

Terms & Conditions

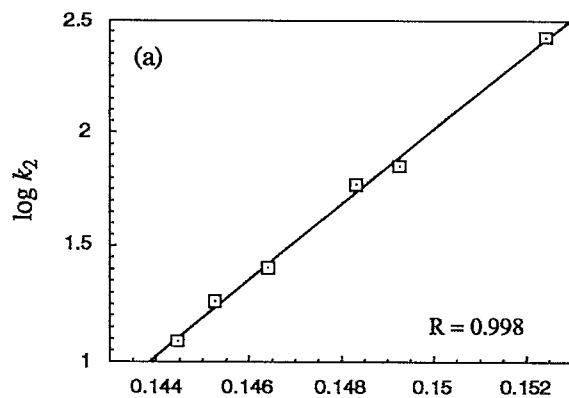
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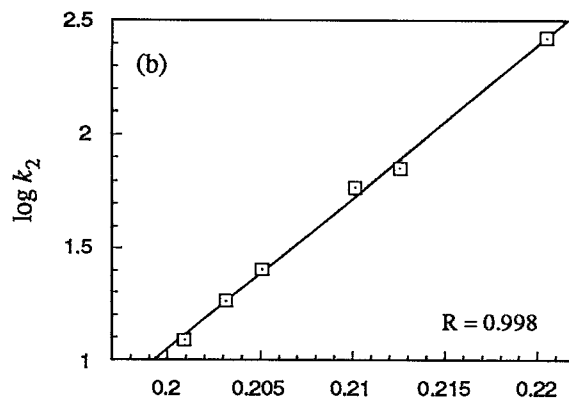
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Suppring Infomation 1



$$\frac{(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d}{|E_{RH} - E_{SL}|} \quad (d = 0.58)$$



$$\frac{(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d}{|E_{RH} - E_{SL}|} \quad (d = 0.40)$$

Figure 13. Plots of $\log k_2$ vs. $[(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d]/|E_{RH} - E_{SL}|$ for the reactions of MnO_4^- with *trans*-chalcones, (a) $E_{RH} = -10.5$ eV, $d = 0.58$; (b) $E_{RH} = -6.5$ eV, $d = 0.40$.

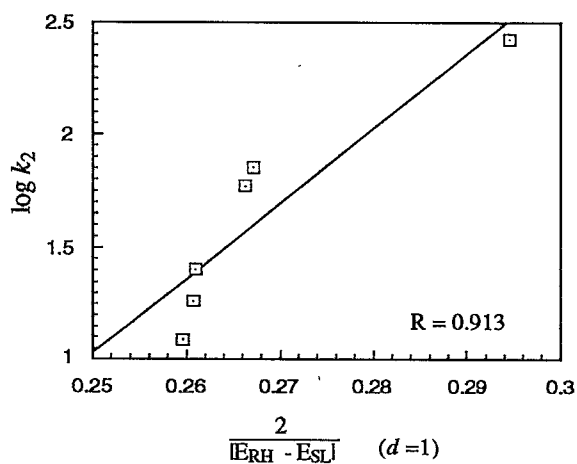


Figure 14. Plots of $\log k_2$ vs. $[(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d]/|E_{RH} - E_{SL}|$ for the reactions of MnO_4^- with *trans*-chalcones, $E_{RH} = -8.5$ eV, $d = 1$.

Supporting Information 2

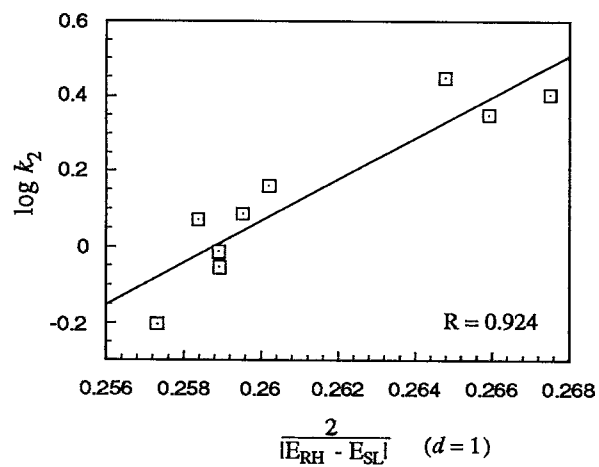


Figure 15. Plots of $\log k_2$ vs. $[(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d]/|E_{RH} - E_{SL}|$ for the reactions of MnO_4^- with methyl cinnamates, $d = 1$ (rate data from ref. 3 and 35).

Supporting Information 3

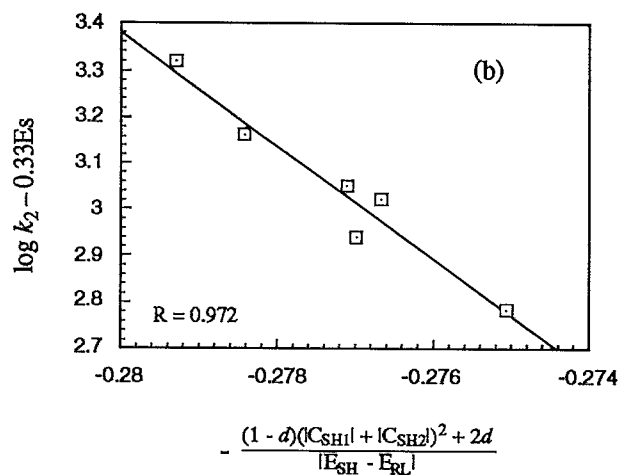
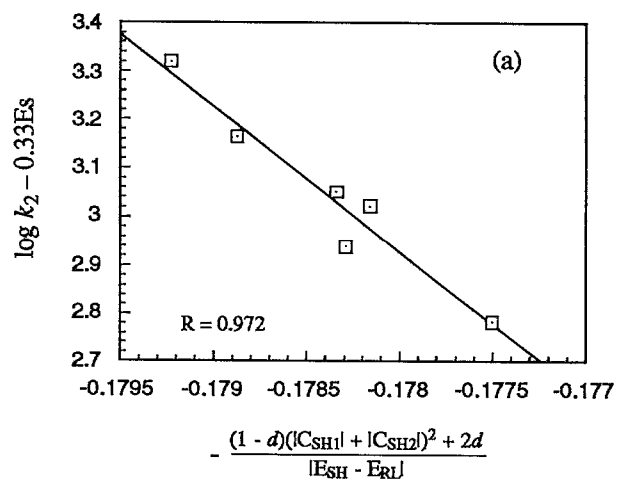


Figure 16. Plots of $\log k_2 - 0.33E_s$ vs. $-\frac{[(1-d)(|C_{SH1}| + |C_{SH2}|)^2 + 2d]}{|E_{SH} - E_{RL}|}$ for the reactions of MnO_4^- with alkyl vinyl ethers, (a) $E_{RH} = 1.5$ eV, $d = 0.93$; (b) $E_{RL} = -2.5$ eV, $d = 0.89$ (rate data from ref. 4).

Suppring Infomation 4

Analyses of Diels-Alder reactions: First, the reactions between 9,10-dimethylantracene and a set of seven nonaromatic *trans*-1,2-disubstituted ethylenes^{38,39} were tested as an example of the reaction between a symmetrical diene and unsymmetrical dienophiles. The rate data of these reactions have been successfully correlated by Charton with the extended form of Hammett equation (Figure 17).³⁹ The reactions were analyzed by use of eq 7 assuming the reaction model in Figure 1 where R is a diene and S is a dienophile. As shown in Figure 18, the plot of $\log k_2$ against $[(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d]/|E_{RH} - E_{SL}|$ reproduced the extended Hammett plot with excellent fidelity when d was taken as 0.80.

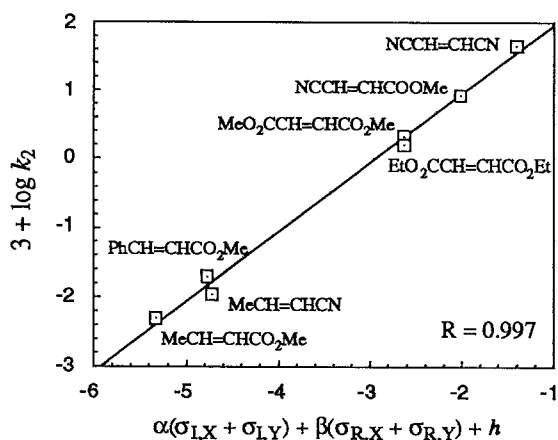


Figure 17. Plot by the extended Hammett equation for the reactions of 9,10-dimethylantracene with *trans*-1,2-disubstituted ethylenes (XCH=CHY); $\alpha = 3.31$, $\beta = 6.14$, $h = -6.23$ (from ref. 39).

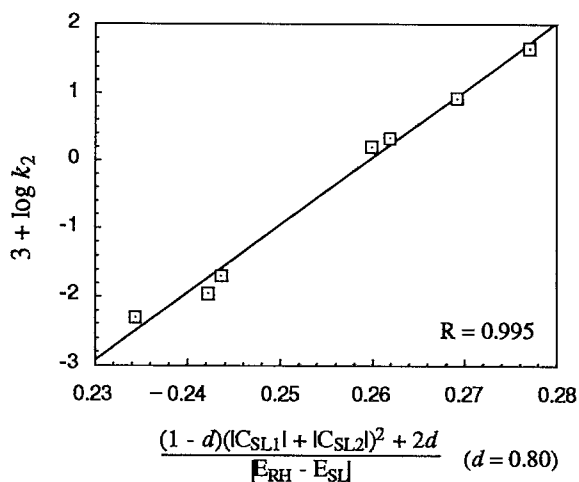


Figure 18. Plots of $\log k_2$ vs. $[(1-d)(|C_{SL1}| + |C_{SL2}|)^2 + 2d]/|E_{RH} - E_{SL}|$ for the reactions of 9,10-dimethylantracene with *trans*-1,2-disubstituted ethylenes; $d = 0.80$ (Data from ref. 38 and 39).

As an example of the Diels-Alder reaction between a symmetrical dienophile and a series of dienes, we next analyzed the reactions of maleic anhydride with anthracene and its benzo derivatives studied by Dewar and Pyron.⁴⁰ It was suggested by them that the reaction involves a cyclic transition state because a linear relationship was found between $\log k_2$ and paraloocalization energies but not between $\log k_2$ and localization energies. If one takes the dienophile as R, and anthracene and its benzo derivatives as S in Figure 1, eq 8 can apply to this case, though these are the reactions with normal electron demand. A plot of $\log k_2$ against $[(1-d)(|C_{SH1}| + |C_{SH2}|)^2 + 2d]/|E_{SH} - E_{RL}|$ is obtained with the best correlation to a straight line when d is taken as 0.76 and this is very similar to the mirror image of the plot given by Dewar and Pyron (Figure 19).

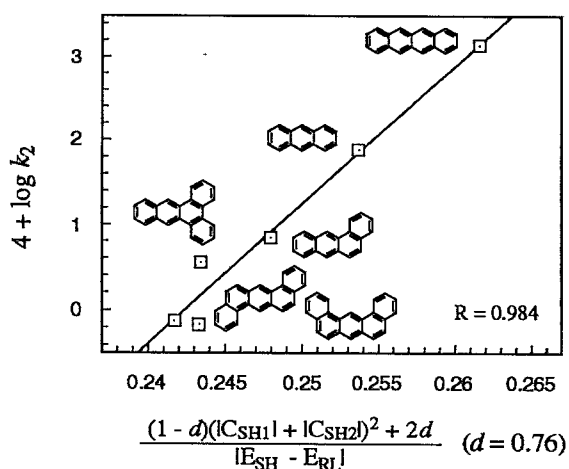


Figure 19. Plot of $\log k_2$ vs. $-[(1-d)(|C_{SH1}| + |C_{SH2}|)^2 + 2d]/|E_{SH} - E_{RL}|$ for the reactions of maleic anhydride with anthracene and its benzo derivatives; $d = 0.76$ (rate data from ref. 40).

References

- (38) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183.
- (39) Charton, M. *J. Org. Chem.* **1966**, *31*, 3745.
- (40) Dewar, M.J..S.; Pyron, R.S. *J. Am. Chem. Soc.* **1970**, *92*, 3098.