SUPPORTING INFORMATION

for

Electron-Withdrawing Substituents Decrease the Electrophilicity of the Carbonyl Carbon. An Investigation with the Aid of ^{13}C NMR Chemical Shifts, ν(C=O) Frequency Values, Charge Densities and Isodesmic Reactions to Interprete Substituent Effects on Reactivity

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Table of Contents

Table S1. IR C=O stretching frequencies (in cm^{-1}) for substituted phenyl acetates (3), phenyl dichloroacetates (2) and phenyl trifluoroacetates (1) RCOOAr.

Ar	σ^a	R		
		CH$_3$	CHCl$_2$	CF$_3$
4-OMe-C$_6$H$_4$	-0.27	1760	1763[b]	1797
4-Me-C$_6$H$_4$	-0.17	1762	1765[b]	1799
H-C$_6$H$_4$	0	1765	1777[b]	1800
4-Br-C$_6$H$_4$	0.23	1761	1767[b]	1801
4-Cl-C$_6$H$_4$	0.23	1764	1762[c]	1804
3-Cl-C$_6$H$_4$	0.37	1770	1783[b]	1804
4-CN-C$_6$H$_4$	0.66	1769	1781[b]	1800
3-NO$_2$-C$_6$H$_4$	0.71	1771	1775[c]	1805
4-NO$_2$-C$_6$H$_4$	0.78	1763	1788; 1767[b]	1806
2,4-(NO$_2$)$_2$-C$_6$H$_3$		1774	1779	1818

[a]Ref. 6. [b]From ref. 3. [c]From ref. 4.

Table S2. IR C=O stretching frequencies (in cm^{-1}) for 0.1 M solutions in CH_2Cl_2 for substituted phenyl acetates (**3**), phenyl dichloroacetates (**2**) and phenyl trifluoroacetates (**1**) RCOOAr.

Ar	σ^a	R		
		CH_3	$CHCl_2$	CF_3
4-OMe-C_6H_4	-0.27	1759	1778; 1761	1796
4-Me-C_6H_4	-0.17	1758	1776	1797
H-C_6H_4	0	1763; 1744	1780	1799
4-Br-C_6H_4	0.23	1760	1784; 1761	1801
4-Cl-C_6H_4	0.23	1763	1788; 1765	1803
3-Cl-C_6H_4	0.37	1766	1784; 1773	1802
4-CN-C_6H_4	0.66	1771	1785; 1770	1802
3-NO_2-C_6H_4	0.71	1772	1787; 1775	1805
4-NO_2-C_6H_4	0.78	1767	1789; 1768	1806
2,4-$(NO_2)_2$-C_6H_3		1790	1802	1820

[a] Ref. 6.

Table S3. IR C=O stretching frequencies (in cm^{-1}) for substituted phenyl acetates RCOOPh (**4**) and methyl acetates RCOOMe (**5**).

R	σ^{*a}	RCOOPh	RCOOMe
CH_3CH_2	-0.1	1762	
CH_3	0	1765	1747
$PhCH_2$	0.215	1760	
$MeOCH_2$	0.520	1775	1754
$PhOCH_2$	0.850	1781	
CH_2Cl	1.05	1759	1759
$CHCl_2$	1.94	1777	1766
CCl_3	2.65	1787	1770
CF_3	2.60	1800	1791

[a]Ref. 10.

Table S4. IR C=O stretching frequencies (in cm^{-1}) for 0.1 M solutions in CH_2Cl_2 for substituted phenyl acetates RCOOPh (**4**) and methyl acetates RCOOMe (**5**).

R	σ^{*a}	RCOOPh	RCOOMe
CH_3CH_2	-0.1	1758; 1715	
CH_3	0	1763; 1744	1739
$PhCH_2$	0.215	1752	
$MeOCH_2$	0.520	1775	1753
$PhOCH_2$	0.850	1779; 1757	
CH_2Cl	1.05	1777	1759
$CHCl_2$	1.94	1780	1766; 1750
CCl_3	2.65	1788; 1770	1769
CF_3	2.60	1799	1788

[a]Ref. 10.

Table S5. Heat of formation values (ΔE_f in kcal mol^{-1}) and C=O bond-orders for phenyl acetates RCOOPh (**4**).

R	ΔE_f	C=O bond-order
CH_3CH_2	-60.94	1.838746
CH_3	-57.67	1.843757
$PhCH_2$	-28.71	1.852833
$MeOCH_2$	-88.43	1.831022
$PhOCH_2$	-53.98	1.880711
CH_2Cl	-56.83	1.842511
$CHCl_2$	-58.53	1.872288
CCl_3	-61.02	1.871240
CF_3	-200.26	1.893330

Table S6. Heat of formation values (ΔE_f in kcal mol^{-1}) and C=O bond-orders for phenyl substituted phenyl acetates (**3**), phenyl dichloroacetates (**2**) and phenyl trifluoroacetates (**1**) RCOOAr.

R

Ar	CH$_3$		CHCl$_2$		CF$_3$	
	ΔE_f	C=O bond-order	ΔE_f	C=O bond-order	ΔE_f	C=O bond-order
4-OMe-C$_6$H$_4$	-95.65	1.845953	-96.48	1.871403	-238.81	1.895021
4-Me-C$_6$H$_4$	-67.16	1.846558	-67.95	1.871981	-210.23	1.895682
H-C$_6$H$_4$	-57.79	1.847150	-58.54	1.872608	-200.76	1.896194
4-Br-C$_6$H$_4$	-49.96	1.850701	-50.51	1.875533	-192.48	1.899559
4-Cl-C$_6$H$_4$	-64.36	1.849716	-64.97	1.874743	-207.00	1.898538
3-Cl-C$_6$H$_4$	-64.26	1.850340	-64.85	1.875416	-206.85	1.899761
4-CN-C$_6$H$_4$	-22.46	1.853217	-22.80	1.877856	-164.50	1.902094
3-NO$_2$-C$_6$H$_4$	-65.88	1.854922	-65.85	1.979208	-207.36	1.904758
4-NO$_2$-C$_6$H$_4$	-66.40	1.859566	-66.35	1.882382	-207.65	1.907062
2,4-(NO$_2$)$_2$-C$_6$H$_3$	-69.96	1.878377	-69.58	1.899659	-209.10	1.928517

About σ* constant

The substituent constants σ* for aliphatic groups have been originally determined with the aid of alkaline and acid hydrolysis of esters RCOOR' by the eqn. (1) where subscripts A and B refer to acidic and basic hydrolysis, respectively. Rate coefficient k_o refers to the reaction of CH_3COOR'.

$$\sigma^* = (1/2.48)[\log(k/k_o)_B - \log(k/k_o)_A] \tag{1}$$

The factor 2.48 is chosen to put σ* values on about the same scale with Hammett σ values. The σ* values thus obtained describe the polar effects of the groups R because the polar effects on the acidic hydrolysis are thought to be small and the steric effects are cancelled by eqn. (1).[10]