Scientific Instruments, 1957, 28, 725.

128. Hayes, U.S.A.E.C., 1953, Document L.A., 1639.

129. Farmer and Bernstein, Science, 1953, 117, 279.

130. Hayes, Anderson and Langham, Proc.Int.Conf. on Peaceful Uses of At. Energy, U.N. Press, New York, 1955, 14, p.67.

131. Pringle, Turchinetz and Funt, Rev.Sci.Int., 1955, 26, 859.

132. Davidson and Feigelson, Int.J.App.Rad. and Iso., 1957, 2, 1.

133. Pauling and Schomaker, J.A.C.S., 1939, 61, 1769.

134. Blicke and Burckhalter, J.A.C.S., 1942, 64, 477.

135. Coonradt, Hartough and Johnson, J.A.C.S., 1948, 70, 2564.

136. Hartough et. al., J.A.C.S., 1946, 68, 2639; 1947, 69, 1012, 1014, 3093, 3096, 3098; 1948, 70, 867.

137. Steinkopf and Hopner, Ann., 1933, 501, 174.

138. Appleby, Sartor, Lee and Kapranos, J.A.C.S., 1948, 70, 1552.

139. Farrar and Levine, J.A.C.S., 1950, 72, 4433.

140. Fries and Hemmecke, Ann., 1929, 470, 1.

141. van Zyl, van Dyke, Heasley, de Jough, Bredeweg and Neckers, Fourth Report on Research under Sponsorship of Petroleum Research Fund, Amer.Chemical Soc., Washinghton, 1960, p.39.

142.a) Crook and Davies, J.C.S., 1937, 1697.

b) Szmuskovicz and Modest, J.A.C.S., 1950, 72, 571.

143. Blicke and Sheets, JA.C.S., 1948, 70, 3768.

144. Challenger and Miller, J.C.S., 1939, 1005.

145. Eaborn and Pande, J.C.S., 1961, 297.

146. Eaborn, Lasocki and Webster, J.C.S., 1959, 3034.

147. Sperry, Ph.D. Thesis, University of Leicester, 1960.

148. de la Mare, Hall, Harris and Hassan, Chem. and Ind., 1958, 1086.

149. Norman and Radda, J.C.S., 1961, 3610.

150. Knowles, Norman and Radda, J.C.S., 1960, 4885.

151. Hammond, J.A.C.S., 1955, 77, 334.

152. Norman and Radda, J.C.S., 1961, 3610 (personal communication from Mackor).

153. O'Reilly and Leftin, J.Phys.Chem., 1960, 64, 1555.

154. Dickens and Linnet, Quart. Rev., 1957, 11, 291.

155. McDaniel and Brown, J.Org.Chem., 1958, 23, 420.

156. Dewar and Schmeising, Tetrahedron, 1959,5, 166.

157. Reference 44, pp. 142-144.

158. Dewar, Mole, Urch and Warford, J.C.S., 3572, 3576.

159. de la Mare and Harvey, J.C.S., 1956, 36; 1957, 131.

160. Weingarten, J.Org.Chem., 1961, 26, 4347.

161. Shatenshtein, Zhur.Fiz.Khim., 1960, 34, 587.

162. Greive and Hey, J.C.S., 1933, 968.

163. Menschutkin, J.Russ.Phys.Chem., 1913, 45, 1710.

164.a)Laver, Ber., 1936, 69, 2618.

b)Laver and Oda, Ber., 1936, 69, 978.

165. Mizuno and Simamura, J.C.S., 1958, 3875.

166. Brown and Stock, J.A.C.S., 1957, 79, 5175.

167. Buckles, Hausman and Wheeler, J.A.C.S., 1950, 72, 2494

168. Eaborn and Waters, J.C.S., 1961, 542.

169. Bastiansen, Acta Chem. Scand., 1949,3, 408.

170. Reference 44, p. 85.

171. Arnett and Wu, J.A.C.S., 1960, 82, 5660.

172. Greasley, Ph.D. Thesis, University of Leicester, 1961.

173. Benkeser, Schroeder and Thomas, J.A.C.S., 1958, 80, 2283.

174. Le Fevre and Turner, J.C.S., 1928, 425.

175. Le Fevre and Le Fevre, J.C.S., 1936, 1130.

176. Berliner and Blommers, J.A.C.S., 1951, 73, 2479.

177. Berliner and Lui, J.A.C.S., 1953, 75, 2417.

178. Reference 44, p. 164.

179. Reference 44, p. 159.

180. Turner, Rec.Trav.Chim., 1929, 48, 821.

181. Kreiter, Bonner and Eastman, J.A.C.S., 1954, 76, 5770.

182. Eaborn, J.C.S., 1956, 4858.

183. Baker, Eaborn and Sperry, J.C.S. 1962,

184. Eaborn, Golesworthy and Lilly, J.C.S., 1961, 3052.

185. Brown and Bortner, Acta. Cryst., 1954, 7, 139.

186. Burns and Iball, Nature, 1954, 173, 635.

187. Wheland, "Theory of Resonance", Wiley and Sons, N.Y. p69.

188. Weisburger and Ray, J.A.C.S., 1950, 72, 4250.

189. Berliner and Shieh, J.A.C.S., 1957, 79, 3849.

190. Grantham, Weisburger and Weisburger, J.Org.Chem. 1961, 26, 1008.

191. Ekert and Langecker, J.Prackt.Chem., 1928, 118, 263.

192. Bell and Gibson, J.C.S., 1955, 3560.

193. Billings and Norman, J.C.S., 1961, 3885.

194. Robertson, Dixon, Goodwin, McDonald and Scaife, J.C.S., 1949, 294.

195. de la Mare, Hilton and Varma, J.C.S., 1960, 4044.