Polar Substituent Constants for Substituted Phenyl Groups. The Extended Taft Equation.

Yoichiro NAGAI, Hideyuki MATSUMOTO, Taichi NAKANO, and Hamao WATANABE
Department of Chemistry, Gunma University, Kiryu, Gunma

(Received February 17, 1972)

Values of the σ^* constants have been defined for some *m*- and *p*-substituted phenyl groups from the ^{29}Si–H coupling constants for a series of *m*- and *p*-substituted phenylsilanes, phenylmethylsilanes, and phenyldimethylsilanes. The σ^* constants for the groups, XC_6H_4, were found to be directly related to the Hammett σ constants for the ring substituents, X. From this correlation the σ^* constants for a number of other substituted phenyl groups have also been calculated. Examples have been presented in which a simple relationship holds between the Taft polar substituent constants including the newly derived σ^* constants and molecular properties for a series of compounds covering both aliphatic and aromatic substances. Correlations of reactivities with the extended σ^* values have been illustrated and the implications of the results are discussed.

It is well known that there exist two important quantitative relationships of very great generality between structure and reactivity, *i.e.*, the Hammett and Taft equations.[1,2] The former applies within

$$\log K/K_0 = \rho\sigma \quad (1)$$

$$\log K/K_0 = \rho^*\sigma^* \quad (2)$$

a great number of reaction series of *m*- and *p*-substituted benzene derivatives, while the latter is followed by a considerable body of aliphatic reaction series involving a wide variety of functional groups, mechanisms, attacking reagents, experimental conditions, *etc.* Both of the two general relationships are based on a rather simple idea that the effect of structure on reaction rates, equilibrium constants, physical properties, *etc.*, is nearly always determined by a single principal factor, the polar effect of the substituent. Although this idea holds, of course, only when other factors such as resonance and steric effects are absent or negligible or vary linearly, there leaves no doubt that numerous instances indeed follow the linear free energy equations. The two relationships are thus associated with very nearly the same physical implications, but it is generally believed that Eq. (1) is applicable only to aromatic reaction series whereas the use of Eq. (2) is limited only to aliphatic reactions. In effect, the scales of the two sets of substituent constants differ much from each other. Since, however, the two linear polar energy relationships have almost identical physical meanings and mathematical forms, it would be anticipated that the two equations could be extended to merging if the two sets of substituent constants are directly related to one another.

An attempt has been made in this work to define Taft σ^* values for some *m*- and *p*-substituted phenyl groups and to determine whether the Taft σ^* constants so derived are linearly related to the Hammett σ constants. It was hoped that such relations would prove to be of value in studying polar effects of substituents on various molecular properties and that a comparison of these properties with the use of the extended Taft equation would indicate the presence or absence of other structural factors.

Polar Substituent Constants for Substituted Phenyl Groups

In order to obtain Taft's polar substituent constant (σ^* values) for substituted phenyl groups, Nagai and coworkers selected NMR values of the ^{29}Si-H coupling constant for series of substituted phenylsilanes, phenylmethylsilanes, and phenyldimethylsilanes.[3] Evidence has been presented that a good correlation exists between reported values[4,5] of $J(^{29}\text{Si-H})$ for hydrosilanes of the general formula $R_1R_2R_3SiH$, where R's could be a phenyl(s), an alkyl(s) and a hydrogen(s), and the sum of the σ^* constants for R_1, R_2, and R_3. The coupling constants follow the equation,

$$J(^{29}\text{Si-H}) = -10.21\sum\sigma^* - 182.9$$

with a correlation coeffecient of 0.994. It is thus possible to evaluate the polar substituent constant for a substisuted phenyl group in question by fitting its NMR parameter to the equation above. The σ^* values so obtained for several substituted phenyl groups are listed in Table 1 in which probable errors are included. Since it has also been shown that the ^{29}Si-H coupling constants for each series of the arylhydrosilanes correlate well with Hammett's σ con-

TABLE 1. POLAR SUBSTITUENT CONSTANTS (σ^*) FOR SUBSTITUTED PHENYL GROUPS AS DETERMINED FROM THE J (^{29}Si–H) VALUES

Group	σ^*	Probable error
p-$N(CH_3)_2C_6H_4$	0.16	±0.01
p-$CH_3OC_6H_4$	0.36	±0.01
p-$CH_3C_6H_4$	0.46	±0.01
m-$CH_3C_6H_4$	0.48	±0.002
p-ClC_6H_4	0.75	±0.01
m-ClC_6H_4	0.85	±0.02

---

[1] a) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, N. Y. (1940), p. 184. b) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

[2] R. W. Taft, Jr., "Steric Effects in Organic Chemistry", ed. by M. S. Newman, John Wiley, N. Y. (1956), p. 556.

[3] Y. Nagai, M. Ohtsuki, T. Nakano, and H. Watanabe, *J. Organometal. Chem.*, **35**, 81 (1972).

[4] B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, **46**, 1399 (1968).

[5] M. A. Jensen, *J. Organometal. Chem.*, **11**, 423 (1968).

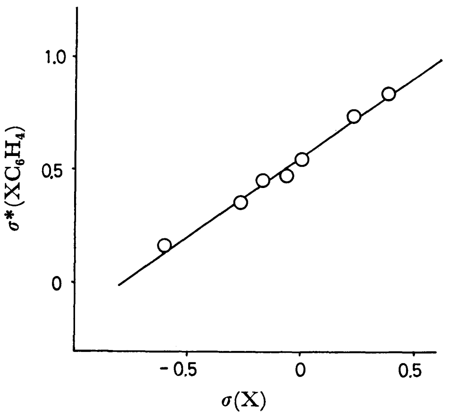

Fig. 1. Relationship between σ and σ^* constants.
σ^* $(XC_6H_4) = 0.720$ $\sigma(X) + 0.575$

stants,[3] the σ^* constants listed in Table 1 are expected to be related to σ constants; two sets of substituent constants are plotted against each other in Fig. 1 which exhibits an excellent linear relationship with a correlation coefficient of 0.995. The regression line can be expressed in terms of the following equation.

$$\sigma^*(XC_6H_4) = 0.72\sigma(X) + 0.58 \tag{3}$$

The value of the intercept, 0.58, agrees well within experimental error with the σ^* value for a phenyl group, 0.60. It follows then that with the use of Eq. (3) one can further proceed to define the σ^* values for a number of other XC_6H_4 groups by scaling σ values of substituents X to fit this expression. Some selected σ^* values thus calculated are summarized in Table 2.[6]

All the substituted phenyl groups listed in Table 2 are more electron-withdrawing than the methyl group as indicated by positive signs of the σ^* values. It is of interest to note that σ^* values of some of the substituted phenyl groups are lower than that of hydrogen, *i.e.*, 0.49. Thus such a substituted phenyl group is shown to be a weaker electron attractor than hydrogen. This is not unexpected since they contain substituents, X, which are +R (by Gould's classification[9]) in nature.

The correctness of the σ^* values for substituted phenyl groups presented in Table 2 can be tested by giving an example of their use for prediction purposes. Taft[2] has quoted the ionization of aliphatic carboxylic acids, RCOOH, in water at 25°C as a typical example of reactions following his equation. For this particular correlation, $\log K = 1.721\sigma^* - 4.65$. Values of the polar substituent constants for *m*- and *p*-substituted benzyl groups can readily be obtained from the values listed in Tables 1 and 2 taking the fall-off factor per methylene group to be 2.8 as suggested by Taft. From the correlation above together with the σ^* values for the benzyl groups, it is possible to predict values of the ionization constant for substituted phenylacetic acids which have been determined by Dippy and Williams.[10] The calculated and observed values of the ionization constant are given in Table 3 for comparison. The agreement between the two sets of values is excellent, thus confirming the σ^* values defined in this work to be quite satisfactory.

TABLE 2. σ^* VALUES FOR SOME SUBSTITUTED PHENYL SUBSTITUENTS CALCULATED BY Eq. (3)

X	σ [a]	σ^*
p-OPh	−0.32	0.35
p-*t*-Bu	−0.20	0.43
p-Et	−0.15	0.47
m-Et	−0.07	0.53
p-Ph	−0.01	0.57
p-F	0.06	0.62
m-OMe	0.12	0.66
p-Br	0.23	0.74
m-OPh	0.25	0.76
m-F	0.34	0.82
m-Br	0.39	0.86
m-CF_3	0.43	0.89
p-CO_2R	0.45	0.90
p-CF_3	0.54	0.96
m-CN	0.56	0.98
p-CN	0.66	1.05
m-NO_2	0.71	1.09
p-NO_2	0.78	1.14

a) See C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry, Vol. 2" Interscience, N. Y. (1964), p. 323.

TABLE 3. PREDICTED AND OBSERVED VALUES OF IONIZATION CONSTANTS FOR SUBSTITUTED PHENYLACETIC ACIDS AT 25°C IN WATER

Substituent	log *K* (calcd)	log *K* (obsd)
p-*t*-Bu	−4.38	−4.42
p-*i*-Pr	−4.36	−4.39
p-Et	−4.36	−4.37
p-Me	−4.37	−4.37
p-MeO	−4.43	−4.36
H	−4.28	−4.31
p-Cl	−4.19	−4.19
p-Br	−4.19	−4.19
p-I	−4.18	−4.18
m-I	−4.14	−4.16
m-Cl	−4.13	−4.14
m-NO_2	−3.98	−3.97
p-NO_2	−3.95	−3.85

---

6) The use of σ° (Ref. 7) or σ^n (Ref. 8) values also gives good correlations with the $J(^{29}Si\text{-}H)$ values, so that the σ° or σ^n values for substituted phenyl groups may be evaluated in a similar fashion. These substituent constants might provide a better choice since they represent inductive constants for the substituted phenyl groups relative to the unsubstituted phenyl group, although in general their values do not differ significantly from σ values. Nevertheless the authors prefer the correlation with σ because of its fundamental importance and of the greater number of substituents for which σ values are available.

7) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

8) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.* Pays-Bas, **78**, 815 (1959).

9) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt-Rinehart-Winston, N. Y. (1964), p. 212.

10) J. F. J. Dippy and F. R. Williams, *Chem. Rev.*, **25**, 151 (1939).

Application of the New σ^* Constants

It is a matter of course that the σ^* values for *m*- and *p*-substituted phenyl groups can be used to correlated a vast number of reaction series with reasonable precisions since they are linearly related to Hammett's σ values. Their utility manifests itself, however, when properties of compounds R–Y are compared, where the groups, R, contain both aliphatic and aromatic substituents. Although not many investigations have been carried out covering such a wide range of compounds under a single set of experimental conditions, Nagai and coworkers have found two typical examples$^{3)}$ following the extended Taft equation. The NMR ^{29}Si-H coupling constants for 30 aliphatic and aromatic hydrosilanes were correlated nicely with $\sum\sigma^*$, where $\sum\sigma^*$ is the sum of σ^* values for the groups on the central silicon atom (Fig. 2). In this relationship the slope is equal to -10.3 Hz/σ^* with a correlation coefficient of 0.996. Figure 3 illustrates a correlation of the methyl ^{13}C–H coupling constants for series of arylmethylsilanes and aryldimethylsilanes with σ^*. In this case $\rho^*=1.68$ Hz/σ^* and $\gamma=0.966$.

The correlation of the ionization of aliphatic$^{2)}$ and aromatic$^{1)}$ carboxylic acids gave a somewhat different picture as shown in Fig. 4. The two independent relationships found in this figure have comparable slopes, the aromatic line being below the aliphatic line by *ca.* 0.5 log unit. These findings furnish convincing justification for the concept that there is a substantial resonance stabilization in the reactant state of aromatic acids that is undoubtedly due to the interaction between an aromatic ring and the carbonyl function.

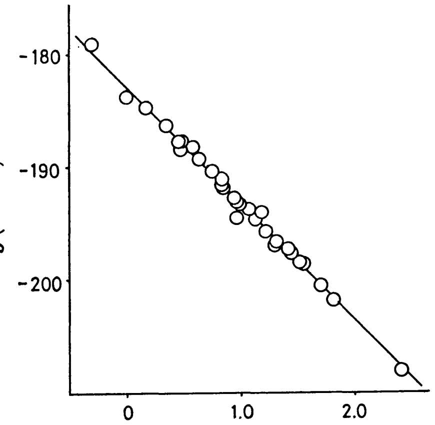

Fig. 2. Correlation of $J(^{29}\text{Si–H})$ for 30 hydrosilanes of general formula $R_1R_2R_3SiH$ with σ^*.
$J(^{29}\text{Si–H})=-10.21\sum\sigma^*-182.9$

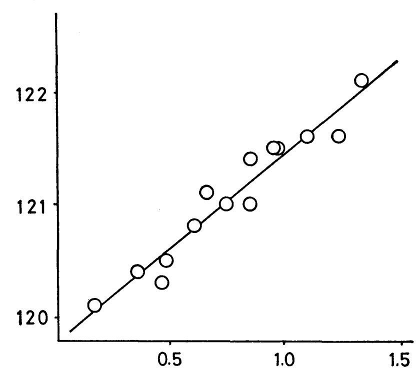

Fig. 3. Correlation of methyl $J(^{13}\text{C–H})$ for phenylmethylsilanes and phenyldimethylsilanes.
$J(^{13}\text{C–H})=1.678\sum\sigma^*+119.8$

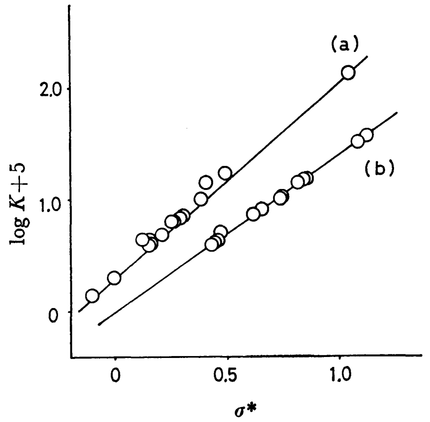

Fig. 4. Correlation of ionization constants for aliphatic and aromatic carboxylic acids with σ^*.
(a) Aliphatic acids; $\log K=1.721\,\sigma^*-4.65$
(b) Aromatic acids; $\log K=1.389\,\sigma^*-5.00$

Perhaps the most interesting generalization concerning the use of the σ^* values for substituted phenyl groups may be drawn from the rate data on the hydrogen abstraction from nuclear substituted aralkylhydrocarbons by polar radicals. In actuality, it has long been recognized that various electron-poor radicals display rather pronounced polar effects in their attack on hydrogens to be abstracted. This general trend has been frequently verified by a number of rate data on the benzylic hydrogen abstractions from series of substituted alkylbenzenes that have been treated within the framework of the Hammett relationship.$^{11)}$ It is

---

11) It might be argued that reactivities of benzylic hydrogens toward abstracting polar reagent such as halogens, alkoxy, and trichloromethyl radicals are better correlated with σ^+ derived by Brown and Okamoto$^{12)}$ than with σ. This idea has been first proposed by Russell$^{13)}$ and supported later on by several other workers.$^{14-18)}$ However, a survey of the existing rate data on the hydrogen abstraction revealed that there are also many instances$^{17)}$ giving a somewhat better fit to the ordinary σ function rather than σ^+. Furthermore, even for some cases in which a better correlation with σ^+ has been reported with emphasis, the difference in the magnitude of correlation coefficient is not significant enough to warrant a definite adoption of the σ^+ correlation.$^{20)}$

12) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

13) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

14) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

15) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Amer. Chem. Soc.*, **85**, 3129 (1963).

16) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963).

17) E. S. Huyser, *ibid.*, **82**, 394 (1960), "Free-Radical Chain Reactions", John Wiley, N. Y. (1970), p. 89.

18) H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1967).

19) J. Hardil and V. Chvalovsky, *Coll. Czech. Chem. Commun.*, **33**, 2029 (1968). See also Ref. 20.

20) Y. Nagai, "Modern Organic Chemistry", ed. by S. Ito *et al.*, Hirokawa, Tokyo, in press.

generally accepted that few if any steric effects are observable on the rate of the hydrogen abstraction processes for a wide variety of structural change in substrate.[21] It is therefore expected that reactivities for benzylic hydrogens toward a given attacking radical species are related only to the polar effects of substituents if resonance effects are absent or constant.

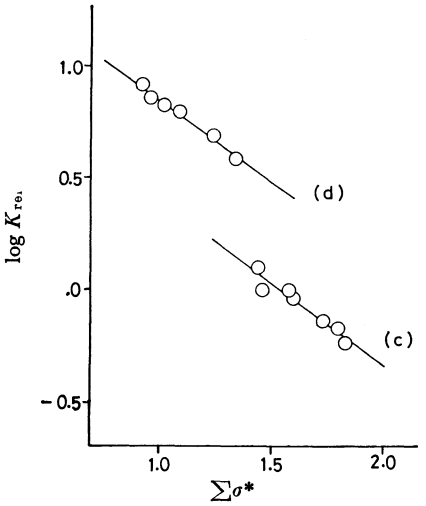

Fig. 5. Plots of relative reactivities for substituted toluenes and ethylbenzenes toward sulfuryl chloride *versus* σ^*.
(c) Toluenes; $\log k_{\rm rel}=-0.741\sum\sigma^*+1.14$
(d) Ethylbenzenes; $\log k_{\rm rel}=-0.731\sum\sigma^*+1.58$

Treatment of the relative reactivities (on a per hydrogen available basis) at 40°C for two series of alkylbenzenes, substituted toluenes and ethylbenzenes, toward sulfuryl chloride in carbon tetrachloride[22] by the Taft equation again gave two independent correlations as shown in Fig. 5. The ρ^* values for the two reaction series are essentially identical. However, the entire body of the rate data cannot be accomodated by a single line. The difference in positions of the two lines is likely to be accounted for by the accelerating hyperconjugation effects of the α-methyl group in ethylbenzene in the transition state which more or less resembles the product state, the benzylic radical. With regard to this point it seemed appropriate to inquire whether the rate data of silicon analogs of alkylbenzenes such as phenylsilane, phenylmethylsilane and phenyldimethylsilanes are incorporated with the extended Taft equation, since the contributing hybrid structures in the transition state of the hydrogen abstraction would require at least partly a silicon-carbon double bond which, unlike a carbon-carbon double bond, has never been positively detected.[23] Relative rate constants for these arylhydrosilanes at 80°C toward the trichloromethyl radical have been obtained in our previous work[24] and a plot of the relative rates *versus* σ^* is shown in Fig. 6. In this case there are once again found three independent straight lines which are closely located each other with comparable σ^* values. However, the whole range of rate data can also be accommodated by a single relationship with an acceptable correlation coefficient, 0.98. This observation is in keeping with the expectation deduced from the inability of silicon to make a double bond and leads to a conclusion that the reactivities for the silicon series thus apparently depend upon solely the polar effects of substituents.

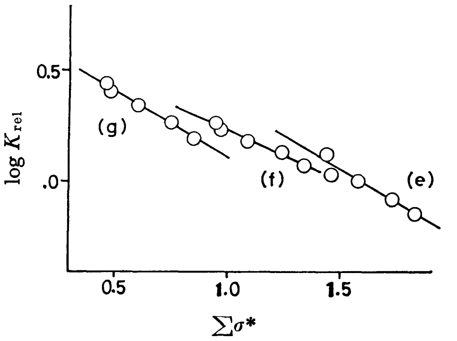

Fig. 6. Plots of relative reactivities for substituted phenylsilanes toward carbon tetrachloride *versus* σ^*.
(e) Phenylsilanes; $\log k_{\rm rel}=-0.595\sum\sigma^*+0.943$
(f) Phenylmethylsilanes; $\log k_{\rm rel}=-0.429\sum\sigma^*+0.652$
(g) Phenyldimethylsilanes; $\log k_{\rm rel}=-0.601\sum\sigma^*+0.702$

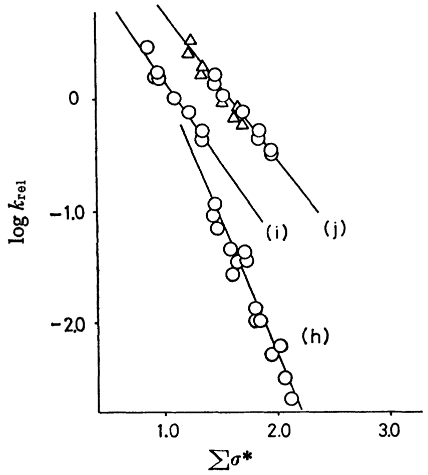

Fig. 7. Plots of relative reactivities for $XC_6H_4CH_2R$ toward the bromine atom in carbon tetrachloride at 80°C *versus* σ^*.
(h) R=hydrogen; $\log k_{\rm rel}=-2.497\sum\sigma^*+2.652$
(i) R=methyl; $\log k_{\rm rel}=-1.441\sum\sigma^*+1.606$
(j) R=phenyl (circles), R=vinyl (triangles);
$\log k_{\rm rel}=-1.309\sum\sigma^*+2.034$

Figure 7 shows correlations between $\sum\sigma^*$ and rates of hydrogen abstraction by the bromine atom from *m*- and *p*-substituted toluenes,[15] ethylbenzenes,[25] diphenylmethanes,[26] and allylbenzenes[26] in carbon tetrachloride at 80°C. To obtain the relative rates expressed in terms of *k*(toluene)=1, the rate ratio of toluene: ethylbenzene: diphenylmethane: allylbenzene was set to be 1: 23: 18: 25, the value being taken from a table compiled by Low and Lee.[26] Also the σ^* value for the vinyl group was calculated as

---

21) G. A. Russell and P. G. Haffley, *J. Org. Chem.*, **31**, 1869 (1966).

22) K. H. Lee, *Tetrahedron*, **25**, 4363 (1969).

23) C. Eaborn, "Organosilicon Compounds", Butterworths, London (1960), p. 86.

24) Y. Nagai, H. Matsumoto, M. Hayashi, E. Tajima, M. Ohtsuki, and N. Sekikawa, *J. Organometal. Chem.*, **29**, 209 (1971).

25) R. L. Huang and K. H. Lee, *J. Chem. Soc.*, *C*, **1966**, 935.

26) T. P. Low and K. H. Lee, *J. Chem. Soc.*, *B*, **1970**, 535.

follows.

$$\sigma^*(CH_2{=}CH) = \sigma^*(CH_3CH{=}CH) - \{\sigma^*(CH_3CH_2CH_2) - \sigma^*(CH_3CH_2)\}$$
$$= +0.360 - (-0.115+0.100) = +0.375$$

As seen in Fig. 7, for the last three series ρ^* values are actually not distinguishable from each other. Among them diphenylmethanes and allylbenzenes seem to be correlated by a single line. The line formed by points for all of the ethylbenzenes is about 0.5 log unit below that defined by series of diphenylmethanes and allylbenzenes. Obviously the accelerating effects of the phenyl and vinyl groups due to resonance interaction with the odd electron developing in the transition state are of the same order of magnitude. The ρ^* value for reactions of toluenes is distinctly larger, in the absolute magnitude, than those for other series. The difference in structural dependence in the hydrogen abstraction from aralkylhydrocarbons has been one of the central subjects for recent years and results regarding this point have been explained mainly in terms of the degree of bond breaking in the transition state.[27] Thus the greater ρ^* values for the toluenes is reflected by the greater ratio of k_H/k_D[28] for the reaction of toluene (4.9) with the bromine atom compared to that for the reaction of ethylbenzene (2.7). Such an explanation advanced for the observed variation in the reaction constant for benzylic hydrogen reactivities toward free radicals implies that the linear free energy relationship would hold only within limited class of compounds. Such is found to be the case not only in this instance but also in many other reactions of the hydrogen abstraction which follow, but even in these cases one may obtain useful informations as to the detailed structure of the transition state.

Figure 8 refers to a similar treatment for bromination rates in chlorobenzene for toluenes (Br_2, 80°C),[19] cumenes (NBS, 70°C),[27] and neopentylbenzenes (NBS, 70°C).[29] Totherow and Gleicher[29] reported a value of 0.45 for the ratio of reactivities of k(neopentylbenzene)/k(toluene) at 70°C while Russell and coworkers[30] obtained a value of 14 for k(cumene)/k(toluene) at 40°C. Although these relative reactivities were determined under different conditions, these are fairly close to allow for direct comparison. The treatment yielded three straight lines with different slopes and this is expected for reactions which involve large differences in the degree of bond breaking in the transition state. It seems significant that the reaction of neopentylbenzenes with the bromine atom shows the smaller substituent dependence than that of toluenes in spite of the fact that neopentylbenzene has a relative rate of one-half that of toluene.[29] In general the ρ values for aralkylhydrocarbons appear to be related to the relative rates of reaction of the parent compounds;[14,31] the faster the reaction of a parent compound, the smaller the ρ value for the reaction series. For this reason the observed tendency for reactions of neopentylbenzenes is anomalous and in keeping with an explanation proposed by Totherow and Gleicher based on unfavorable steric interactions between a substrate and an attacking reagent.[29]

Comparison of chlorination rates for aliphatic and aromatic series of compounds with the aid of the Taft equation discloses yet another interesting point. Extensive studies have been made by Migita, Nagai, and Kosugi[32,33] of the chlorination of systematized series of aliphatic compounds under certain conditions,

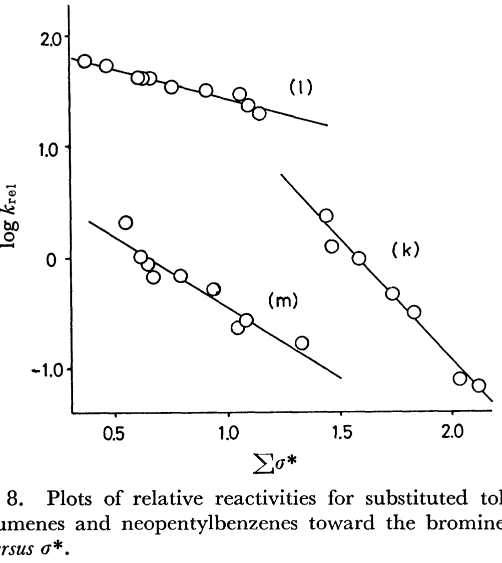

Fig. 8. Plots of relative reactivities for substituted toluenes, cumenes and neopentylbenzenes toward the bromine atom *versus* σ^*.

(k) Toluenes; $\log k_{rel} = -2.198 \sum\sigma^* + 3.462$

(l) Cuments; $\log k_{rel} = -0.542 \sum\sigma^* + 1.971$

(m) Neopentylbenzenes; $\log k_{rel} = -1.280 \sum\sigma^* + 0.831$

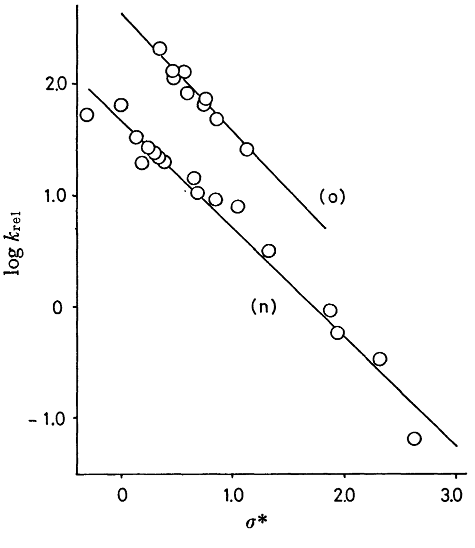

Fig. 9. Plots of relative reactivities of R–CH_3 toward photochlorination at 40C° *versus* σ^*.

(n) R=alkyl; $\log k_{rel} = -0.955\,\sigma^* + 1.698$

(o) R=aryl; $\log k_{rel} = -1.050\,\sigma^* + 2.647$

---

[27] G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

[28] K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, **80**, 3033 (1958).

[29] W. D. Totherow and G. J. Gleicher, *ibid.*, **91**, 7150 (1969).

[30] G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

[31] M. M. Martin and G. J. Gleicher, *ibid.*, **86**, 233 (1964).

[32] M. Kosugi, T. Migita, and Y. Nagai, *Nippon Kagaku Zasshi*, **92**, 477 (1971).

[33] Y. Nagai, M. Kosugi, K. Takeuchi, and T. Migita, *Tetrahedron*, **26**, 2791 (1970).

while Russell and Williamson[34] have obtained relative rate data for the chlorination of a series of substituted toluenes including a wide range of substituents. Since both of the measurements were conducted under very nearly the same conditions, relative reactivities for compounds of either types can be readily compared with a considerable degree of reliability, if the two sets of rate data are combined. This can immediately be done since a reactivity ratio of k(toluene)/k(t-BuCl) was found by Russell[35] to be 1.1 : 0.12. The results were treated using the Taft equation to give correlations shown in Fig. 9. Strikingly enough, there were found two parallel lines and this finding indicates that the stabilization by resonance interaction between an aromatic ring and the reaction site amounts to about 0.5 log unit corresponding 0.7 kcal/mol. That is, this value holds regardless of the substituents present on the phenyl group.

Conclusions

Many useful informations as to the effect of structure on molecular properties can be obtained by correlating reactivities or physical measurements with a set of Taft polar substituent constants including values for substisuted phenyl groups which we have defined. Some instances following the extended Taft equation have been illustrated. The treatment of this type is especially instructive when comparing reactivities or physical properties of groups of benzylic type. The new polar substituent constants have general utility in the identification of the specific resonance or steric effects. Deviations from the extended Taft relationship provide a measure of such effects and this use of the σ^* values has been exemplified.

The authors are grateful to Professor T. Migita of Gunma University who made a number of valuable suggestions on this topic.

---

[34] G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

[35] G. A. Russell, *ibid.*, **80**, 4997 (1958).