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BROMINATION OF STILBENES . NON-LINEAR FREE ENERGY RELATIONSHIP

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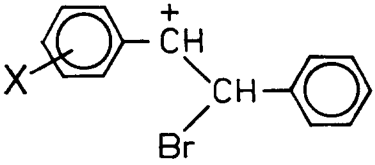
The linear correlation of the rates of bromination of substituted styrenes (1) with σ^+ shows that the transition state approaches closely that of the defining reaction, t-cumyl chlorides solvolysis (2), in which the intermediate is an α-aryl carbonium ion. The examination of the products of reaction (3) in acetic acid confirms this conclusion ; besides the dibromo derivative, only the α-acetoxy β-bromo and no β-acetoxy α-bromo isomer is obtained, indicating that the intermediate resembles a free carbonium ion wherein the charge is localised on the α-carbon, independent of the substituent character.

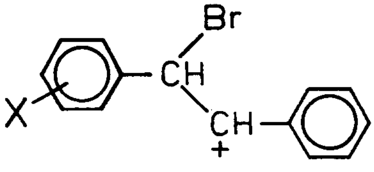
This result prompted us to undertake the study of the stilbene system where two aryl groups are in competition so that one group *must* be in the β-position relative to the incipient carbonium ion centre.

Second order rate constants for the bromination of 12 monosubstituted trans-stilbenes were measured by various techniques under identical conditions (in methanol containing 0.2 M NaBr at 25°C). Figure 1 shows that the data can be correlated (4) neither by σ nor by σ^+.

Whereas σ and σ^+ are defined by reactions with a single reaction centre, stilbene bromination can proceed via two transition states leading to the carbonium ion intermediates I and II.



(I)



(II)

TABLE I

Experimental and calculated rate constants for bromination of monosubstituted stilbenes in methanol (0.2 M NaBr) at 25°C.

X	$(\log k_1/k_o)_{calc}$	$(\log k_2/k_o)_{calc}$	$\log k_{calc}$	$\log k_{exp}$
1- p-NMe_2	(8.57)	(4.41)	(9.78)	8.34
2- p-OH	4.57	0.58	5.78	5.93
3- p-OMe	3.85	0.43	5.06	4.89
4- p-Me	1.50	0.28	2.73	2.47
5- m-Me	0.28	0.13	1.72	1.80
6- H	-0.07	0.02	1.49	1.51
7- p-Cl	-0.65	-0.33	1.05	0.89
8- p-Br	-0.83	-0.33	1.00	0.91
9- m-Cl	-2.06	-0.55	0.68	0.72
10- m-CF_3	-2.69	-0.63	0.58	0.54
11- p-CF_3	-3.15	-0.80	0.41	0.43
12- p-NO_2	-3.99	-1.17	0.04	0.02

The experimental rate constant will, therefore, be the sum of two constants, k_1 and k_2, which obey independent $\rho\sigma$ relationships (6). Hence, k_1 should be correlated by σ^+ and k_2 by σ, with ρ_2 less negative than ρ_1 on account of the intervening CHBr group.

$$\log k_1/k_o = \rho_1\sigma^+ \qquad \log k_2/k_o = \rho_2\sigma$$

$$k_{exp}/k_o = 10^{\rho_1\sigma^+} + 10^{\rho_2\sigma} \text{ ; where } k_o = 0.5\ k_{stilbene}$$

The path leading to I will be preferred by stilbenes with strongly electron-donating substituents since $\rho_1\sigma^+ \gg \rho_2\sigma$. Calculations for compounds 2 and 3 (see Table I) indicate (7) that ρ_1 is of the order of -5. For substituents with small σ and σ^+ values, the relative importance of the two terms will be determined by the difference between ρ_1 and ρ_2 and between σ and σ^+. For the strongest electron-attractors, for which $\sigma \simeq \sigma^+ > 0$, it is safe to assume that the first term will be small with respect to the second, since ρ_2 can hardly be greater than $0.5\ \rho_1$ (8). Confirming this assumption, compounds 9 to 12 are accurately correlated by σ, with $\rho_2 = -1.53 \pm 0.08$ (Figure 2).

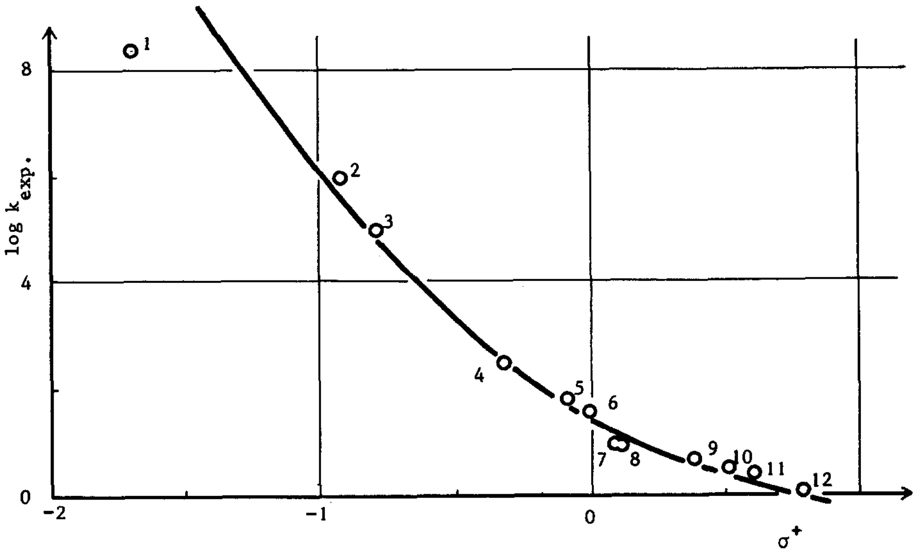


FIG.1 - Bromination of stilbenes : non-linear reactivity correlation.

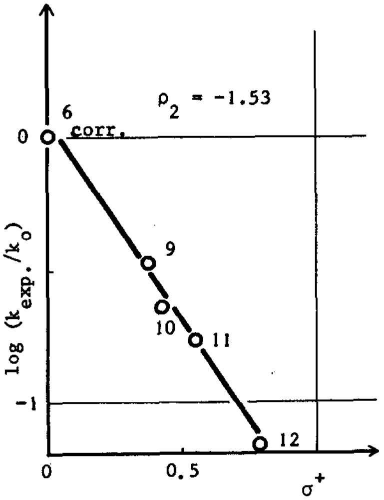


FIG.2 - Linear correlation with σ, for strong electron-attractors : $\rho_2 = -1.53$.

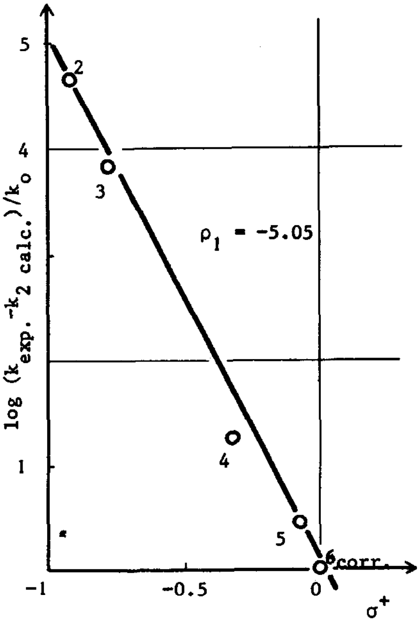


FIG.3 - Linear correlation of log k_1 calc. with σ^+, for electron-donating substituants .

Since $k_1 = k_{exp} - k_2$, and k_2 can be calculated from $\rho_2 = -1.53$, we can obtain ρ_1 (= -5.05 ± 0.25) from the data for electron-donating substituents (Figure 3).

The value of ρ_1 is in the same range as that obtained for other reactions leading to α-aryl carbonium ion intermediates, *e.g.* methanolysis of t-cumyl chlorides (2) (-4.82) ; bromination of styrenes in methanol - NaBr (1) (-4.28). There is an interesting analogy between our results and those of the hydrolysis of 1,2-diarylethanols (10) which involves rate-determining carbonium ion deprotonation. The corresponding ρ values are -3.77 (α-aryl) and -1.00 (β-aryl). The similarity of the transmission factors in the two reactions (bromination, 0.30 ; hydrolysis, 0.27) might lead us to conclude that the bromine atom plays little or no part in charge stabilization in stilbene bromination. However, since the reaction media are very different, this agreement may be entirely fortuitous.

For electron-donating substituents, therefore, an α-carbonium ion is formed ; in the case of electron-attracting substituents, the charge is not on the α-carbon but on an atom or atoms one-removed, *i.e.* the β-carbon or possibly the bromine atom. Recent studies, (3,11) however, suggest that even in the second case an open carbonium ion mechanism is more likely than that involving a bromonium ion.

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4) The curvature of the σ plot is not due to competition between electrophilic attack by bromine and by tribromide ion on the double bond. The value of Q ($k_{Br_2} / k_{Br_3^-}$) is in the range where k_{exp} and k_{Br_2} have the same dependence on substituent effects (5).

   For p-NMe_2 , Q = 20 ; H , Q = 43 ; p-NO_2 , Q = 17.

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6) We are indebted to Professor B.M. Wepster for valuable discussions on this topic.

7) Compound 1 (X = p-NMe_2) has been neglected from our calculations since the usually quoted (9) σ^+ (-1.7) appears to be an exalted value.

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