401. *Aromatic Reactivity. Part XXV.*[1] *A Re-examination of a Recent Quantitative Treatment.*

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Arguments are presented to the effect that recent conclusions by Norman and Radda, derived from an extension of the Yukawa–Tsuno treatment of substituent effects, are unsoundly based.

Norman and Radda[2] recently described an examination of quantitative treatments of aromatic substitution. We disagree with both their methods and their conclusions, and we here set out our arguments because Norman and Radda included and, we believe, misused results for cleavages of aryl–metal bonds reported in our papers.

Yukawa and Tsuno[3] showed that the effects of substituents in electrophilic side-chain reactions and some aromatic substitutions could be correlated by the equation $\log k_{\text{rel}} = \rho[\sigma + r(\sigma^+ - \sigma)]$, where σ is the Hammett substituent constant, derived from ionization of benzoic acids in water at 25°,[4] σ^+ is the Brown electrophilic substituent constant derived from solvolysis of αα-dimethylbenzyl chlorides in 90% acetone at 25°,[5] and r is a measure of the relative contribution by polarizability effects, with a value zero for the ionization of the acids and unity for the solvolysis of the chlorides. The novelty in Norman and Radda's examination lies in conclusions based on a so-called extension of the Yukawa–Tsuno treatment to a number of the aryl–metal cleavages (to which, in fact, the treatment had already been extended[3,7–10]). The reactions included in their survey are shown in the table, along with values of ρ and r listed by them, the values of r being calculated (in our opinion unwisely, as discussed below) by use of σ^n-constants (ref. 6) rather than σ-constants for some *para*-substituents. From these values Norman and Radda conclude that r is linearly related to ρ with high precision, and we make the following comments.

Reaction	$-\rho$	r
Protodestannylation ($HClO_4$–H_2O–EtOH)	4·0	0·47
Protodegermylation (H_2SO_4–AcOH–H_2O)	4·4	0·62
Protodegermylation ($HClO_4$–MeOH–H_2O)	4·9	0·67
Protodesilylation (H_2SO_4–AcOH)	5·7	0·70
Bromodesilylation (Br_2–AcOH–H_2O)	6·8	0·79
Nitration	7·3	1·07
Bromination (molecular)	8·8	1·20

(*a*) Yukawa and Tsuno[3] listed five aromatic substitutions, *viz.*, nitration, molecular bromination, ionic bromination, protodesilylation in aqueous-methanolic perchloric acid, and bromodeboronation; Norman and Radda use two of these and ignore the others.

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[1] Part XXIV, Baker, Bott, and Eaborn, preceding paper.

[2] Norman and Radda, *Tetrahedron Letters*, 1962, 125.

[3] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

[4] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 194; McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

[5] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[6] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[7] Eaborn and Pande, *J.*, 1961, 297.

[8] Eaborn and Waters, *J.*, 1961, 542.

[9] Eaborn and Pande, *J.*, 1961, 3715.

[10] Eaborn and Pande, *J.*, 1961, 5082.

For ionic bromination,[11] which obeys the Yukawa–Tsuno equation better than do the other reactions,[3] the values of ρ and r, $-5{\cdot}276$ and $1{\cdot}145$, respectively, listed by Yukawa and Tsuno (who use σ- not σ^n-constants, which makes no significant difference for present purposes) clearly fall far from the Norman and Radda " line," but possibly omission of this reaction can be justified because the results, although some of the most accurate available for aromatic substitutions, refer only to *m*- and *p*-Me, -Bu^t, and -Ph groups.[11] For bromodeboronation,[12] however, results are available for more, and for a wider range of, substituents than for nitration and molecular bromination; and they conform to the Yukawa–Tsuno equation better than do those for the last two reactions.[3] * The values of ρ and r, namely, $-3{\cdot}84$ and $2{\cdot}29$, derived by Yukawa and Tsuno for this reaction (r would be $2{\cdot}18$ if σ^n-constants were used) are in extreme disagreement with the linear relation noted by Norman and Radda, and if these values are used along with those listed by Norman and Radda the correlation coefficient for the relation is changed from 0·965 to —0·004. If the " minimum " rate constant for the *p*-OMe substituent, which may be considerably in error,[12] is omitted, an r value of 1·53 applies,[14] which is still in serious disagreement with Norman and Radda's generalization.†

(*b*) The available data for molecular bromination in acetic acid [16] and for nitration [17,18] are such that it is wrong to use the calculated r values in a quantitative analysis. For example, ρ values (on which the calculated r values depend) are derived from rate factors for *meta*-substituents,[2,3] and in the references cited by Norman and Radda the only *meta*-substituents listed, along with the percentages of *meta*-substitution and the corresponding ρ values, are as follows: (i) molecular bromination,[16] Me, 0·3%, $\rho = -10{\cdot}7$; (ii) nitration,[17] Me, 3·5%, $\rho = -5{\cdot}79$ (a rather less likely value of 1·6% for *meta*-nitration of toluene reported by Knowles, Norman, and Radda [18] corresponds with a ρ value of $-1{\cdot}65$); Bu^t, 8·5%, $\rho = -6{\cdot}0$ (or $-4{\cdot}8$ if the results of Knowles *et al.*[18] are used); Cl, 0·9%, $\rho = -8{\cdot}2$; Br, 1·2%, $\rho = -7{\cdot}6$; I, 1·8%, $\rho = -5{\cdot}7$. Since Norman and Radda rightly say that it is necessary to omit data based on low *meta*-percentages, it is difficult to see how they could derive ρ values for these reactions with any confidence.

(*c*) For nitration, combination of reported rate factors [17] with the ρ value of $-7{\cdot}3$ listed by Norman and Radda corresponds to the following values of r: *p*-F, 0·33; *p*-OMe, 0·34; *p*-Me, 0·61; *p*-Ph, 0·78; *p*-Cl, 0·98; *p*-Bu^t, 1·03; *p*-Br, 1·16; *p*-I, 1·54. This spread of values shows how arbitrary is the r value of 1·07 assigned to this reaction by Norman and Radda, and underlines the unwisdom of making quantitative comparisons of r values from reaction to reaction. The ρ and r values of $-6{\cdot}377$ and $0{\cdot}897$, respectively, listed by Yukawa and Tsuno [3] give, we believe, a rather better plot than those derived by Norman and Radda, but it would be pointless, with the data available, to try to select any definite values of ρ or r.

(*d*) We can find no basis for the combination of ρ and r values ($-8{\cdot}8$ and $1{\cdot}20$) which Norman and Radda assign to molecular bromination. The annexed Figure shows a plot

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* The rate constants for bromodeboronation [12] may be generally in error by 10—15%,[13] but this is unimportant for our purposes.

† The high r value for this reaction is possibly to be associated with the unusual mechanism [12] which may operate. A reaction should not, of course, be omitted from a general analysis of electrophilic aromatic substitutions simply because its mechanism seems unusual, since the mechanisms are not known with certainty for any of the substitutions, and a possible mechanism for protode-stannylation and -plumbylation [15] is analogous to that proposed for protodeboronation.

[11] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, pp. 134, 237.

[12] Kuivila and Hendrickson, *J. Amer. Chem. Soc.*, 1952, **74**, 5068; Kuivila and Benjamin, *ibid.*, 1955, **77**, 4834.

[13] Stock and Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 1668.

[14] Tsuno, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 1959, **16**, 197.

[15] Eaborn and Pande, *J.*, 1960, 1566.

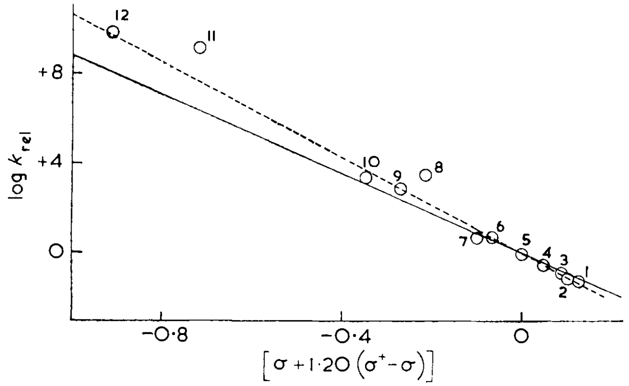
[16] Ref. 11, pp. 131, 135—142, 237.

[17] Ref. 11, pp. 85, 88, 237.

[18] Knowles, Norman, and Radda, *J.*, 1960, 4885.

of log k_{rel} against $[\sigma + 1{\cdot}20(\sigma^+ - \sigma)]$ (σ^n-values being used where available), and the solid line has the Norman–Radda slope of $-8{\cdot}8$. The broken line, which is clearly very much more satisfactory, has a slope of $-10{\cdot}6$. (In assessing the reliability of ρ and r values it is interesting that Yukawa and Tsuno[3] use $\rho = -8{\cdot}82$ and $r = 1{\cdot}66$ to fit the same data.)

(*e*) For the various desilylations[19-21] and degermylations[7,10] Norman and Radda derive r values which increase progressively with $-\rho$, in accord with the relation they wish to establish. However, there are excellent linear free-energy relations between the effects of substituents in these reactions,[7,10,19,20] which means that the balance of polarization and polarizability effects of the substituents is effectively the same in all of them. The linear relations between the reactions are more exact than the Yukawa–Tsuno plots for the separate reactions, and thus, while it is possible to assign slightly different values of r to the reactions (for example, by assigning extra weight to certain substituents) (cf. refs. 7, 10), it is fruitless to seek quantitative significance in the differences. Within the normal accuracy of application of the Yukawa–Tsuno equation to these reactions a single value of r of $0{\cdot}67$ is very satisfactory for them all, although ρ (as calculated by Norman and Radda) varies from $-4{\cdot}4$ to $-6{\cdot}8$.



Plot of log k_{rel} in bromination against $[\sigma + 1{\cdot}20(\sigma^+ - \sigma)]$.
1, *p*-Br. 2, *p*-I. 3, *p*-Cl. 4, *m*-Ph. 5, H. 6, *m*-Me. 7, *p*-F. 8, *p*-Ph. 9, *p*-Bu^t. 10, *p*-Me. 11, *p*-NHAc. 12, *p*-OMe.
The solid line has the Norman–Radda slope of $-8{\cdot}8$. The broken line has a slope of $-10{\cdot}6$.

(*f*) Norman and Radda ignore results for protodeplumbylation.[9] While only four substituents were studied, they were carefully chosen to include *m*-Cl, which enables the value of ρ to be fixed (at $-2{\cdot}42$), and *p*-Cl, *p*-Me, and *p*-OMe, which enable the value of r to be derived with reasonable accuracy, and with greater certainty than for, say, nitration. With a value of ρ of $-2{\cdot}42$ and σ^n-constants, the best (least squares) Yukawa–Tsuno plot corresponds to $r = 0{\cdot}63$; this is seriously in disagreement with Norman and Radda's generalization, particularly since the r value is greater than in protodestannylation, which has a markedly higher ρ value. Again, however, a linear free-energy relation applies between the substituent effects in the two reactions[9] as satisfactorily as the Yukawa–Tsuno equation applies to protodeplumbylation, so that it is meaningless to derive different r values for the two reactions.

(*g*) We conclude that the linear relation between ρ and r which Norman and Radda observed[2] results from omission of data for some reactions and misuse of those for others,

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[19] Eaborn and Webster, *J.*, 1957, 4449; 1960, 179.
[20] Deans and Eaborn, *J.*, 1959, 2299.
[21] Deans, Eaborn, and Webster, *J.*, 1959, 3031.

and has no sound basis. We accept, of course, that r shows a general tendency to increase with ρ, for this, if the Yukawa–Tsuno equation applies, is equivalent to the generalization that the importance of polarizability effects tends to increase with the " electron demand " as roughly measured by the rate factor, f_p^{Me}, for the *p*-methyl substituent. Not only has this generalization been used in many discussions in this series of papers,[7,22-24] but also exceptions * to it have been noted.[8,22,23,25]

We believe the Yukawa–Tsuno treatment to be useful. It applies satisfactorily to a wide range of reactions,[3] and by its use substituent effects in electrophilic cleavages of aryl–metal bonds have been related to those in other reactions.[7-10] It has also been used, for example, to interpret semiquantitatively the variability of the effect of a *p*-Ph group in electrophilic aromatic substitution and to show that there is nothing particularly abnormal about it.[23] Nothing is to be gained, however, by claiming that this treatment, and others similar, are better than broad generalizations, to which exceptions are to be expected. Thus Knowles, Norman, and Radda [18] derived an equation somewhat similar to the Yukawa–Tsuno equation (though less securely based—see, for example, ref. 13) and concluded that the relative balance of polarization and polarizability effects for *p*-Me and *p*-Bu$^{\mathrm{t}}$ groups was such that the hyperconjugative order of activation (*p*-Me $>$ *p*-Bu$^{\mathrm{t}}$) could be expected in some reactions and the opposite, inductive order in others; they thus considered that the inductive order in nitration was explained,[18] and by their reasoning they would reach the same conclusion on the basis of the Yukawa–Tsuno treatment. However, the Knowles–Norman–Radda and the Yukawa–Tsuno treatment both predict the activation order *p*-Me $>$ *p*-Bu$^{\mathrm{t}}$ for nitration; the relevant characteristics of nitration (such as the values of f_p^{Me}, ρ, or r), while not precisely known, as we have seen, certainly lie between those for protodesilylation and molecular bromination, in both of which the hyperconjugative order applies; and thus no amount of manipulation of the parameters in such treatments can lead to interpretation of the opposite order in nitration. Indeed, far from explaining the inductive order for nitration, as Knowles *et al.* suggest,[18] application of the Yukawa–Tsuno and related treatments serves to emphasize its anomaly.

Finally, we criticize Norman and Radda's use of σ^n- in place of σ-constants in the Yukawa–Tsuno equation. In so far as the equation applies, any two reactions with a reasonable separation of r values could be used to define the substituent constants, but those chosen have the great advantage that accurate results are available for a large number of substituents. It is irrelevant that there is a small amount of resonance interaction between some substituents and the reaction centre in the ionization of benzoic acids, although r is, by definition, zero, which is Norman and Radda's objection to the use of σ-constants; it merely means that reactions in which there are no such interactions (and to which σ^n-values apply) have small negative values of r. An attractive feature of the Yukawa–Tsuno equation is that it permits analysis of substituent effects in terms of experimental data for two well-studied reactions; and it is undesirable that experimental σ-constants should be replaced by calculated σ^n-constants, for the latter are available for

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* Accurate experimental results are available for a large number of electrophilic substitutions in toluene.[26] If the Yukawa–Tsuno equation applied precisely, and if r decreased with $-\rho$, the value of the ratio $\log f_p^{\mathrm{Me}}/\log f_m^{\mathrm{Me}}$ ($= R$) should fall with the value of $-\rho$ ($= \log f_m^{\mathrm{Me}}/\sigma_m$), but the following data (selected from ref. 26, in which reaction conditions and original sources are indicated) show that this is by no means consistently the case; molecular bromination, $\rho = -10{\cdot}7$, $R = 4{\cdot}57$; molecular chlorination, $\rho = -10{\cdot}1$, $R = 4{\cdot}19$; ionic bromination, $\rho = -5{\cdot}8$, $R = 4{\cdot}45$; nitration (30°), $\rho = -7{\cdot}0$, $R = 3{\cdot}54$; protodesilylation ($HClO_4$–AcOH), $\rho = -4{\cdot}5$, $R = 3{\cdot}95$; sulphonylation, $\rho = -4{\cdot}6$, $R = 4{\cdot}63$; mercuration (90°), $\rho = -3{\cdot}3$, $R = 4{\cdot}56$; isopropylation, $\rho = -2{\cdot}2$, $R = 4{\cdot}72$. Over this range of ρ values, the value of R would fall linearly from 5·4 to 2·9 if the Norman–Radda relation between ρ and r applied.

[22] Eaborn and Taylor, *J.*, 1961, 247.

[23] Eaborn and Taylor, *J.*, 1961, 1012.

[24] Baker, Eaborn, and Taylor, *J.*, 1961, 4927; Baker and Eaborn, *J.*, 1961, 5077; Baker, Eaborn, and Sperry, *J.*, 1962, 2382.

[25] Eaborn and Taylor, *J.*, 1961, 2388.

[26] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323.

relatively few substituents and have values which, being derived from several reactions, depend on assumptions made in their calculation and on the nature and number of reactions used.[6] It is noteworthy that, in our experience, Yukawa–Tsuno plots are better with σ- than with σ^n-constants.

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