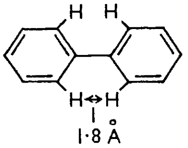
757. *The Kinetics and Mechanisms of Addition to Olefinic Substances. Part VII.*[1] *Some Observations relating to Linear Free-energy Relations in Reactions of Olefinic Substances.*

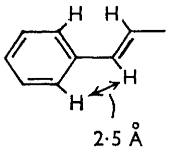
By P. B. D. de la Mare.

Applications of linear free-energy relations in correlating substituent effects in addition of halogens to olefinic substances, and in the unimolecular solvolyses of allylic halides, with those established for aromatic substitutions and for the unimolecular solvolyses of arylalkyl halides are discussed, with particular reference to steric effects on the electron-releasing power of aryl groups.

In biphenyl, maximum conjugation between the aryl groups would require a planar conformation (I), in which the 2- and 2′-hydrogen atoms are only about 1·8 Å apart. It is considered (cf. ref. 2) that the resulting non-bonding repulsions significantly reduce conjugation in these compounds. In ω-styryl compounds (II), one of these repulsions is absent in a planar configuration, and it might therefore be expected that steric inhibition of conjugation would be less prominent in the latter system.



(I)



(II)

Berliner and Blommers[3] recognised this structural feature when they discussed the low efficiency of transmission of structural effects through the biphenyl system. They used Hammett's reaction constants,[4,5] ρ, as a measure of the efficiency of transmission; for *meta*- and *para*-substituted benzoic acids $\rho = 1{\cdot}0$, and for the 3′- and 4′-substituted biphenyl-4-carboxylic acids (on the same scale) $\rho = 0{\cdot}37$. Inductive effects, however, play a large part in these systems; this is probably why substituents still more powerfully affect the strengths of β-substituted acrylic acids ($\rho =$ *ca.* $2{\cdot}2$),[6] and why the interposition of an extra phenyl group reduces substituent effects even more markedly (ρ for *meta*- and *para*-substituted cinnamic acids,[5] 0·47).

More suitable reactions for the illustration of factors influencing conjugative effects would be those involving much electron-demand at the reaction centre. Orr and Kharasch[7] have discussed in this connection the addition of 2,4-dinitrobenzenesulphenyl chloride to substituted styrenes, and noticed that the *p*-methoxyl group promotes an abnormally high reactivity, as judged in comparison with its σ-value. For such reactions, however, the Hammett equation is known to have only very limited predictive power;[8] and H. C. Brown and his co-workers[9] have more recently proposed the adoption of a set of " electrophilic substituent constants," σ^+, which serve to correlate structural effects in electrophilic aromatic substitutions with those in unimolecular solvolyses of arylalkyl halides. These electrophilic substituent constants give considerable weight to conjugative

---

[1] Part VI, Ballinger, de la Mare, and Williams, *J.*, 1960, 2467.

[2] (*a*) de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086; (*b*) Beavan, Hall, Lesslie, and Turner, *J.*, 1952, 854; Howlett, *J.*, 1957, 4353; 1960, 1055.

[3] Berliner and Blommers, *J. Amer. Chem. Soc.*, 1951, **73**, 2479.

[4] Hammett, *Trans. Faraday Soc.*, 1938, **34**, 156.

[5] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[6] Charton and Meislich, *J. Amer. Chem. Soc.*, 1958, **80**, 5940.

[7] Orr and Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 1201.

[8] Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525; de la Mare, *J.*, 1954, 4450.

[9] Brown and Okomoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913; 1958, **80**, 4979.

effects.[9,10] It is interesting, therefore, to consider to what extent they predict reactivities in olefinic systems. Some results are available for illustration of this matter.

Addition of Halogens to Olefinic Compounds.—The addition of chlorine to olefinic compounds in acetic acid is generally a second-order process,[11] of kinetic form: $-d[Cl_2]/dt = k_2[\text{Olefin}][Cl_2]$. The electrophilic reagent which attacks the olefin is believed, from a study of the effects of added electrolytes, to be molecular chlorine, and the subsequent stages of the reaction are considered not to affect comparisons of effects of substituents.[12] These effects have been studied by Robertson and his co-workers; most of the results have been summarised elsewhere.[13] One series of compounds suitable for consideration in terms of linear free-energy relations is the series of β-substituted acrylic acids, $RR'C{:}CH{\cdot}CO_2H$. In compounds of this type, initiation of attack by an electrophile must be at the α-carbon atom,[14] to which electrons can be released mesomerically by β-substituents; so the relative rates might be expected to be linearly related to the electrophilic substituent constants for *para*-substituents, $\sigma_p{}^+$. Table 1 summarises the data,[13,15] which are plotted in Fig. 1.

TABLE 1. *Rates* (k_2, *at* 25°, *in acetic acid*) *of addition of chlorine to* β-*substituted acrylic acids*, $RR'C{:}CH{\cdot}CO_2H$.

R	Me	Ph	Me	H	CO_2H
R′	Me	H	H	H	H
k_2 (l. mole^{-1} min.$^{-1}$)	51	4·9	0·62	0·018	0·00011
$\log_{10} (k_2{}^R/k_2{}^H)$	3·45	2·43	1·54	0·00	−3·00 *
$\Sigma\sigma_p{}^+$ (ref. 9)	−0·62	−0·18	−0·31	0·00	0·42

* The experimental rate-coefficient for this compound is for the *cis*-, whereas the remainder refer to *trans*-isomers; so this value has been corrected for the rate-factor of three, expected between maleic and fumaric acid,[13] and for the statistical factor, since this compound has two equivalent positions for attack; these corrections do not greatly affect the logarithmic plot.

FIG. 1. *Rates of addition of chlorine to β-substituted acrylic acids*, $RR'C{:}CH{\cdot}CO_2H$.

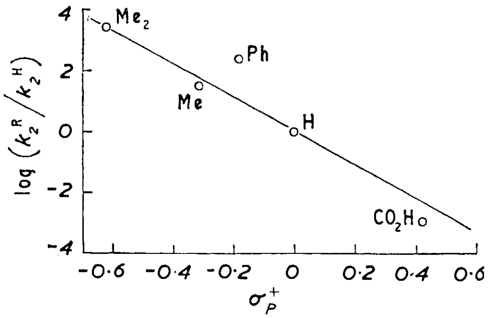
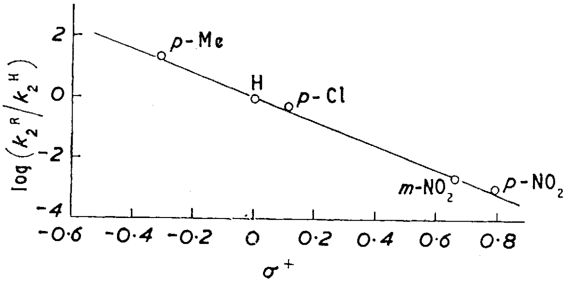


FIG. 2. *Rates of addition of chlorine to substituted* trans-*cinnamic acids*, $R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$.



The points representing the effects of two, one, and no methyl groups define a reasonable straight line, thus indicating that methyl groups behave approximately additively. This line, which has a slope of $\rho = ca. -5{\cdot}5$, passes satisfactorily near the point which represents the effect of the carboxyl substituent. The value of the slope indicates that, for these substituents, electronic effects on reaction rates are quantitatively rather more important than for the solvolysis of 1-aryl-1-methylethyl halides ($\rho = -4{\cdot}6$), but less than for nitration ($\rho = -6$) or for molecular halogenation of aromatic compounds ($\rho = ca. -11$).[10a]

---

[10] (*a*) de la Mare and Ridd, " Aromatic Substitution: Nitration and Halogenation," Butterworths, 1959, p. 159; (*b*) Van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[11] White and Robertson, *J.*, 1939, 1509.

[12] Robertson, Dixon, Goodwin, McDonald, and Scaife, *J.*, 1949, 294.

[13] de la Mare, *Quart. Rev.*, 1949, **3**, 126.

[14] Ingold and Smith, *J.*, 1931, 2742.

[15] Evans, Watson, and Robertson, *J.*, 1950, 1624.

All these reactions involve much electron-demand at the reaction centre, and in all of them demand can to a substantial degree be satisfied in the transition state.

The point which in Fig. 1 represents the behaviour of the phenyl substituent, however, lies *ca.* 1·5 logarithmic units above the line; cinnamic acid is at least thirty times more reactive than would be predicted from σ^+. It is suggested, therefore, that for the steric reason already discussed (cf. structures I and II) it is easier to bring the styryl than the biphenylyl system towards coplanarity in the transition state, and hence the phenyl group is more nearly able to exert its full conjugative power through an olefinic than through an aryl system. An equivalent illustration of the same point is that in aromatic substitution,[2a,10a] and in the solvolyses of arylalkyl halides,[9] a single methyl group is superior in electron-releasing power to a phenyl group; but in the corresponding additions to unsaturated compounds, despite the fact that the deactivating inductive effect of the latter group would be promoted by its nearness to the reaction centre, the order is reversed and a phenyl group is considerably superior to a methyl group.

Support for the present theory can be derived by comparing the structural effects on the rates of addition of chlorine to substituted acrylic acids (Fig. 1) and to substituted cinnamic acids, for which the results are given in Table 2 and Fig. 2.[13,15]

TABLE 2. *Rates* (k_2 *at* 25°, *in acetic acid*) *of addition of chlorine to substituted cinnamic acids, trans*-$R\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$.

R	*p*-Me	H	*p*-Cl	*m*-NO_2	*p*-NO_2
k_2 (l. mole^{-1} min.$^{-1}$)	103	4·9	2·4	0·011	0·0049
$\log_{10} (k_2^R/k_2^H)$	1·32	0·00	−0·30	−2·65	−3·00
σ^+ (ref. 9)	−0·31	0·00	0·11	0·66	0·79

The relative rates are well predicted by the values of σ^+; and the slope of the plot is $\rho^+ = -3{\cdot}9$. The electron-demand in the reaction can still be satisfied to a considerable degree by electron-release from conjugating substituents, despite the fact that a phenylene group has been interposed between the substituent and the reaction centre.

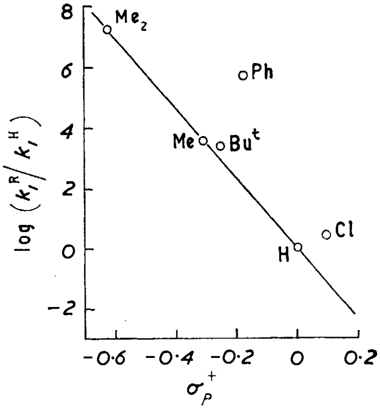


FIG. 3. *Relative rates of unimolecular solvolyses of allylic halides,* $RR'C{:}CH\cdot CH_2Cl$.

For reactions of aromatic systems to which H. C. Brown's substituent constants would be considered appropriate, the interposition of an extra phenylene group seems to make transmission of substituent effects much less effective.[2a,16] Thus for molecular chlorination a methyl group activates the *para*-position in toluene by a factor of 820; but it activates the 4'-position in 4-methylbiphenyl only by a small factor.[2a,10a,16] Similarly, whereas nitrobenzene is less reactive than benzene in halogenation by an estimated factor of about 10^6, 4-nitrobiphenyl is less reactive than biphenyl by a factor of 500, and the difference would be even larger if the comparison were made, as it should be, for *para*-substitution.

---

[16] de la Mare, " Theoretical Organic Chemistry," Kekulé Symposium, Butterworths, London, 1958, pp. 219—229.

Again, for nucleophilic displacement,[17] the 4-nitro-group in 2,4-dinitrobromobenzene activates the bromine substituent by a factor of some 10^5; but the 4′-nitro-group in 4-bromo-3,4′-dinitrobiphenyl activates the bromine atom by a factor of only 12. Comparison with the olefinic systems above supports the view that steric hindrance to coplanarity is more important in determining effects of conjugative origin relayed through biaryl than through styryl systems.

Bromine additions have not been discussed here in detail, since the kinetic forms and mechanisms are more complicated; but the effects of alkyl and of phenyl substituents on third-order bromine addition (kinetic form: $-\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = k_3[\text{Olefin}][\mathrm{Br}_2]^2$) are very similar to those already discussed for chlorine addition.[13,18] Clearly, as in aromatic substitution, these reactions are closely related and evoke similar extents of electron-release in the transition state.

Unimolecular Solvolysis of Allylic Halides.—In the unimolecular (S_N1) mechanism for allylic halides, $\mathrm{RR'C{:}CH{\cdot}CH_2Cl}$, electron-demand at the reaction site is very great and can readily be satisfied by conjugating or hyperconjugating 3-substituents. Table 3 summarises results given by Vernon,[19] which are plotted in Fig. 3; the compounds could not all be examined at the same temperature or in the same solvent, but correction for this would not much affect a logarithmic plot of this kind. Once again, the points which represent the influence of two, one, and no alkyl groups define a reasonable straight line. This gives $\rho = ca.\ -11{\cdot}7$; the response of the system to electron-release is very large. Conjugating substituents (Cl, Ph) give points which represent a reactivity greater than would be predicted from the values of σ^+; that for the phenyl group involves a rate greater by a factor of some 3500. So here we have a second example of an olefinic system in which a single phenyl group is considerably superior to a methyl group in its power of electron-supply.

TABLE 3. *Relative rates of unimolecular solvolysis of allylic halides,* $\mathrm{RR'C{:}CH{\cdot}CH_2Cl}$.

R	Me	Ph	Me	Bu^t	Cl
R′	Me	H	H	H	H
Rel. rate of solvolysis (S_N1; k_1^R/k_1^H) ...	*ca.* $1{\cdot}5 \times 10^7$	*ca.* 5×10^5	$3{\cdot}6 \times 10^3$	$2{\cdot}3 \times 10^3$	3·1
$\log_{10} k_1^R/k_1^H$)	7·18	5·70	3·56	3·36	0·49
$\sum\sigma_p^+$	−0·62	−0·18	−0·31	−0·25	0·11

This discussion suffices to illustrate that σ^+ constants can be extended only with very limited predictive power from aromatic to the structurally related olefinic systems; and it draws attention again to the variable electronic effects of the phenyl group. This group, as Berliner and Liu pointed out,[20] can satisfactorily be treated only in terms of a multiplicity of substituent constants; van Bekkum, Verkade, and Wepster's general extension [10b] of this view, to which Dickinson and Eaborn's treatment [21] is similar, may eventually prove to be more useful than either, or both, of the series of substituent constants now currently popular.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

[*Received, March* 30*th*, 1960.]

---

[17] Berliner, Newman, and Riaboff, *J. Amer. Chem. Soc.*, 1955, **77**, 478.

[18] de la Mare and Robertson, *J.*, 1950, 2838.

[19] Vernon, *J.*, 1954, 423.

[20] Berliner and Liu, *J. Amer. Chem. Soc.*, 1953, **75**, 2417.

[21] Dickinson and Eaborn, *J.*, 1959, 3036.