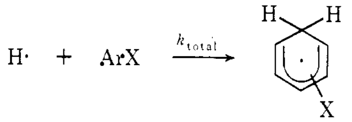
Addition of Hydrogen Atoms to Substituted Benzenes. Use of the Hammett Equation for Correlating Radical Reactions[1,2]

William A. Pryor,* T. H. Lin, J. P. Stanley, and R. W. Henderson

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received January 27, 1973*

Abstract: Isomer distribution data are reported for the addition of tritium atoms, generated by photolysis of thiophenol-*t*, to monosubstituted benzenes at 40°. These data are combined with literature values of the total rate constant for the addition of H atoms to substituted benzenes, and relative rate constants are calculated for the rate of addition to the ortho, meta, and para positions (so called partial rate factors). A Hammett correlation of the meta and para partial rate factors gives a ρ of -0.24 ± 0.09; a correlation of meta data only gives a ρ of -0.28 ± 0.12. These ρ values are compared with values derived from studies of H atoms generated by aqueous radiolysis. A compilation is given of Hammett ρ values for the abstraction of hydrogen from the benzylic position of toluenes by various free radicals and the addition of radicals to monosubstituted benzenes. Unexpectedly, the ρ values for the two reactions are quite similar for the five of the six radicals for which both ρ values are known; it is suggested that this similarity may be general. The use of the Hammett equation to correlate radical reactions is discussed.

The hydrogen atom adds to aromatic compounds to form a cyclohexadienyl radical.[3-7] Kinetic data for this reaction (eq 1) have been published from a



(1)

ortho, meta, and para isomers

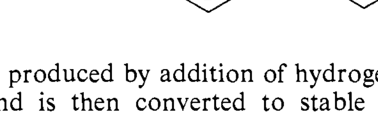
number of laboratories using aqueous solutions of the aromatic compounds and high energy radiolysis of water to generate the H atoms. The techniques used in these studies give the total rate constant for eq 1 and do not distinguish the partial rate constants k_o, k_m, and k_p for addition to the carbons ortho, meta, or para to the X substituent. Despite the fact that the fraction of the hydrogen atoms which add to each of the three isomeric positions in the aromatic compounds was not determined, the data for eq 1 have been correlated using the Hammett equation. Since it was not possible to decide whether σ_m or σ_p values should be used with the data available, Anbar, Meyerstein, and Neta[8] and Neta and Schuler[9] correlated the values of k_{total} with both meta and para σ values. Using this method, they obtain Hammett correlations with ρ values of -0.7 and -0.4, respectively. Neta[3b] has reviewed and recalculated these data and obtains a ρ of -0.45.

The Hammett correlation of data for eq 1 using both σ_m and σ_p is unusual, and the use of this method for obtaining Hammett ρ values is untested. Also, since the reaction of substitution at the ortho position is unknown, it must be assumed either that no ortho substitution occurred or that the amount of substitution at that position is constant and independent of the X substituent.

A more precise treatment[10,11] of this problem requires what are termed partial rate factors; in this analysis, the isomeric composition of the radicals produced in eq 1 is combined with values of k_{total}, and partial rate constants for each of the three positions are deduced (eq 2). Values of k_m then can be correlated with σ_m and k_p with σ_p.

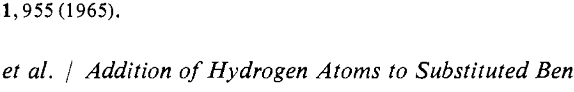
$$k_{\text{total}} = 2k_o + 2k_m + k_p \tag{2}$$

We here present data on the position of substitution by tritium atoms in a series of eight monosubstituted benzenes (eq 3 and 4). The cyclohexadienyl radical **1**



1

(all three isomers) (3)



(4)

is produced by addition of hydrogen and tritium atoms and is then converted to stable products by further

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(1) This research was supported in part by National Institutes of Health Grant 11908 and National Science Foundation Grant GP 3820.

(2) This publication is part VI in the series, "Reactions of the Hydrogen Atom in Solution." Previous publications in this series: (a) part I, W. A. Pryor, J. P. Stanley, and M. G. Griffith, *Science*, **169**, 181 (1970); (b) part II, W. A. Pryor and J. P. Stanley, *Intra-Sci. Chem. Rep.*, **4**, 99 (1970); (c) part III, W. A. Pryor and M. G. Griffith, *J. Amer. Chem. Soc.*, **93**, 1408 (1971); (d) part IV, W. A. Pryor and J. P. Stanley, *ibid.*, **93**, 1412 (1971); (e) part V, W. A. Pryor and R. W. Henderson, *ibid.* **92**, 7234 (1970).

(3) (a) R. A. Holroyd in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, pp 467–476; (b) P. Neta, *Chem. Rev.*, **72**, 533 (1972).

(4) L. M. Dorfman, I. A. Taub, and R. E. Buehler, *J. Chem. Phys.*, **36**, 3051 (1962).

(5) A. MacLachlan and R. L. McCarthy, *J. Amer. Chem. Soc.*, **84**, 2519 (1962).

(6) P. Neta and R. H. Schuler, *Radiat. Res.*, **47**, 612 (1971).

(7) P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, **75**, 1654 (1971).

(8) M. Anbar, D. Meyerstein, and P. Neta, *Nature (London)*, **209**, 1348 (1966).

(9) P. Neta and R. H. Schuler, *J. Amer. Chem. Soc.*, **94**, 1056 (1972).

(10) (a) G. H. Williams, *Chem. Soc., Spec. Publ.*, No. **24**, 25, 36 (1970); "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960; (b) J. E. Leffler and E. Grunwald, "Rates and Equilibrium of Organic Reactions," Wiley, New York, N. Y., 1963, pp 196–204; (c) D. H. Hey, *Advan. Free-Radical Chem.*, **2**, 47 (1967).

(11) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

reaction (eq 4). The tritium atoms were generated by photolyzing a solution of tritium-labeled thiophenol and the substituted benzenes (eq 5); we have described[2] the

$$\mathrm{PhSH^*} \xrightarrow[\text{In ArX solution}]{3000\ \text{Å}} \mathrm{PhS\cdot} + \mathrm{H\cdot^*} \qquad (5)$$

use of thiol photolysis to generate H atoms and have shown that this system gives data much like those produced in aqueous radiolysis.

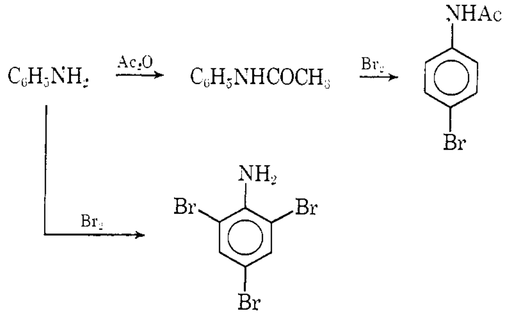
Our analysis of the isomer distribution in eq 3 and 4 can be combined with absolute rate constants for k_{total} from the literature to construct a Hammett equation correlation using partial rate factors. In addition to the usual kinetics assumptions, our analysis necessitates that three requirements be met. (1) The rate of attack at the three positions in a monosubstituted benzene by tritium or hydrogen atoms must parallel the rate of production of the three final substituted products. That is, the isomer distribution in eq 3 must parallel that of the final products isolated from eq 4. This assumption is common to all work on homolytic aromatic substitution and, to the extent to which it has been examined, it appears to be satisfied.[10a,12] (2) The rate constants k_{total} usually are measured using hydrogen atoms, whereas we have measured the isomer distribution using tritium atoms. Therefore, the combination of the two sets of data requires that the isotope effects on eq 3 and 4 be independent of the nature of the substituent X. Again, what limited data that are available suggest that this assumption is acceptable.[13] (3) The rate constants were measured in aqueous solution, whereas we have measured our isomer distributions in organic media. Our own limited data suggest that the H atom shows only a small solvent effect in its reactions and that relative values of k_{total} and isomer distributions probably are not very sensitive to the nature of the solvent.[2d]

Experimental Section

Irradiation. All the chemicals were purified by distillation or vacuum distillation. Mixtures of tritiated thiophenol (2×10^{11} dpm/mol) and the compounds to be studied were placed in quartz tubes, degassed, and irradiated for 6 hr with Rayonette lamps (nominally 3000 Å) using a merry-go-round photochemical reactor. Except where indicated otherwise, the solutions were 2:1 mole mixtures of substrate to thiophenol.

After the irradiation, thiophenol was removed by washing with aqueous NaOH and water. The irradiated substrates were then vacuum distilled and degraded.

Degradation. Aniline was degraded using the following scheme.[14a]



The activity distribution was determined from the specific activities of acetanilide, *p*-bromoacetanilide, and tribromoaniline.

Toluene and acetophenone were oxidized to benzoic acids, which were converted to aniline *via* the Schmidt reaction.[14b] Benzonitrile and methyl benzoate were hydrolyzed and saponified, respectively, to benzoic acids which were similarly converted to aniline. Bromobenzene was converted to benzoic acid by means of the Grignard reaction, which was in turn converted to aniline. Nitrobenzene was reduced to aniline by refluxing with Sn–HCl.

The degradation of phenol was performed by a scheme quite similar to that of aniline; counting phenol, *p*-bromophenol, and tribromophenol (first two counted as phenoxyacetic acid[15] derivatives) afforded the desired activity distribution.

All the above derivatives were purified by means of recrystallization, refluxing with methanol (to remove exchangeable tritium), Norit treatment, and vacuum sublimation until reproducible specific activities were obtained.

Aniline was photolyzed with various concentrations of thiophenol for different times. Neither the ratio of reactants nor the duration of the photolysis had any effect on the fraction of the product which contained tritium in the meta position, and it is probable that the complete isomer distribution is not changed.

Results

The tritium distribution in the recovered aromatic substrates is given in Table I. The pattern is rather similar to that found for the phenyl radical (Table II), the radical for which the most data have been pub-

Table I. Activity Distribution in Recovered ArX Compounds after Substitution by Tritium Atoms at 40°

				% activity distribution		
Substrate	Runs[a]	Hr[b]	Ratio[c]	Ortho	Meta	Para
Aniline	6	6	2	67.0	19.1	13.9
Phenol	1	6	2	63.5	20.1	16.4
Toluene	2	6	2	45.7	41.2	13.1
Ethylbenzene	1	6	2	45.3	42.0	12.7
Cumene	1	6	2	44.9	42.8	12.3
Acetophenone	1	6	2	57.0	30.0	13.0
Benzonitrile	1	6	2	42.0	45.2	12.8
Bromobenzene	1	6	2	41.8	43.8	14.4
Methyl benzoate	3	6	2	48.1	24.9	27.0
Nitrobenzene	1	6	2	49.0	24.6	26.4
Aniline	1	4	40		18.3	
Aniline	1	4	4		18.9	
Aniline	1	4	1.3		17.5	
Aniline	1	1	1.3		18.3	

[a] Number of duplicate runs analyzed (each in at least duplicate) to give average quoted; in general, agreement between duplicates was better than ±1%. [b] Hours irradiated at 40° with 3000-Å light. [c] Mole ratio of substrate/thiophenol.

Table II. Data on the Phenylation of ArX[a]

	%			Partial rate factors		
X	Ortho	Meta	Para	F_o	F_m	F_p
OCH_3	70	15	15	4.2	0.9	1.9
CH_3	65	20	15	2.4	0.7	1.1
C_2H_5	51	28	21	1.4	0.76	1.1
i-C_3H_7	30	42	28	0.58	0.81	1.1
CN	60	10	30	6.5	1.1	6.1
Br	56	29	16	2.2	1.1	2.2
CO_2CH_3	57	18	25	3.0	0.9	2.7
NO_2	62	10	28	5.5	0.9	4.9
F	55	30	15	1.7	0.92	0.93
Cl	57	26	17	1.8	0.81	1.1
I	52	32	17	2.0	1.3	1.3

[a] G. H. Williams, *Chem. Soc., Spec. Publ.*, No. **24**, 36 (1970).

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(12) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 261 ff.

(13) P. Neta and L. M. Dorfman, *J. Phys. Chem.*, **73**, 413 (1969).

(14) (a) W. A. Bonner, *J. Amer. Chem. Soc.*, **79**, 2469 (1957); (b) T. H. Lin and H. M. Pohlit, *Anal. Biochem.*, **28**, 150 (1969).

(15) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956, p 264.

lished.[10a,16] The greatest differences in the substitution pattern for H· and Ph· occur for meta and para substitution in benzonitrile and for meta substitution in nitrobenzene.

Our choice of values of the rate constants for the partial rate factor analysis requires some discussion. Numerous laboratories[17] have reported values of k_{total} for eq 3, but the agreement is not always what might be wished. The difficulties are numerous, including the fact that absolute rate constants generally are measured by flash techniques, and these absolute k's probably are less precise than relative rate constants would be. In addition, total rates are measured and it is not always clear whether addition to the ring, addition to the X group (where possible), or hydrogen abstraction from the X group (*e.g.*, as in toluenes) is the predominant process.[3b] However, a comparison of the reactivities of alkyl-X and Ar-X substrate pairs[17,18] suggests that addition to the aromatic ring is the predominant process for all of the compounds studied here. Therefore, we have used the total rate constants as reported without any correction for processes other than addition to the aromatic ring.

Table III gives the rate constants we have selected to calculate partial rate factors. We used two criteria in our choice of rate constants: we selected the most recent publications and have used the minimum number which provide all of the k's we require. We, therefore, have used two publications by Neta, *et al.*,[9,13] and one by Gold.[19] The studies of Neta, Schuler, and Dorfman utilize H atoms and esr techniques to obtain k_{total}; for these, we assume that the kinetic isotope effects on eq 3 and 4 are independent of the substituent X. Brett and Gold[19] measured the rate of appearance of tritiated substrate in aqueous radiolysis of aromatics, and their work is more directly comparable to ours. (They measured relative rate constants, but these can be put on the scale of Neta, *et al.*, using benzonitrile as the common substrate.) For aniline, the rate constant at pH 7 for the unprotonated NH_2 group was used.[18]

Table III. Total Rate Constants for Addition of H-Atoms to ArX Compounds and Calculated Partial Rate Factors

X	10^{-9} k_{total}, M^{-1} sec^{-1}	—Partial rate factors— F_o	F_m	F_p
H	1.1[a]	(1.0)	(1.0)	(1.0)
NH_2	2.6[a,e]	4.7	1.36	2.0
OH	1.4[a]	2.4	0.77	1.27
CH_3	1.6[c]	2.0	1.76	1.14
C_2H_5				
i-C_3H_7				
$COCH_3$	1.2,[a] 1.1[d]	1.87	0.98	0.86
CN	0.64,[a] 0.66,[c] 0.68[d]	0.74	0.79	0.45
Br	0.88[c]	1.05	1.00	0.67
CO_2CH_3[b]	0.85[a]	1.12	0.58	1.26
NO_2	1.0[d]	1.39	0.70	1.50

[a] P. Neta and R. H. Schuler, *J. Amer. Chem. Soc.*, **94**, 1056 (1972). [b] The rate constant for a benzoate ester has not been reported; the values given above are for benzoic acid at pH 1 [P. Neta and R. H. Schuler, *J. Phys. Chem.*, **76**, 2673 (1972)]. This point was excluded from the Hammett correlation but is included here for completeness. [c] Calculated from relative rate constants in C. I. Brett and V. Gold [*Chem. Commun.*, 148 (1971)] using benzonitrile to obtain absolute rate constants. Note that this work gives rate constants for tritium atom addition whereas the data of Neta, *et al.*, is for H atoms. We assume that isotope effects in these systems are small and vary negligibly with X. See discussion in text. [d] P. Neta and L. M. Dorfman, *J. Phys. Chem.*, **73**, 413 (1969); [e] At pH 7; P. Neta and R. H. Schuler, *J. Phys. Chem.*, **76**, 2673 (1972).

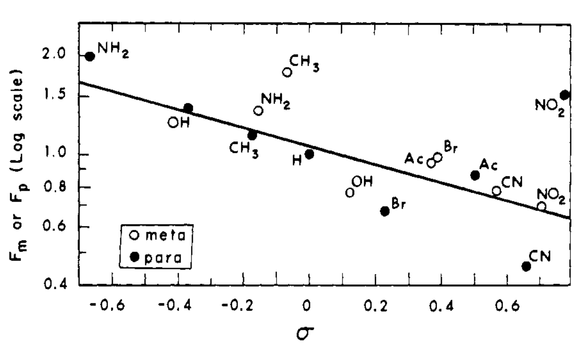

Figure 1. A plot of the partial rate factors for substitution by hydrogen atoms in monosubstituted benzenes at 40° *vs.* Hammett σ values. The substituent in the aromatic ring is shown beside each point. The ρ value (slope) and standard deviation are -0.24 ± 0.09; excluding the points for p-NO_2 and p-CN the ρ is -0.28 ± 0.07; the correlation for meta substituents is $\rho = -0.31 \pm 0.13$.

Table III gives the calculated partial factors, F_o, F_m, and F_p, where these quantities are defined[10] as in eq 6:

$$F_i = \frac{s(k_{total})(\text{fraction substitution at } i\text{th position in ArX})}{k_{benzene}} \tag{6}$$

s, the statistical correction, equals 6 for F_p and 3 for F_o and F_m; k_{total} is the total rate constant for the addition of H atoms to all three positions in ArX; and $k_{benzene}$ is the total rate constant for reaction of H atoms with benzene.

Discussion

Figure 1 shows a plot of F_m *vs.* σ_m and F_p *vs.* σ_p. The combined correlation[20,21a] gives a ρ of -0.24 ± 0.09,

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[16] G. H. Williams, *Chem. Soc., Spec. Publ.*, **No. 24**, 36 (1970).

[17] M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

[18] P. Neta and R. H. Schuler, *J. Phys. Chem.*, **76**, 2673 (1972).

[19] C. I. Brett and V. Gold, *Chem. Commun.*, 148 (1971).

[20] (a) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); see Table XIV; (b) *J. Amer. Chem. Soc.*, **81**, 3020 (1959); (c) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (d) O. Exner, "Advances in Linear Free Energy Relationships," N. B. Chapman and J. Shorter, Ed., Plenum Press, London, 1972, pp 1–69; (e) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963); (f) A. A. Zavitsas and J. A. Pinto, *J. Amer. Chem. Soc.*, **94**, 7390 (1972); (g) A. P. G. Kieboom, *Tetrahedron*, **28**, 1325 (1972); (h) B. M. Wepster, *J. Amer. Chem. Soc.*, **95**, 102 (1973), and references cited therein; (i) C. K. Hancock, *J. Chem. Educ.*, **42**, 608 (1965); (j) P. R. Wells, "Linear Free Energy Relations," Academic Press, New York, N. Y., 1968, pp 11–15, 29; (k) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas Belg.*, **78**, 815 (1959); (l) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

[21] (a) Jaffe (ref 20b) has shown that meta and para data often can be correlated together. (b) We have chosen to cite standard deviations obtained from the least-square analysis rather than the correlation coefficient values which were used by Jaffe[20a] and have been widely adopted. In this, we have been guided by the discussion of Exner[20d] who has stated: "The comparison of correlation coefficients is of little value if the degrees of freedom are not considered. . . The standard deviation gives the absolute precision with which data are reproduced or new ones predicted. . . Earnest warning is also necessary against correlations with few degrees of freedom and conclusions drawn from them. . . In general no satisfactory statistical procedure has so far been given for the Hammett equation." Table IV gives all these measures of goodness of fit: standard deviation of ρ, standard error of estimate, and the correlation coefficient. (c) Although relative rate constants as well as isomer distributions for the T· + ArX reactions could have been obtained by techniques similar to those we have used here (*e.g.*, see ref 2), our present data cannot be used for this purpose. Because of experimental difficulties, we did not include a standard reactant in each run,

Table IV. Hammett Equation Correlations for Hydrogen Abstraction from Toluenes by Radicals[a]

Radical	Temp, °C	ρ Meta only	ρ Meta and para
Hydrogen atom	40	−0.11[b]	−0.10[b]
Methyl	100	−0.21[c]	−0.17[c]
tert-Butyl	30	+0.96[d]	+0.99[d]
$\cdot CH_2CO_2H$	130	−0.65[e]	−0.99[e]
Phenyl	60	−0.14[f]	−0.19[f]
Phenyl	60	−0.32[g]	−0.48[g]
Phenyl	100	−0.42[h]	−0.51[h]
p-$CH_3C_6H_4\cdot$	60	−0.09[i]	−0.12[i]
p-$BrC_6H_4\cdot$	60	−0.66[j]	−0.29[j]
p-$NO_2C_6H_4\cdot$	60	−0.56[k]	−0.52[k]
$\cdot CCl_3$	50	−1.67[l]	−1.59[l]
tert-Butoxy	50	−0.36[m]	−0.34[m]
$ROO\cdot$	90	−1.96[n]	−0.76[n]
tert-$BuOO\cdot$	30	−0.73[o]	−0.76[o]
$(CH_3)_2N\cdot$	134	−0.96[p]	−1.66[p]
$Cl\cdot$ (in CCl_4)	40	−0.65[q]	−0.78[q]
$Cl\cdot$ (in CCl_4)	70	−0.88[r]	−0.84[r]
$.SO_2Cl$ (?)	40	−0.53[s]	−0.57[s]
$Cl\cdot$ (in CCl_4)	60		−0.46[t]
$Cl\cdot$ (in benzene)	60		−0.98[u]
$Cl\cdot$ (in benzene)	40	−0.82[v]	−0.82[v]
$Cl\cdot$ (in PhCl)	80	−0.90[w]	−0.75[w]
$Cl\cdot$ (in PhCN)	80		−0.73[x]
$Cl\cdot$ (in $PhNO_2$)	80		−0.47[y]
$Br\cdot$ (in CCl_4)	80	−1.70[z]	−1.88[z]
$Br\cdot$ (in benzene)	80		−1.79[aa]
$Br\cdot$ (in benzene)	60		−1.61[ab]
$Br\cdot$ (in PhCl)	80	−1.31[ac]	−1.61[ac]
$Br\cdot$ (in PhBr)	80		−1.59[ad]
$Br\cdot$ (in $PhCF_3$)	60		−1.00[ae]
$Br\cdot$ (in $PhNO_2$)	80		−0.32[af]
? γ-radiolysis	25	−0.72[ag]	−0.70[ag]
$(CH_2)_5N\cdot^+$	16		−1.46[ah]
$Ph_2\dot{C}O\cdot$	22		−1.66[ai]

[a] Literature data were statistically analyzed by a computer program using formulas given in G. W. Snedecor ["Statistical Methods," 4th ed, Iowa State College Press, Ames, Iowa, 1946, pp 118, 137, 139]. σ values were taken from J. E. Leffler and E. Grunwald ["Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963]. Normal σ values were used even if σ^+ values improved the correlation, for reasons discussed in the text. The footnotes give the standard deviation (s_ρ) of ρ, the number of data points (n), the standard error of estimate (the square root of variance) (SE), the absolute value of the correlation coefficient (r), and the literature reference. For uniformity, and in conformity with practice in this field, all ρ values are given to two decimal places; *this is not always warranted* by the precision of the data. Values of s_ρ in the footnotes should be examined to determine the defensible significant figures for each ρ value. Likewise, s_ρ, SE, and r values are given to two decimals, except r values greater than 0.995 have been rounded down to 0.99 rather than up to 1.00.

[b] R. W. Henderson and W. A. Pryor, Abstract, Rocky Mountain Regional American Chemical Society Meeting, June 1972, ORGN-13: meta, 0.07, 5, 0.03, 0.68; meta and para, 0.04, 8, 0.03, 0.72.

[c] W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969): meta 0.05, 3, 0.01, 0.98; meta and para, 0.06, 6, 0.03, 0.83. (*p*-Phenoxy was excluded.)

[d] W. A. Pryor, W. H. Davis, and J. P. Stanley, *J. Amer. Chem. Soc.*, **95,** 4754 (1973): meta, 0.08, 10, 0.07, 0.97; meta and para, 0.06, 23, 0.08, 0.96.

[e] E. I. Heiba, R. M. Dessau, and W. J. Koehl, *ibid.*, **91**, 138 (1969): meta, 0.06, 4, 0.02, 0.99; meta and para, 0.16, 10, 0.10, 0.91.

[f] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85,** 3754 (1963): meta, 0.003, 3, 0.001, 0.99; meta and para, 0.07, 6, 0.06, 0.80. (*p*-Phenoxy was excluded.)

[g] W. A. Pryor, J. T. Echols, and K. Smith, *ibid.*, **88**, 1189 (1966): meta, 0.04, 3, 0.02, 0.99; meta and para, 0.11, 5, 0.06, 0.93.

[h] E. A. Trosman and Kh. S. Bagdasar'yan, *Russ. J. Phys. Chem.*, **38**, 1466 (1964): meta, 0.10, 4, 0.06, 0.95; meta and para, 0.07, 8, 0.06, 0.95. (*p*-CN and *p*-NO_2 were excluded.)

[i] W. A. Pryor, J. T. Echols, and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966): meta, 0, 2, 0, 1.00 (note only two meta points); meta and para, 0.02, 6, 0.02, 0.94.

[j] *Ibid.*: meta, 0.11, 3, 0.01, 0.99; meta and para, 0.10, 7, 0.08, 0.79. If the *p*-NO_2 point is excluded, $\rho = -0.94 \pm 0.07$; SE = 0.02; $r = 0.99$.

[k] *Ibid.*: meta, 0.04, 5, 0.02, 0.99; meta and para, 0.06, 12, 0.07, 0.93. If the point for *p*-PhO is excluded, $\rho = -0.58 \pm 0.05$; SE = 0.05; $r = 0.96$.

[l] E. S. Huyser, *ibid.*, **82**, 394 (1960): meta, 0.19, 4, 0.07, 0.99; meta and para, 0.20, 7, 0.10, 0.96. (*p*-Methoxy was excluded.)

[m] A. A. Zavitsas, *ibid.*, **94,** 7390 (1972): meta, 0.07, 3, 0.02, 0.98; meta and para, 0.03, 5, 0.02, 0.99. (Also see extensive data of other workers referred to in this paper.)

[n] G. A. Russell, *ibid.*, **78,** 1047 (1956): meta, 0.60, 3, 0.06, 0.96; meta and para, 0.06, 8, 0.06, 0.98. (*p*-Methoxy was excluded.)

[o] J. A. Howard and J. H. B. Chenier, *ibid.*, **95**, 3054 (1973): meta, 0.05, 6, 0.03, 0.99; meta and para, 0.10, 14, 0.13, 0.91.

[p] C. J. Michejda and W. P. Hoss, *ibid.*, **92,** 6298 (1970); meta, 0.05, 3, 0.02, 0.99; meta and para, 0.36, 6, 0.19, 0.92.

[q] G. A. Russell and R. C. Williamson, *ibid.*, **86**, 2357 (1964): meta, 0.16, 4, 0.06, 0.94; meta and para, 0.06, 9, 0.06, 0.98. Substrate is 1 *M* and authors find no difference between CCl_4 and benzene as solvent.

[r] C. Walling and B. Miller, *ibid.*, **79,** 4181 (1957): meta, 0.08, 5, 0.04, 0.99; meta and para, 0.08, 9, 0.06, 0.97. Authors find CCl_4 and benzene solvents give different results.

[s] K. H. Lee, *Tetrahedron*, **25,** 4363 (1969): meta, 0.08, 4, 0.03, 0.98; meta and para, 0.04, 7, 0.02, 0.98. Also see E. C. Kooyman, R. van Helden, and A. F. Bickel, *Kon. Ned. Akad. Wetensch. Proc., Ser. B*, **56,** 75 (1953); R. van Helden and E. C. Kooyman, *Recl. Trav. Chim.*, **73**, 269 (1954).

[t] J. Hradil and V. Chralovsky, *Collect. Czech. Chem. Commun.*, **33**, 2029 (1968): 0.02, 6, 0.02, 0.97. Solvent is CCl_4 and substrate is 0.1 *M*.

[u] *Ibid.*: 0.09, 6, 0.08, 0.98.

[v] K. H. Lee and T. O. Teo, *J. Chem. Soc., Perkin Trans. 2*, in press: meta, 0.02, 4, 0.01, 0.99; meta and para, 0.04, 8, 0.02, 0.99.

[w] J. Hradil and V. Chralovsky, *Collect. Czech. Chem. Commun.*, **33,** 2029 (1968): meta, 0.03, 3, 0.01, 0.99; meta and para, 0.03, 7, 0.03; 0.99.

[x] *Ibid.*: 0.12, 6, 0.10, 0.95.

[y] *Ibid.*: 0.03, 6, 0.02, 0.99.

[z] C. Walling, A. L. Riege, and D. D. Tanner, *J. Amer. Chem. Soc.*, **85,** 3129 (1963): meta, 0.069, 6, 0.044, 0.99; meta and para; 0.16, 17, 0.21, 0.95.

[aa] R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85,** 3142 (1963): 0.22, 7, 0.19, 0.96.

[ab] J. Hradil and V. Chralovsky, *Collect. Czech. Chem. Commun.*, **33,** 2029 (1968): 0.09, 6, 0.08, 0.99.

[ac] *Ibid.*: meta, 0.05, 3, 0.02, 0.99; meta and para, 0.07, 7, 0.07, 0.99.

[ad] *Ibid.*: 0.10, 6, 0.08, 0.99.

[ae] *Ibid.*: 0.05, 6, 0.04, 0.99.

[af] *Ibid.*: 0.01, 6, 0.01, 0.99.

[ag] J. Weiss, *Radiat. Res.*, **45,** 252 (1971): meta, 0.13, 10, 0.20, 0.88; meta and para, 0.07, 17, 0.17, 0.93.

[ah] R. S. Neale and E. Gross, *J. Amer. Chem. Soc.*, **89**, 6579 (1967): meta and para, 0.08, 10, 0.08, 0.99.

[ai] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965): meta and para; 0.59, 6, 0.24, 0.81.

where the error limits are the standard deviation from the least-squares analysis.[21b] If the points for *p*-nitro and *p*-cyano, which lie furthest off the line in Figure 1, are omitted, ρ is changed only slightly to -0.28 ± 0.07. The points for these substituents also are far off the least-squares line in the Hammett correlation of the combined "best" data for phenyl radical.[16] In fact, they lie much further from the least-squares line correlating phenylation data than they do in Figure 1. The combined F_m and F_p correlation of the addition of phenyl radicals to benzenes is poor: ρ is $+0.3 \pm 0.2$.

If only meta values are used, as is common,[11,16,20c,g] our H-atom substitution data give a ρ of -0.28 ± 0.12. The ρ value for the phenyl radical using only meta data[16] gives a ρ of 0.1 ± 0.1.

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and changes in light intensity, etc., do not permit calculations of relative rate constants from the activity in each substrate. In studies of homolytic aromatic substitution it is not unusual to obtain rate and product data from separate studies.[10,16] (d) Other correlations also can be cited. The ortho data can be correlated using the techniques of ref 11; the correlation is fair, but nothing new is learned. Correlations using σ^+ in place of σ give similar ρ values and slightly but not significantly poorer correlations.

Thus, our data indicate a ρ of -0.3 ± 0.1 for the addition of the H-atom to monosubstituted benzenes. This value is not very different from the values of -0.4, -0.45, and -0.7 reported by Anbar, Meterstein, and Neta,[6] by Neta,[3b] and by Neta and Schuler.[9] In retrospect, it is perhaps not surprising that these ρ values agree reasonably well with ours although they were obtained by correlations of total rate constants with what amounts to weighted averages of σ_m and σ_p. The rate constants for eq 3 vary only by a factor of about 4 (Table III), and the distribution of activity among the three positions varies only slightly as the X substituent is changed (Table I). In addition, the hydrogen atom is only very slightly electrophilic, and since the measured ρ value is so close to zero it changes very little as any given data point is varied

These ρ values, in agreement with previous studies, demonstrate that the H atom is very nearly nonpolar, but with some slight electrophilic character.[2,3,9,13,17–19] The phenyl radical[16] also is found to have very little polar character. In striking contrast with these data, the addition of the solvated electron to substituted benzenes correlates in a Hammett equation with a ρ of 3.1, demonstrating, as expected, a large amount of nucleophilic character for this charged species from aqueous radiolysis.[22]

It is interesting that the substitution pattern for toluene, ethylbenzene, and cumene is almost identical for the H atom (Table I), but this is not true for the phenyl radical (Table II). Apparently, as would be expected, the H atom behaves as a small species which is relatively insensitive to steric hindrance.

Precision of the Correlation of Radical Reactions by the Hammett Equation. The relatively large standard deviations in our ρ values require comment. Jaffe[20a] has shown that poor correlations can be expected for data from Hammett treatments which yield small ρ values. Since free-radical reactions on the average have ρ values which are closer to zero than do ionic reactions,[23] radical reactions will not be correlated by the Hammett equation as well as are ionic reactions. Furthermore, the controversy[12,20e] over whether σ, σ^+, or even σ^- values[20f] should be used in radical reactions only serves to point out the fact that radical reactions should be correlated[20c,d] by a special set of homolytic σ values; despite some interesting attempts, the standard reaction which should be used to define these σ^H values has not been satisfactorily characterized. Thus, radical reactions normally are correlated with a function which is derived from ionic reactions, originally was only meant to handle them,[20c] and fits even ionic reactions only poorly for reactions with small ρ.[20a] Nonetheless, even relatively poor correlations of radical reactions by the Hammett equation can categorize radicals as being electrophilic or nucleophilic in polar type, and this has proven to have wide utility in understanding radical reactivity patterns.[12,16,20c,e,f,21c,d] Furthermore, in order to categorize a set of reactions or reagents mechanistically, it is only necessary to know whether ρ is positive or negative and one significant figure is ample for most purposes.

Use of the Hammett Equation for Radical Reactions. Table IV lists ρ values for the hydrogen abstraction reactions of radicals with toluenes, and Table V gives similar data for the addition of radicals to benzenes. (We believe these tables include all of the data in the literature; if there are omissions, we would appreciate being informed.) The data tabulated include the ρ value, the standard deviation of the slope obtained by linear regression analysis, the number of data points, the standard error of estimate (also called the standard deviation from regression and the square root of variance), and the correlation coefficient. In both tables, the correlations of both the meta-substituted derivatives alone and the meta and para together are given. The correlation of meta data alone generally is better, but often the difference is not statistically significant.

Table V. Hammett Correlations of the Addition of Radicals to Substituted Benzenes[a]

Radical	Temp, °C	ρ	
		F_m only	F_m and F_p
Hydrogen atom	40	−0.28[b]	−0.24[b]
Methyl	*c*	+1.07[c]	+1.36[c]
Cyclohexyl	90	+1.05[d]	+1.51[d]
$\text{PhC}\equiv\text{C}\cdot$	*e*	−1.42[e]	−1.54[e]
$\cdot\text{CN}$	15–20	−0.39[f]	−0.51[f]
Phenyl	*g*	+0.09[g]	+0.31[g]
$p\text{-CH}_3\text{C}_6\text{H}_4\cdot$	20	+0.03[h]	+0.41[h]
$p\text{-ClC}_6\text{H}_4\cdot$	20	−0.29[i]	−0.19[i]
$p\text{-NO}_2\text{C}_6\text{H}_4\cdot$	20	−0.69[j]	−0.38[j]
$p\text{-CH}_3\text{OC}_6\text{H}_4\cdot$	20	+0.18[k]	+0.51[k]
Oxygen atoms (^{3}P)	30	−1.42[l]	−1.58[l]
$\text{PhCO}_2\cdot$	60	−1.70[m]	−1.79[m]
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\cdot$	60	−1.18[n]	−1.48[n]
$p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\cdot$	60	−2.81[o]	−2.84[o]
$i\text{-C}_3\text{H}_7\text{OCO}_2\cdot$	60	−2.13[p]	−3.18[p]

[a] See footnote *a* in Table IV. The footnotes list in order: the reference, the standard deviation of the slope, the number of data points, the standard error of estimate, and the correlation coefficient. [b] This work: meta, 0.12, 8, 0.10, 0.69; meta and para, 0.09, 15, 0.14, 0.60. If p-NO$_2$ and p-CN are excluded, $\rho = -0.28 \pm 0.07$; SE = 0.10; $r = 0.77$. [c] See data of M. Szwarc, E. Eliel, and W. Waters summarized by G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, pp 101 and 106. Rate data are those of Szwarc, *et al.*, at 85°; isomer distribution data are those of Eliel for toluene at 110° and unpublished data of Waters, *et al.*, at 130–145°: meta 0.59, 6, 0.33, 0.67; meta and para, 0.38, 11, 0.36, 0.76. [d] J. R. Shelton and C. W. Uzelmeier, *Intra-Sci. Chem. Rep.*, **3**, 293 (1969): meta, 0.16, 8, 0.11, 0.93; meta and para, 0.27, 15, 0.31, 0.84. [e] G. Martelli, P. Spagnolo, and M. Tiecco, *J. Chem. Soc. B*, 1413 (1970): meta, 0.13, 6, 0.07, 0.98; meta and para, 0.09, 12, 0.07, 0.98. Temperature not reported, but probably 15–20°. See footnote *f.* [f] P. Spagnolo, L. Testaferri, and M. Tiecco, *J. Chem. Soc. B*, 2006 (1971): meta, 0.06, 8, 0.03, 0.93; meta and para, 0.10, 18, 0.09, 0.78. [g] Data summarized by G. H. Williams, *Chem. Soc., Spec. Publ.*, **24,** 36 (1970) (temperature not stated): meta, 0.07, 13, 0.07, 0.34; meta and para, 0.15, 26, 0.22, 0.39. [h] R. Ito, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965): meta, 0.02, 5, 0.02, 0.58; meta and para, 0.27, 9, 0.28, 0.50. [i] *Ibid.*: meta, 0.04, 5, 0.02, 0.97; meta and para, 0.28, 9, 0.29, 0.25. [j] *Ibid.*: meta, 0.07, 5, 0.04, 0.98; meta and para, 0.20, 9, 0.21, 0.59. [k] *Ibid.*: meta, 0.17, 5, 0.11, 0.52; meta and para, 0.23, 9, 0.24, 0.65. [l] E. Grovenstein, Jr., and A. Mosher, *J. Amer. Chem. Soc.*, **92**, 3810 (1970): meta, 0.18, 7, 0.09, 0.96; meta and para, 0.23, 13, 0.20, 0.90. If p-methoxy is excluded, $\rho = -1.36 \pm 0.18$; SE = 0.14; $r = 0.92$. [m] M. E. Kurz and M. Pellegrini, *J. Org. Chem.*, **35,** 990 (1970): meta, 0, 2, 0, 1 (note only two points); meta and para, 0.49, 4, 0.21, 0.93. [n] *Ibid.*: meta, 0.13, 3, 0.05, 0.99; meta and para, 0.24, 6, 0.14, 0.95. [o] *Ibid.*: meta, two points only; meta and para: 0.32, 4, 0.14, 0.99. [p] P. Kovacic, C. G. Reid, and M. E. Kurz, *ibid.*, **34**, 3302 (1969): meta, 0.09, 5, 0.04, 0.99; meta and para, 0.52, 9, 0.32, 0.92.

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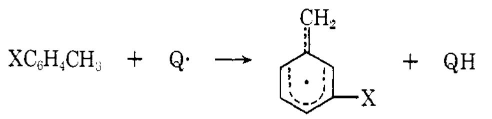
(22) W. V. Sherman, *J. Phys. Chem.*, **70**, 2872 (1966).

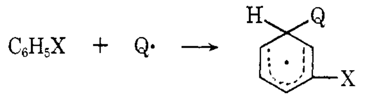
(23) Compare, for example, the distribution of absolute values of ρ in Table V and in ref 20a.

Points for p-methoxy,[24] p-phenoxy, p-phenyl, p-nitro, and p-cyano often lie far from the line defined by the meta substituents alone. Often the use of σ^+ rather than σ values improves the fit of the electron-donating substituents, since it allows for some "extra" resonance interaction between the substituent and the benzylic position. Similarly, the use of σ^- can improve the fit of the electron-withdrawing substituents. However, the use of the σ^+ scale for treating radical reactions appears to be overdone; there is no reason to assume that the extra resonance for a radical reaction is accurately measured by the σ^+ scale, and the only rationalization for its use, other than an empirical and often marginal improvement in fit, is that a σ^H scale is not available. It appears more reasonable to utilize the approach first recommended by van Bekkum and Taft:[20i–l] meta substituents should be used and para substituents examined only with regard to how well they are correlated by the line for meta compounds and as a probe of the "extra" resonance which develops at the transition state.[25a,b]

Comparison of ρ Values for Reactions with Toluenes and with Benzenes. Table VI lists ρ values for six radicals from Tables IV and V for which data are available both for the toluene (eq 7) and the benzene (eq 8) reaction series. (The ρ values tabulated in Table VI are those for the combined meta and para correlations, but a similar table leading to similar conclusions can be constructed from the data for meta derivatives.[25c]) It is not obvious that there need be any correlation between these two sets of ρ values. However, as Table VI shows, if the values for the methyl radical are excluded, the approximation can be suggested: $\rho_{\text{toluene}} \cong \rho_{\text{benzene}}$. Several remarks need be made about this relation. Firstly, the data on the methyl radical do not obey it. The data on the methylation of benzenes are from several different laboratories, at different temperatures, and were not intended for use in a Hammett correlation. It appears worthwhile to reexamine the addition of methyl radicals to benzenes. Secondly, the ρ values in each pair were not measured at the same temperature, and the effect of temperature on these ρ values is not known. Thirdly, all of the radicals are rather similar and give rather similar ρ values which are near zero. Clearly, more data on a greater variety of radicals are required if this relation is to be tested.



(7)



(8)

Table VI. Comparison of ρ Values for Hydrogen Abstraction from Meta- or Para-Substituted Toluenes and Addition to the Meta and Para Positions of Benzenes by a Series of Radicals[a]

	H-abstract from toluenes		Addition to benzenes	
Radical	ρ	Temp, °C	ρ	Temp, °C
Hydrogen atom	−0.1	40	−0.2	40
Methyl	−0.2	100	+1.4	85–145
Phenyl	−0.3	60	+0.3	[d]
p-$CH_3C_6H_4\cdot$	−0.1	60	+0.4	20
p-$XC_6H_4\cdot$	−0.3[b]	60	−0.2[c]	20
p-$NO_2C_6H_4\cdot$	−0.5	60	−0.4	20

[a] Data from Tables IV and V. Also see ref 25c. [b] X is Br. [c] X is Cl. [d] Various temperatures.

"Extra" **Resonance.** The ratio log (F_p/F_m) is a measure of the "extra" resonance stablization possible when the substituent can interact with the odd electron directly.[11,16,20c,g,l,26] For the eight substituents studied here, this value is positive for three (OH, NH_2, and NO_2) and negative for four (CH_3, CN, Br, and Ac). It is interesting how little these values match our traditional ideas about the ability of substituents to stabilize a positive or negative charge; *i.e.*, whether the substituent is electron donating or withdrawing. Presumably some para substituents confer "extra" resonance stabilization on the transition state for the addition of H atoms to benzene rings, whereas some stabilize the substrate more than they do the transition state.

In contrast, none of the values of log (F_p/F_m) are negative for addition of phenyl radicals to benzenes. The values range from a high of 0.74 for NO_2 to values of about 0 for F and I. The average value is 0.29 for eleven substituents (data from Table II). The reasons for the differences in the pattern of log (F_p/F_m) values for H atoms and phenyl radicals is not entirely clear, but these differences dramatically emphasize the problems in establishing a σ^H scale.

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(24) The methoxy substituent also is suspect when hydrogen abstraction from toluenes is studied since hydrogen often is abstracted from it almost as well as from the methyl group. For example, the ratio of rate constants for hydrogen abstraction from anisole relative to toluene is: 1.81 for the methyl radical [W. A. Pryor, *et al.*, *J. Org. Chem.*, **34**, 2018 (1969)]; 1.14 for the H-atom [R. W. Henderson and W. A. Pryor, Abstract, Rocky Mountain American Chemical Society Meeting, June 1972]; 0.91 for the *tert*-butoxy radical [H. Sakurai, A. Hosoma, and M. Kumada, *J. Org. Chem.*, **35**, 993 (1970)]; 0.45 for the benzophenone ketyl radical [C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965)]; and 0.08 for the *tert*-butylperoxy radical [J. A. Howard and J. H. B. Chenier, *ibid.*, **95**, 3054 (1973)]. Jaffee has commented on the variability of the σ value for the p-methoxy group even in ionic reactions (see p 230, ref 20a).

(25) (a) As a practical matter, the inclusion of a few para substituents generally changes ρ so slightly that mechanistic considerations are unchanged (see Tables IV and V). Often, however, para substituents such as p-methoxy or p-nitro must be discarded since they lie so far from the line defined by other substituents studied. As usually practiced, the selection of substituents to be studied is not particularly systematic, however, and it appears that the examination of more meta substituents often would lead to a more precisely defined ρ. (b) The problem of enhanced resonance for para substituents may be more pronounced for reaction of benzenes than for toluenes. With the benzene series, substitution in the para position at a greatly enhanced rate may lead to a reduced reactivity at the meta position, and F_p values often are far off the line defined by the F_m substituents. (c) In principle, we prefer to restrict the correlation to meta derivatives. However, so few meta derivatives were studied for some of these radicals that the ρ values may not be reliable; *e.g.*, ρ for p-bromophenyl is more negative than that for p-nitrophenyl. For this reason, Table VI has been constructed using both meta and para derivatives.

(26) R. W. Taft, private communication.