AN EXAMINATION OF QUANTITATIVE TREATMENTS OF AROMATIC SUBSTITUTION

R.O.C. Norman and G.K. Radda

Dyson Perrins Laboratory, The University, Oxford

THE inadequacy of the Hammett equation in the form $\log \underline{f} = \sigma^+\rho$ for correlating the rates of aromatic substitution has recently been pointed out by Yukawa and Tsuno[1] and by Knowles et al.[2] Both groups of investigators recognized that the limitation of this equation is that it takes no account of the extent of formation of the new σ-bond between reagent and aromatic nucleus in the rate-determining addition step of the reaction; as the new bond is more fully formed, conjugation between an electron-releasing para-substituent and the nucleus is increased and the substituent becomes better able to delocalize the charge on the aromatic ring. In Yukawa and Tsuno's empirically derived equation (1), the parameter $(\sigma^+-\sigma)$ was taken as a measure of the ability of the substituent to interact mesomerically and $\underline{r}$ as a measure of the extent of the interaction in a given reaction, σ^+-values being derived from an arbitrarily chosen reaction (the solvolysis of cumyl chlorides) in which such interaction occurs in the transition state. Knowles et al. derived a new substituent parameter, σ_p, as a measure of the potential of the substituent to delocalize positive charge, and deduced empirically that the extent to which it was required to do so in a given reaction was proportional to the reagent parameter, ϕ (equation 2).

$$\log \underline{f} = \sigma\rho + (\sigma^+-\sigma)r\rho \ \ldots\ldots\ (1); \qquad \log \underline{f} = \sigma_G\phi + \sigma_p\phi^2 \ \ldots\ldots\ (2)$$

[1] Y. Yukawa and Y. Tsuno, Bull. Chem. Soc. (Japan) 32, 965, 971 (1959).

[2] J.R. Knowles, R.O.C. Norman and G.K. Radda, J. Chem. Soc. 4885 (1960).

We have extended Yukawa and Tsuno's treatment by increasing the number of reactions involving direct substitution of the aromatic nucleus. Rho-values were calculated from rate data for meta-substituents and the unsubstituted compound, but it was necessary to omit data based on very low meta-percentages since small errors would give large errors in ρ; most of the reactions used were those involving displacement on a meta-substituted compound, e.g. protodesilylation. Values of r were obtained from equation (1), σ^n-constants[3] rather than σ-constants being used in their derivation since the latter, obtained from the ionization constants of benzoic acids, include resonance interaction between para-substituents and the carboxyl group. Inspection of the results (tabulated) leads to two useful conclusions.

(i) The parameter r increases regularly with ρ. More significantly, it is related linearly to ρ with high precision (correlation coefficient = 0.965), the line having gradient 0.14 and intercept on the r-axis -0.07.

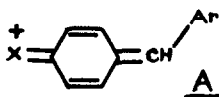| Reaction[4]	ρ	r
Protodestannylation $(HClO_4-H_2O-EtOH)$	4.0	0.47
Protodegermylation $(H_2SO_4-HOAc-H_2O)$	4.4	0.62
Protodegermylation $(HClO_4-MeOH)$	4.9	0.67
Protodesilylation (H_2SO_4-HOAc)	5.7	0.70
Bromodesilylation $(Br_2-HOAc-H_2O)$	6.8	0.79
Nitration	7.3	1.07
Bromination (Br_2)	8.8	1.20

Hence, for aromatic substitutions, equation (1) may be written: $\log f = \sigma\rho + (\sigma^+-\sigma)(a\rho + b)\rho$, where a and b are constants. This equation, like (2),

[3] H. van Bekkum, P.E. Verkade and B.M. Wepster, Rec. Trav. Chim. 78 815 (1959).

[4] Data for protonolyses and brominolysis are from the papers of C. Eaborn et al., J. Chem. Soc. 2299 (1959), 179 (1960), 297, 542, 5082 (1961); and for nitration and bromination from P.B D. de la Mare and J.H. Ridd, Aromatic Substitution, Butterworths, London (1959); ref. 2.

is a quadratic in the reagent parameter; the two equations are of similar

form, based on different sets of parameters. The existence of this re-

lationship supports the view[2] that, as the extent of formation of the new

σ-bond in the transition state increases, not only does a larger fraction

of unit positive charge reside on the aromatic system (increasing ρ) but

also conjugation between a <u>para</u>-substituent and the aromatic nucleus is

more complete (increasing $\underline{r}$).

(ii) For all reactions other than aromatic substitutions quoted by

Yukawa and Tsuno, $\underline{r}$ is larger than predicted from the relation between $\underline{r}$

and ρ in (i).[5] In a typical example, the equilibrium of a benzhydrol with

its carbonium ion, $Ar_2CH.OH + H^+ \rightleftharpoons Ar_2CH^+ + H_2O$, there should be strong

conjugation between a <u>para</u>-substituent and the carbonium ion (i.e. structure

$\underline{A}$ should be an important contributor to the hybrid); hence $\underline{r}$ should be large.

However, the positive charge can now be delocalized over two aromatic rings

and the aliphatic CH group, so that ρ is smaller relative to $\underline{r}$ than ex-

pected. The same is true of reactions such as the solvolysis of cumyl

chlorides, in which there is significant conjugation between mesomerically-

releasing <u>para</u>-substituents and the developing carbonium ion in the tran-

sition state, while the charge is delocalized both by the aromatic nucleus

and by the α-carbon atom. The relation of $\underline{r}$ to ρ in these and related

reactions therefore gives some indication of the extent of resonance inter-

action in the transition state compared with the charge to be delocalized

by the aromatic nucleus and its substituent.

[5] The ρ-values for reactions (11) and (22) in ref. 1 should be divided by
2 & 3 respectively, since the data refer to di- and tri-substituted
compounds.