amino)-α-methylstyrene, b.p. 125–127° at 10 mm., was obtained. After recrystallization from methanol, the olefin, m.p. 74–75°, was obtained in 23% yield (lit.[19] m.p. 74°). The olefin was treated with methyl iodide in benzene to form the quaternary salt, dec. 213°, and the product transformed into the chloride with silver chloride. The chloride was dissolved in methanol and precipitated with diethyl ether, dec. 200°.

Anal. Calcd. for $C_{12}H_{18}NCl$: C, 68.07; H, 8.59; N, 6.62. Found: C, 68.30; H, 8.88; N, 6.85.

The chlorides were prepared from the corresponding olefin and carbinol by treatment with hydrogen chloride at room temperature in absolute ethanol. The *meta* derivative decomposed at 160°; *para*, at 130°.

Kinetic Measurements.—The procedures used for the kinetic measurements were similar to those previously described[11f] with one exception. In the case of the carboxylate, the weighed potassium metal was added to 100 ml. of absolute ethanol under a nitrogen atmosphere to form the potassium ethoxide solution. Sufficient potassium ethoxide was present to neutralize the carboxylate group and to react with the acid developed in the hydrolysis. After the solution was brought to reaction temperature in a constant temperature bath, the weighed chlorides were added to the solution and mixed rapidly by vigorous agitation. After 3 to 5 min., a 5 ml. "zero time" sample was removed and placed in 100 ml. of acetone at 0°.

The excess potassium ethoxide was titrated with 0.030 *N* hydrochloric acid using bromochlorophenol in ethanol solution as the indicator. Typical kinetic runs are summarized in Table V.

Acknowledgment.—We wish to acknowledge the valuable assistance provided by Mr. T. Inukai who synthesized several of the intermediates required in this study.

TABLE V

RATE DATA FOR THE SOLVOLYSIS OF *t*-CUMYL CHLORIDE CONTAINING CHARGED SUBSTITUENTS

Time, hr.	*x*, ml.	*a* − *x*, ml.	k_1, hr.$^{-1}$
A. *m*-(Potassium carboxylate)-*t*-cumyl chloride in ethanol at 25.0°			
0	5.690		
0.250	4.270	1.420	2.18
.417	3.840	1.850	1.90
.583	3.330	2.360	2.05
.916	2.910	2.780	1.89
1.250	2.670	3.020	1.80
∞	2.310		
		Average	1.96 ± 0.09
B. *p*-(Trimethylammonium chloride)-*t*-cumyl chloride in 90% aqueous acetone at 55.0°			
0	1.790	4.710	
1.08	2.380	4.120	0.124
1.83	2.730	3.770	.121
2.42	2.995	3.505	.122
2.92	3.250	3.250	.127
4.58	3.870	2.630	.127
6.75	4.580	1.920	.133
7.42	4.750	1.750	.133
18.83	6.060	0.440	.126
∞	6.500		
		Average	0.127 ± 0.0034

LAFAYETTE, IND.

[19] V. Braun, *Ann.*, **472**, 43 (1929).

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Electrophilic Substituent Constants[1,2]

BY HERBERT C. BROWN AND Y. OKAMOTO[3]

RECEIVED FEBRUARY 28, 1958

An excellent linear relationship is observed between log (k/k_H) for sixteen *meta* substituted *t*-cumyl chlorides and the Hammett *meta* substituent constants. The reaction constant, −4.54, is used to calculate a total of forty-one electrophilic substituent constants. The degree of constancy exhibited by these and other electrophilic substituent constants in representative aromatic substitutions and electrophilic side-chain reactions is examined. The data are used to estimate substituent constants for additional groups not examined in the *t*-cumyl system. These substituent constants correlate the available data on electrophilic aromatic substitution and electrophilic side-chain reactions with reasonably good precision.

The solvolysis of substituted *t*-cumyl chlorides offered a promising route to electrophilic substituent constants[4a–d] capable of correlating the available data on electrophilic aromatic substitution[5a] and side chain reactions.[5b] With additional constants now available,[4e–h] it appears appropriate to assemble these constants and to examine their utility in treating the available data for electrophilic reactions.

The Substituent Constants.—The reaction constant, ρ, for the solvolysis of the *t*-cumyl chlorides in 90% aqueous acetone at 25° was previously calculated to be −4.62 by a least squares treatment of log (k/k_H) for the solvolysis of several *t*-cumyl derivatives (*m*-Me, *m*-Et, *m*-F, *m*-Cl, *m*-Br, *m*-I and *m*-NO_2) *versus* the corresponding Hammett substituent constants. With data for many additional groups now available, it appeared desirable to redetermine the value of the reaction constant.

In Fig. 1 is shown a plot of log (k/k_H) for the solvolysis *versus* the available values of the Hammett substituent constants.[6] Least squares treatment of all sixteen points for which both σ_m and log k values are available (MeO–, MeS–, Me–, Et–,

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[1] Directive Effects in Aromatic Substitution. XXX.

[2] This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[3] Post-doctorate research assistant on a National Science Foundation Grant (G-2752), 1956–1957.

[4] (a) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957); (b) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957); (c) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); (d) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957); (e) H. C. Brown, Y. Okamoto and T. Inukai, *ibid.*, **80**, 4964 (1958); (f) Y. Okamoto and T. Inukai, *ibid.*, **80**, 4969 (1958); (g) Y. Okamoto, T. Inukai and H. C. Brown, *ibid.*, **80**, 4972 (1958); (h) Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4976 (1958).

[5] (a) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[6] These constants are taken from the compilation by D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

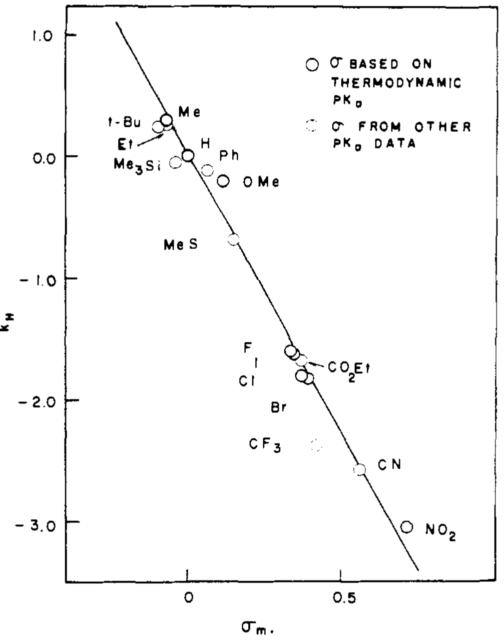

Fig. 1.—Solvolysis of the *meta* substituted *t*-cumyl chlorides in 90% aqueous acetone at 25°.

TABLE I

ELECTROPHILIC SUBSTITUENT CONSTANTS

Substituent	σ_m	σ_m^+	σ_p	σ_p^+
Dimethylamino			−0.83	$(-1.7)^a$
Anilino				$(-1.4)^a$
Amino	−0.16	$(-0.16)^a$	− .66	$(-1.3)^a$
Hydroxy	$.121^b$		$-.37^b$	$(-0.92)^a$
Acetylamino	.21		− .01	$(-.6)^a$
Benzoylamino				$(-.6)^a$
Methoxy	$.115^b$	.047	$-.268^b$	− .778
Phenoxy	$.252^b$		$-.320^b$	(− .5)
Methylthio	.15	.158	.00	− .604
Methyl	$-.069^b$	− .066	$-.170^b$	− .311
Ethyl	− .07	− .064	$-.150^b$	− .295
Isopropyl		− .060	$-.151^b$	− .280
t-Butyl	− .10	− .059	$-.197^b$	− .256
Phenyl	.06	.109	− .01	− .179
3,4-C_4H_4(β-Naphthyl)			$.042^b$	− .135
Carbethoxymethyl		$(-.01)^a$		$(-.164)^a$
Chloromethyl		$(.14)^a$		$(-.01)^a$
Hydrogen	0	0	0	0
Trimethylsilyl	−0.04	0.011	−0.07	0.021
Fluoro	$.337^b$	.352	$.062^b$	− .073
Chloro	$.373^b$	.399	$.227^b$	.114
Bromo	$.391^b$	.405	$.232^b$	.150
Iodo	$.352^b$	.359	.18	.135
Carboxy		.322		.421
Carbomethoxy		.368		.489
Carboethoxy	.37	.366	.45	.482
Trifluoro	.42	.520	.54	.612
Cyano	$.56^c$	.562	$.660^b$	.659
Nitro	$.710^b$	.674	$.778^b$	.790
Carboxylate (K^+)	− .1	− .028	.0	− .023
Trimethylammonium (Cl^-)	1.01	.359	.88	.408

[a] Values in parentheses are estimated σ-constants from data on electrophilic reactions other than the solvolysis of *t*-cumyl chlorides. See Table II. [b] Thermodynamic data with estimated uncertainty of ±0.02. [c] Thermodynamic datum with estimated uncertainty of ±0.05.

t-Bu–, Ph–, Me_3Si–, H–, F–, Cl–, Br–, I–, EtO_2C–, F_3C–, NC– and O_2N–)[7] leads to a value for the reaction constant of −4.45.

The σ-constants are based on benzoic acid ionization data of greatly variable quality.[6] In some cases the uncertainty in the pk_a values is sufficiently large as to introduce an uncertainty in the values of the substituent constants, σ, of ±0.10 unit. Consequently, it has been proposed that reaction constants be calculated only from substituent constants based on thermodynamic dissociation constants in water.[6] The uncertainties in these values are considerably smaller, usually no greater than ±0.02 unit. Least squares treatment of the eight "thermodynamic" points (MeO–, Me–, H–, F–, Cl–, Br–, I– and O_2N–) leads to a slightly different value for the reaction constant, −4.54. (The thermodynamic point for the cyano group was omitted because of the disagreement between different workers as to the correct thermodynamic dissociation constant for *m*-cyanobenzoic acid.[6]) Since the latter reaction constant is based on more precise data for the σ-constants, this value, $\rho = 4.54$, has been adopted for the calculation of the σ_p^+-constants.

In Table I we have summarized all of the available electrophilic substituent constants based on the solvolysis of the *t*-cumyl chlorides together with the corresponding Hammett substituent constants.

It is of interest to compare the extent of the agreement between the σ_m-constants derived from ionization data and the σ_m^+-constants calculated by the above procedure. In the case of the eight "thermodynamic" points, the average deviation is ±0.019. If we include all sixteen points for which both σ_m and σ_m^+ are available, the average deviation becomes ±0.027.

In electrophilic reactions strong resonance interactions occur between electron-supplying substituents and the electron-deficient centers of the reacting systems. Consequently, it has long been recognized that the Hammett substituent constants are not satisfactory for treating electrophilic substituent reactions. Indeed, it has been argued that the resonance interactions of the substituent will vary so markedly in different reactions as to render it impossible to represent the effect of the substituent by a constant, as required in the Hammett treatment.[8] Consequently, it is of interest to calculate σ^+-constants from data from different electrophilic reactions in order to compare the range of variation observed in these constants. For this comparison[9] we have selected the following reactions: (A) solvolysis of the *t*-cumyl chlorides; (B) uncatalyzed bromination of aromatic derivatives in acetic acid at 25°[8a,10]; (C) uncatalyzed chlorination of aromatic derivatives in acetic acid

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(7) Because of the wide variation in the σ-values for the trimethylammonium group and the large discrepancy observed in the σ_m- and σ_m^+-values, this charged group is not included in this treatment. See discussion in ref. 4h.

(8) (a) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954); (b) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953); (c) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955). For more favorable views see (d) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952); (e) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 164 (1956); (f) N. C. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957).

(9) A similar treatment for a somewhat more limited series of substituents and reactions was recently reported by Deno and Evans, ref. 8f.

(10) H. C. Brown and L. M. Stock, THIS JOURNAL, **79**, 1421 (1957), and unpublished work.

TABLE II

VALUES OF ELECTROPHILIC SUBSTITUENT CONSTANTS CALCULATED FROM VARIOUS REACTIONS

	Reaction								
	A	B	C	D	E	F	G	H	
	Solvolysis of *t*-cumyl chloride	Un-catalyzed bromination	Un-catalyzed chlorination	Nitration	Protonolysis of $ArSiMe_3$	Ionization of Ar_2CHOH	Ionization of Ar_3COH	I.r. spectra of acetophenones	Selected value of σ^+
Substituent	$\rho =$ −4.54	$\rho =$ −12.14	$\rho =$ −8.06	$\rho =$ −6.22	$\rho =$ −4.32	$\rho =$ −4.74	$\rho =$ −3.44	$\rho =$ −12.30	
p-Dimethylamino		−1.58			−1.74	−2.00	−1.55		−1.7
p-Anilino							−1.39		−1.4
p Amino							−1.37	−1.14	−1.3
p-Hydroxy		−0.969			−0.933		−0.833		−0.92
p-Acetylamino		− .750					− .469		− .6
p-Benzoylamino		− .750					− .419		− .6
p-Methoxy	−0.778	− .826			−0.736	−0.801	− .721		
p-Phenoxy		− .645				− .364			− .5
p-Methyl	− .311	− .278	−0.365	−0.278	− .305	− .306	− .297	−0.325	
p-Ethyl	− .295				− .299				
p-Isopropyl	− .280				− .287				
p-*t*-Butyl	− .256	− .240	− .323		− .275				
p-Phenyl	− .179	− .262	(− .378)	− .167	− .127				
p-Trimethylsilyl	.021				− .041				
p-Fluoro	− .073		− .100	.012	.028	− .028		.081	
p-Chloro	.114		.055	.133	.201	.070	.107	.081	
p-Bromo	.150		.074	.152	.231	.091		.162	
p-Iodo	.135			.055			.101	.162	
p-Carboethoxy	.482			.490					
p-Nitro	.790						.933	.732	
p-Chloromethyl			− .062	.035					− .01
p-Carboethoxymethyl				− .164					− .16
m-Amino								− .162	− .16
m-Methoxy	.047	− .054							
m-Methyl	− .066	− .061	− .087	− .079	− .083				
m-*t*-Butyl	− .059	− .065	− .097						
m-Fluoro	.352							.406	
m-Chloro	.399			.479		.422	.426	.406	
m-Bromo	.405			.477					
m-Iodo	.359			.346					
m-Carboethoxy	.366			.337					
m-Chloromethyl				.137					.14
m-Carboethoxymethyl				− .01					− .01

at 25°[8a,11]; (D) nitration of aromatic derivatives by nitric acid in acetic anhydride or in nitromethane at 0° and 25°[12]; (E) protonolysis of substituted phenyltrimethylsilanes by perchloric acid in aqueous methanol at 51.2°[13]; (F) ionization of diphenylcarbinols in aqueous sulfuric acid[8c,f]; (G) ionization of triphenylcarbinols in aqueous sulfuric acid[8c,f]; and (H) infrared absorption frequency for carbonyl stretching band.[14]

Ideally, the values of the reaction constant should be based on reaction data for *meta* substituents and the substituent constants based upon thermodynamic dissociation constants of benzoic acids. Unfortunately, the available data deal primarily with the effect of *para* substituents, with too few *meta* substituents examined to utilize this procedure. Consequently, we have plotted the results *versus* the electrophilic substituent constants (Figs. 2–4, 6, 12) and have estimated the reaction constants from a least squares treatment of the data. The individual values of the substituent constants were then estimated from the relationship $\sigma^+ = 1/\rho \log (k/k_H)$. The results are summarized in Table II to facilitate ready comparison.

In the case of the *p*-methyl substituent, data are available for each of the reactions examined in Table II. The seven reactions, B–H, lead to an average value for this electrophilic substituent constant of −0.308 ± 0.021, as compared to the σ^+-constant of −0.311 derived from the *t*-cumyl chloride system. Similarly six reactions (C–H) result in an average value for the *p*-chloro substituent of 0.108 ± 0.039, as compared to the σ^+-value of 0.114 derived from the *t*-cumyl chloride solvolysis.

The *p*-methoxy group possesses a large resonance contribution in electrophilic reactions. Consequently, such a group might be expected to exhibit a large variation in the value of the constant calculated in this way from experimental data from reactions of widely different electronic demand.

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[11] H. C. Brown and L. M. Stock, THIS JOURNAL, **79**, 5175 (1957), and unpublished work.

[12] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *ibid.*, **76**, 4525 (1954); C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931); C. K. Ingold and F. R. Shaw, *ibid.*, 575 (1949); M. J. S. Dewar, T. Mole, D. S. Urch and E. W. T. Warford, *ibid.*, 3572 (1956); M. J. S. Dewar, T. Mole and E. W. T. Warford, *ibid.*, 3576 (1956).

[13] C. Eaborn, *ibid.*, 4858 (1956).

[14] R. N. Jones, W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957).

TABLE III

REACTION CONSTANTS FOR ELECTROPHILIC SUBSTITUTIONS IN BENZENOID DERIVATIVES

Reaction	Reaction constant, ρ^a	s^b	r^c	n^d	Fig.	Ref.
Bromination of monosubstd. benzenes by bromine in HAc at 25°[e]	−12.14	0.604	0.987	8	2	8a, 10
Chlorination of monosubstd. benzenes by chlorine in HAc at 25°[f]	− 8.06	.190	.987	9	3	8a, 11
Nitration of monosubstd. benzenes by nitric acid in nitromethane or acetic anhydride at 0° or 25°	− 6.22	.287	.980	13	4	12
Bromination of monosubstd benzenes by hypobromous acid and perchloric acid in 50% aq. dioxane at 25°	− 5.78	.076	.998	7	5	16
Protonolysis of aryltrimethylsilanes by perchloric acid in 72% aq. methanol at 50°	− 4.32	.326	.972	12	6	13
Protonolysis of aryltrimethylsilanes by sulfuric acid in HAc	− 4.60	.248	.980	14	7	17
Brominolysis of aryltrimethylsilanes in HAc at 25°	− 6.04	.175	.990	14	8	18
Brominolysis of benzeneboronic acids in 20% HAc and 0.40 M NaBr at 25°[g]	− 4.44	.114	.992	16	9	19
Bromination of polymethylbenzenes by bromine in nitromethane at 25°	− 8.10	.101	.995	11	10	20

[a] The reaction constant ρ is based only on σ^+-values derived from the *t*-cumyl solvolyses (Table I). [b] The standard deviation of the experimental measurements from the regression line. [c] The correlation coefficient. [d] The number of compounds involved in the calculation of ρ. [e] The *para* partial rate factor for biphenyl estimated from rate data and an assumed value of 50% substitution in the *para* position. [f] The biphenyl point deviates seriously (Fig. 3) and was not included in the calculations. [g] The *p*-methoxy point deviates seriously and was omitted from the calculations.

However, even in the case of this group, the average value (from reactions B, E–G), −0.771 ± 0.042, is in excellent agreement with the σ^+-value of −0.778 derived from the standard reaction. Finally, even in the case of the *p*-dimethylamino group, where resonance contributions must be very large, the available data from four reactions (B, E–G) exhibit good internal consistency, and lead to an average constant for this group of −1.72 ± 0.15.

The excellent agreement realized in these comparisons[15] between the σ^+-constants obtained from the solvolysis of the *t*-cumyl derivatives and the average values calculated from other reaction data is highly encouraging. Moreover, it suggests that data from these reactions may be used to calculate tentative σ^+-constants for groups which have not been examined in the *t*-cumyl system. Accordingly, such values are listed in the last column of Table II and are given (in parentheses) in the compilation of σ^+-values in Table I.

Correlation of Electrophilic Aromatic Substitution Data.—Our primary objective in developing this set of σ^+-constants has been the quantitative correlation of directive effects in aromatic substitution. Accordingly, with the extended list of such constants now available, it appeared appropriate to test their utility for this purpose. In addition to the substitution reactions examined in Table II, we have examined the utility of the σ^+-constants for the following additional reactions: bromination by hypobromous acid. catalyzed by perchloric acid, in 50% aqueous dioxane at 50°[16]; protonolysis of aryltrimethylsilanes by sulfuric acid in acetic acid[17]; brominolysis of aryltrimethylsilanes in acetic acid at 25°[18]; brominolysis of benzeneboronic acids at 25°[19]; and bromination of substituted polymethylbenzenes in nitromethane at 25°.[20]

Reaction constants for these reactions, obtained by a least squares treatment of the available data in each case, are summarized in Table III together with the results of a statistical analysis of the correlation realized in this treatment.

Previously, insufficient data were available to permit the independent treatment of bromination and chlorination. Accordingly, data for these similar reactions were treated together as a single halogenation reaction with $\rho = -11.35$.[5a] With additional data available, both σ^+-constants and partial rate factors, individual treatment is now feasible.

Considering the enormous range of reactivity covered by the bromination reaction, the correlation with the σ^+-constants is excellent. On the other hand, no correlation is realized with the σ-constants (Fig. 2).

The situation is less satisfactory in the case of the chlorination results (Fig. 3). The point for biphenyl appears to deviate seriously from the linear relationship.[21] The calculated value for ρ, −8.06, also appears to be out of line with the value −12.1 estimated for the related bromination reaction. This unexpected value for the chlorination reaction constant arises primarily from the data for the monohalobenzenes, which correlate poorly with the partial rate factors for the alkylbenzenes (Fig. 3).

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(15) Only in the case of the *p*-acetylamino and the *p*-benzoylamino groups does there appear to be a major discrepany between the σ^+ constants calculated from the bromination data (B) and the corresponding constants obtained from the ionization of the substituted triarylcarbinols in sulfuric acid (G). Possibly protonation of the acylamino groups occurs in the latter reaction and modifies their ability to stabilize the carbonium ion.

(16) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956); P. B. D. de la Mare and J. T. Harvey, *ibid.*, 131 (1957); P. B. D. de la Mare and M. Hassan, *ibid.*, 3004 (1957).

(17) Private communication by Dr. C. Eaborn.

(18) C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 4449 (1957).

(19) H. G. Kuivila and A. R. Hendrikson, THIS JOURNAL, **74**, 5068 (1952); H. G. Kuivila and C. E. Benjamin, *ibid.*, **77**, 4834 (1955).

(20) G. Illuminati and G. Marino, *ibid.*, **78**, 4975 (1956); G. Illuminati, *Ricerca Sci.*, **26**, 2752 (1956).

(21) It should be mentioned that this point is based on an assumed value (60%)[8a] for *para* substitution. An unusually large amount of *ortho* substitution in this system would improve the situation. Dr. P. B. D. de la Mare is investigating the isomer distribution in this reaction.

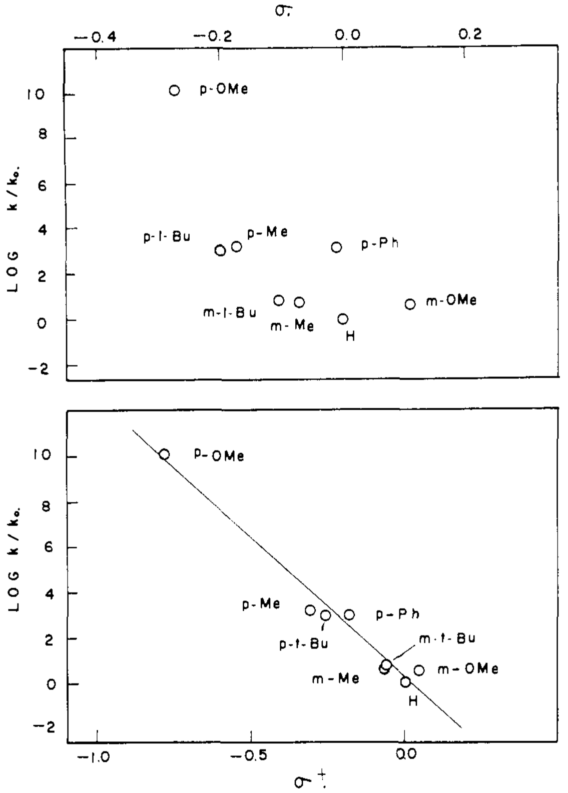

Fig. 2.—Bromination of monosubstituted benzenes in acetic acid.

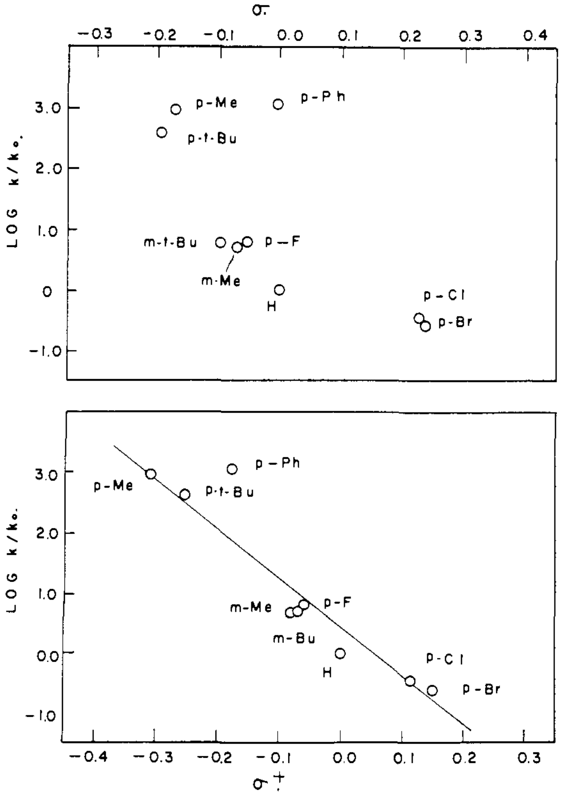

Fig. 3.—Chlorination of monosubstituted benzenes in acetic acid.

We plan to examine the chlorination of these monohalobenzenes.

Of the simple aromatic substitution reactions, nitration has been the most extensively studied. Unfortunately, the investigators have utilized different solvents and different temperatures, so that the data are not strictly comparable. Considering the possible effects of these minor variations in the experimental conditions, the correlation of the partial rate factors with the σ^+-constants can be considered satisfactory (Fig. 4). It should be compared with the corresponding plot based on the σ-constants (Fig. 4).

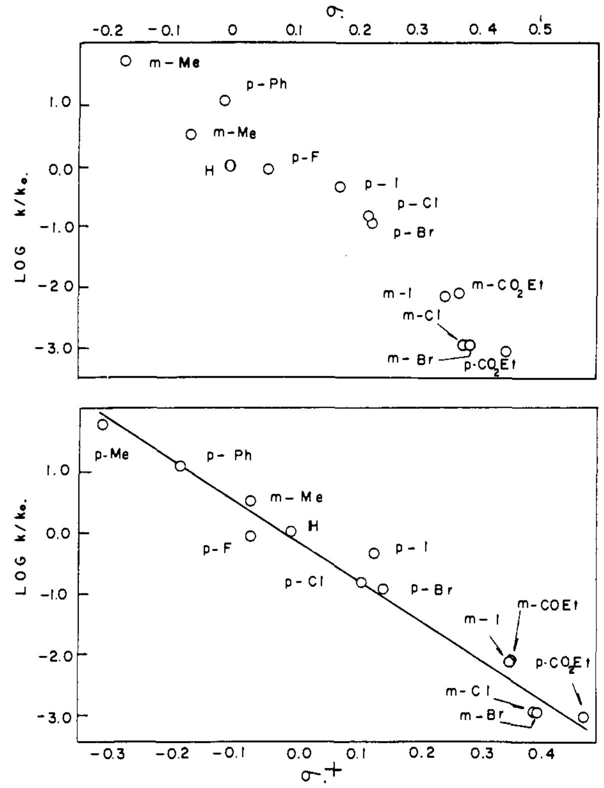

Fig. 4.—Nitration of monosubstituted benzenes in nitromethane or acetic anhydride.

The recent results of P. B. D. de la Mare and his co-workers on the bromination of aromatics by hypobromous acid, catalyzed by perchloric acid, yields an excellent correlation with the σ^+-constants (Fig. 5).

The determination of accurate partial rate factors for aromatic substitutions frequently offers major experimental difficulties. In the case of some substituents, one isomer may be formed in predominant amount, and it becomes a difficult problem to determine minor amounts of the product accurately. The protonolysis of aryltrimethylsilanes (Figs. 6 and 7), and the brominolysis of aryltrimethylsilanes and benzeneboronic acids (Figs. 8 and 9) offer a convenient means to determine partial rate constants by a direct experimental rate measurement, without the necessity for an accurate analysis for minor components of the reaction product. In these four cases, the experimental

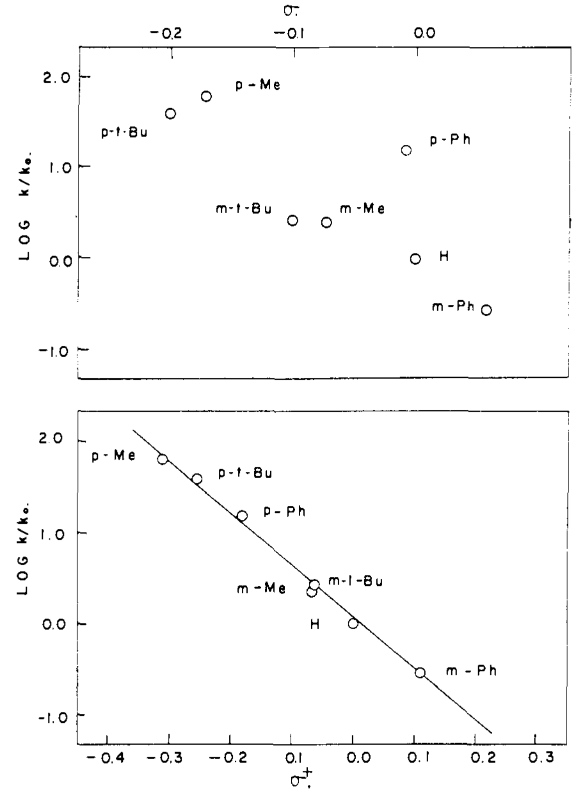

Fig. 5.—Bromination of monosubstituted benzenes in aqueous dioxane by hypobromous acid, catalyzed by perchloric acid.

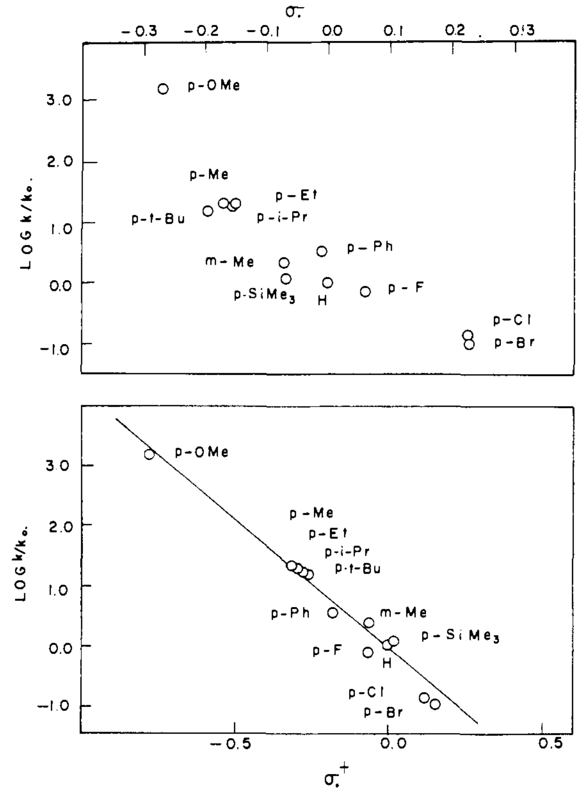

Fig. 6.—Protonolysis of phenyltrimethylsilanes by perchloric acid in 72% aqueous methanol.

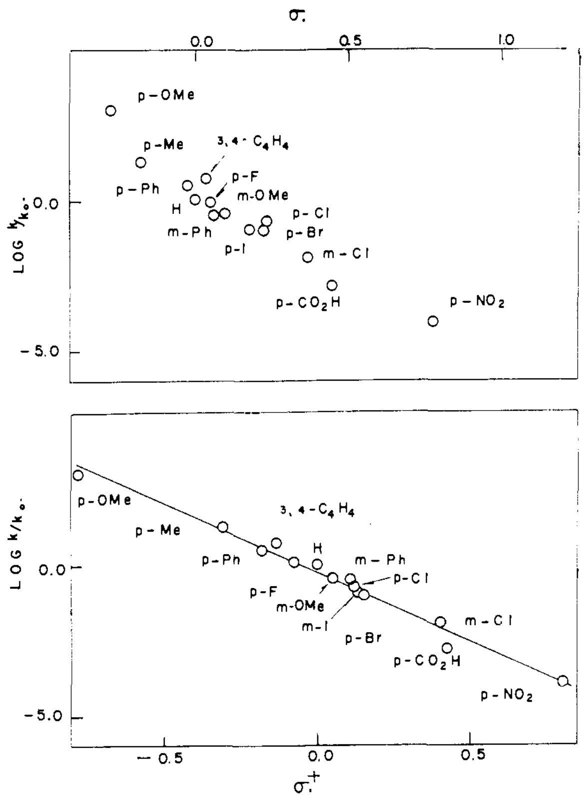

Fig. 7.—Protonolysis of phenyltrimethylsilanes by sulfuric acid in acetic acid.

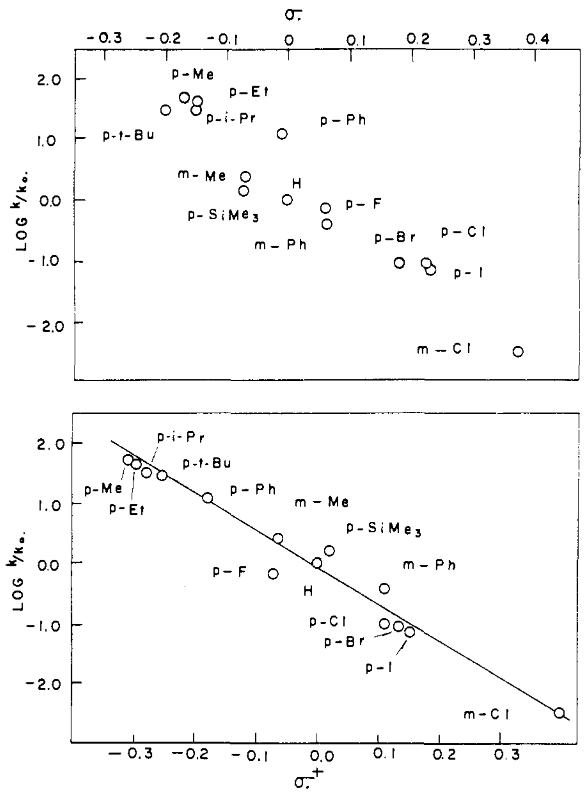

Fig. 8.—Brominolysis of phenyltrimethylsilanes in acetic acid.

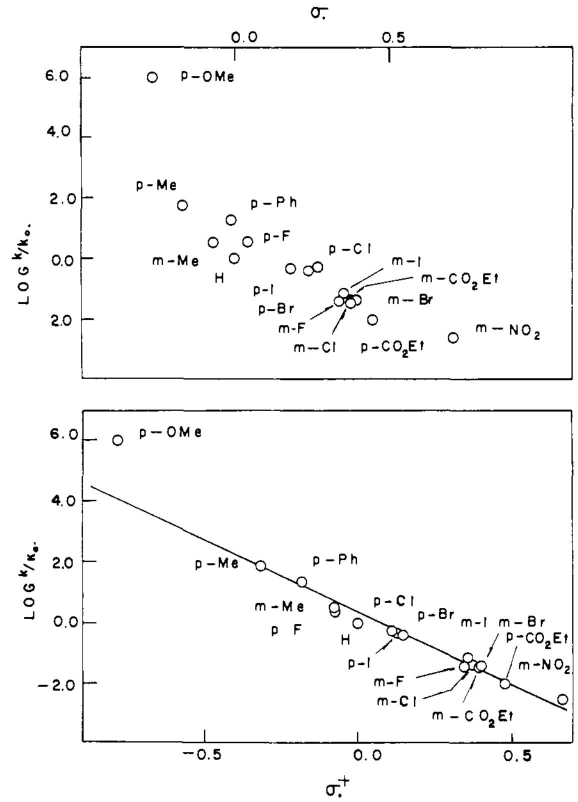

Fig. 9.—Brominolysis of benzeneboronic acids in 20% acetic acid.

rate data exhibit an excellent correlation with the electrophilic substituent constants.[22]

Illuminati and Marino have developed an alternative procedure for determining the partial rate factors by a direct measurement of substitution rates.[20] Comparison of the rates of bromination of the monosubstituted mesitylenes with that of mesitylene itself yields the *meta* partial rate factors, m_f. Similarly, comparison of the monosubstituted durenes with durene itself yields the *para* partial rate factors, p_f. Excellent agreement between these rate factors and the σ^+-substituent constants is observed (Fig. 10). The fact that the partial rate factors for both methyl and the halogens agree so well with the σ^+-values suggests that the relatively poor correlation exhibited by the partial rate factors for these groups in the chlorination reaction (Fig. 3) may not be real.

In conclusion the available data on aromatic substitution exhibit a gratifying correlation with the electrophilic substituent constants. Additional data of high accuracy will be required to provide a realistic evaluation of the precision which may be realized in predicting rates and isomer distributions in the substitution of aromatics.

Correlation of Electrophilic Aromatic Side-chain Reactions.—Recently we examined the utility of the σ^+-constants in correlating the available data from electrophilic side-chain reactions.[5b] An excellent correlation was realized. With additional constants available, we have extended our examination of the correlation to include the new values and applied them to several representative electrophilic reactions: solvolysis of *t*-cumyl chlorides in ethanol at 25°[4g]; solvolysis of triphenylcarbinyl chlorides in 40% ethanol–60% ethyl ether at 0°[23]; thermal rearrangement of α-phenylethyl chlorocarbonates in dioxane at 80°[24]; acid-catalyzed rearrangement of phenylpropenylcarbinols in 60% aqueous dioxane at 30°[25]; migration aptitudes in the acid-catalyzed rearrangement of diphenylmethylcarbinyl azides[26]; equilibrium constants for carbonium ion formation from triarylcarbinols in aqueous sulfuric acid at 25°[8c,f]; equilibrium constants for the ionization of triphenylcarbinyl chlorides in liquid sulfur dioxide at 0°[27]; and the frequency shifts in the infrared stretching frequency of the carbonyl groups in substituted

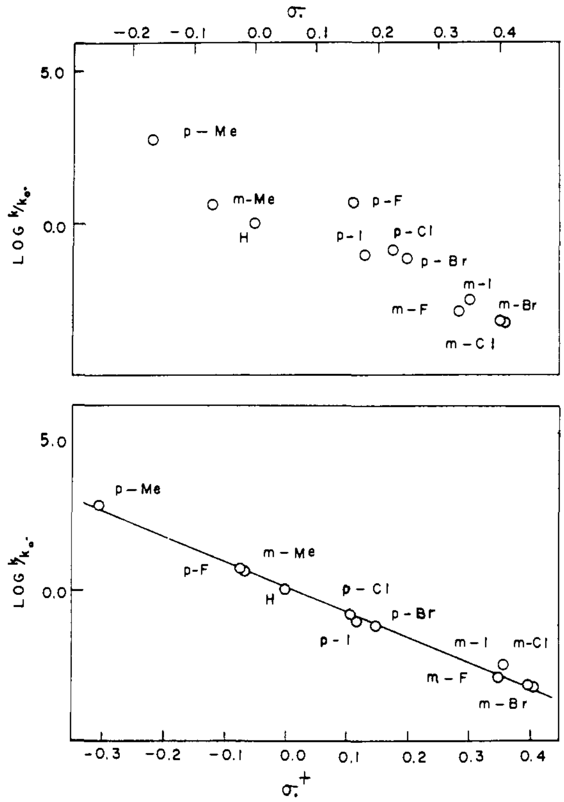

Fig. 10.—Bromination of polymethylbenzenes in nitromethane.

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[22] Only in the case of the *p*-methoxy group is a serious deviation observed in the brominolysis of benzeneboronic acid. This value is based on a major experimental extrapolation, which might have introduced some experimental complication. Alternatively, the reaction of this derivative may involve a change in the rate-determining stage. It is highly desirable that this exception be carefully re-examined to ascertain whether or not it constitutes a real deviation from the proposed correlation.

[23] A. C. Nixon and G. E. K. Branch, THIS JOURNAL, **58**, 492 (1936).

[24] K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1955).

[25] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1096 (1947).

[26] S. N. Ege and K. W. Sherk, THIS JOURNAL, **75**, 254 (1953).

[27] The data represent equilibrium constants for the ionization to form an ion-pair

$$(C_6H_5)_3CCl \xrightarrow{SO_2,\ 0°} (C_6H_5)_3C^+Cl^-$$

The authors wish to express their appreciation to Professor N. Lichtin for his generosity in permitting this examination of his data prior to the complete publication of his results.

TABLE IV

REACTION CONSTANTS FOR ELECTROPHILIC AROMATIC SIDE CHAIN REACTIONS

Reaction	Reaction constant, ρ[a]	s[b]	r[c]	n[d]	Ref.
Solvolysis of *t*-cumyl chlorides in 90% aq. acetone at 25°	−4.54[f]	0.154	0.992	8	[e]
	−4.45[g]	.178	.989	16	[e]
Solvolysis of *t*-cumyl chlorides in ethanol at 25°	−4.67	.074	.998	16	4g
Solvolysis of triphenylcarbinyl chlorides in 40% ethanol–60% ethyl ether at 60°	−2.57	.099	.994	8	23
Thermal rearrangement of α-phenylethyl chlorocarbonates in dioxane at 80°	−3.01	.031	.999	14	24
Acid-catalyzed rearrangement of phenylpropenylcarbinols, $XC_6H_4CH(OH)CH{=}CHCH_3$, in 60% aqueous acid at 30°	−2.97	.155	.978	7	25
Migration aptitudes in the acid-catalyzed rearrangement of diphenylmethylcarbinyl azides	−2.69	.091	.997	5	26
Equil. constants for carbonium ion formation from triphenylcarbinols in aq. sulfuric acid at 25°	−3.64	.512	.995	12[h]	8c,f
Equil. constants for ionization of triphenylcarbinyl chlorides to ion-pairs in sulfur dioxide at 0°	−3.73	.234	.981	15	27
Frequency shifts in the infrared stretching frequency of the carbonyl group in substd. acetophenones	−12.30	.906	.980	10	14, 28

[a] The reaction constant ρ is based only on σ^+-values derived from the *t*-cumyl solvolyses (Table I). [b] The standard deviation of the experimental measurements from the regression line. [c] The correlation coefficient. [d] The number of compounds involved in the calculation of ρ. [e] This study. [f] Obtained from a least squares treatment of the eight *meta* thermodynamic points (MeO–, Me–, H–, F–, Cl–, Br–, I–, O_2N–). [g] Obtained from a least squares treatment of all *meta* points (MeO–, MeS–, Me–, Et–, *t*-Bu–, Ph–, Me_3Si–, H–, F–, Cl–, Br–, I–, EtO_2C–, F_3C–, NC–, O_2N). [h] Values for *p*-*t*-Bu and *p*-*i*-Pr derivatives omitted since authors report these values are less accurate and they deviate seriously from the linear relationship followed by remaining compounds.

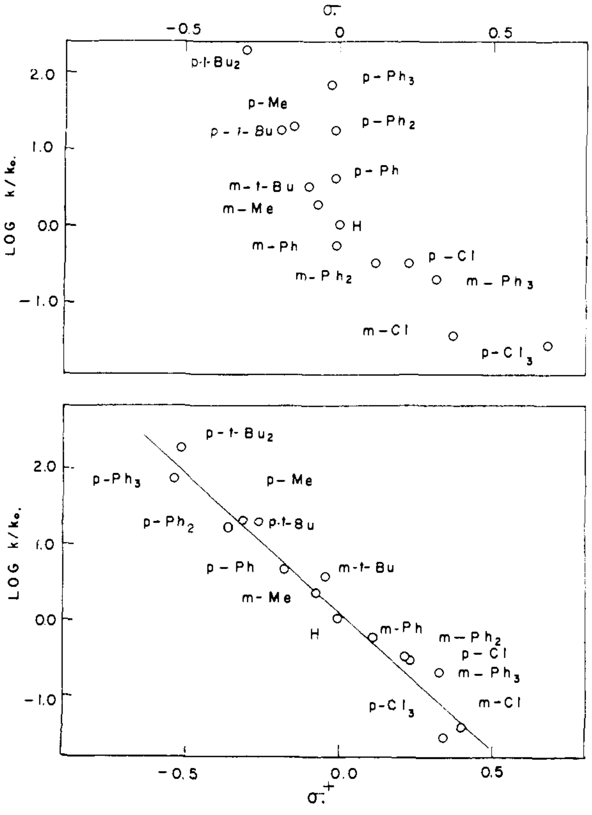

Fig. 11.—Ionization of triphenylcarbinyl chlorides in liquid sulfur dioxide.

acetophenones.[14,28] The results of a statistical analysis of the correlation achieved are summarized in Table IV.

It was pointed out previously that the σ^+-constants did not correlate the data on rates of solvolysis of the benzyl tosylates.[29] With this one exception, the σ^+-constants have been quite satisfactory in correlating numerous reactions of wide diversity.

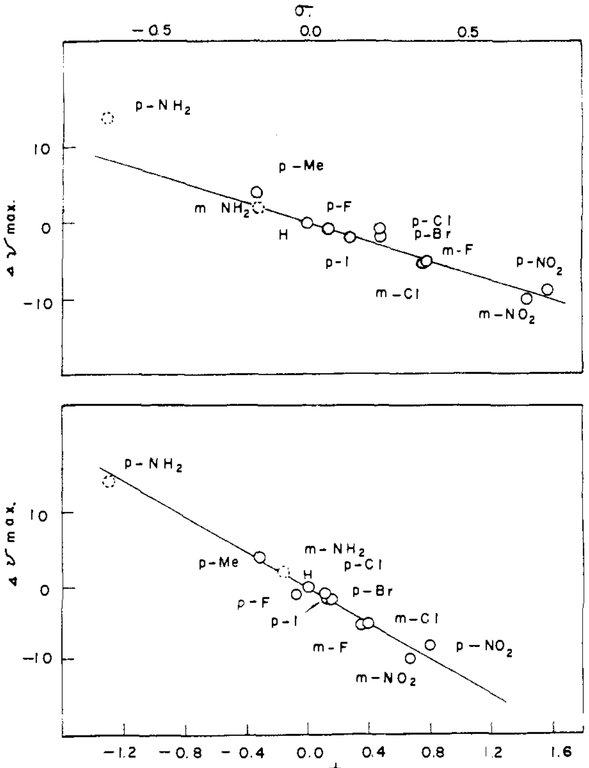

Fig. 12.—Frequency shifts in the infrared stretching band for the carbonyl groups in acetophenones.

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(28) See C. N. R. Rao and G. B. Silverman, *Curr. Sci.* (*India*), **26**, 375 (1957), for a discussion of this question and a summary of the pertinent literature.

(29) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953). See also F. T. Fang, J. K. Kochi and G. S. Hammond, *ibid.*, **80**, 563 (1958); G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *ibid.*, **80**, 568 (1958); G. S. Hammond and C. E. Reeder, *ibid.*, **80**, 573 (1958).

The arguments which have been presented on why the Hammett treatment should fail in reactions involving large resonance interactions with the substituents appear quite reasonable.[8] It is possible that the correlations in Table IV appear better than they should because the data include relatively few *meta* substituents to permit an accurate determination of the true reaction constant.

On the other hand, data for numerous *meta* substituents are available for the ionization of triphenylcarbinyl chlorides in liquid sulfur dioxide (Fig. 11) and the frequency shifts in the infrared stretching frequency of the carbonyl group in substituted acetophenones (Fig. 12). Moreover, in these cases the reaction constants range from $\rho = -3.73$ to -12.30. Nevertheless the correlation with the σ^+-constants must be considered quite satisfactory.

The ability of these groups to correlate such diverse reactions suggests that there must be some fundamental property of substituent groups which is represented by the individual σ^+-constants.

Acknowledgment.—The invaluable assistance of Mr. T. Inukai and L. M. Stock with the statistical analysis is gratefully acknowledged.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Solvent Effects in the Reactions of Free Radicals and Atoms. II. Effects of Solvents on the Position of Attack of Chlorine Atoms upon 2,3-Dimethylbutane, Isobutane and 2-Deuterio-2-methylpropane[1]

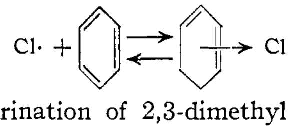
BY GLEN A. RUSSELL

RECEIVED JANUARY 16, 1958

In the presence of a number of aliphatic solvents the photochlorination of 2,3-dimethylbutane produces 60% of 1-chloro-2,3-dimethylbutane and 40% of the 2-isomer. In the presence of certain aromatic solvents, and some non-aromatic materials, 2-chloro-2,3-dimethylbutane becomes the major reaction product. In 8 *M* benzene the 2-isomer is formed in 90% yield while in 12 *M* carbon disulfide the yield of 2-isomer is greater than 95% of the total yield of chloro-2,3-dimethylbutanes. This solvent effect, controlling the products of the reaction has been demonstrated to occur in the attack of the chlorine atom upon the hydrocarbon. It is concluded that chlorine atoms form a π-complex with the aromatic nucleus by an acid–base type interaction. These complexes are less reactive and therefore more selective than a free chlorine atom. The results indicate a method by which the reactivity and selectivity of free radicals and atoms can be altered and controlled. The importance of specific solvent effects in other free radical reactions is discussed.

It has been generally assumed that solvents have little effect upon the course and rate of free radical reactions.[2] This conclusion appears to be based mainly upon the effect of solvents, usually of varying polarity, upon the rate of homolytic dissociation, for example of hexaphenylethanes.[3] The absence of solvent effects on the over-all rate of polymerization of styrene,[4] and the copolymer structure observed in vinyl copolymerizations[5] have been noted.[6] However, it was felt that it would be worthwhile to obtain data in other systems from which the magnitude of the solvent effect could be judged. The first free radical reaction that we examined was the photochlorination of a branched-chain hydrocarbon. Here, on the basis of admittedly scanty evidence, it had been suggested that the highly electrophilic chlorine atom should associate with the π-electrons of an aromatic solvent.[7]

All of the experimental evidence that we have obtained has been in agreement with this prediction. Aromatic solvents can dramatically alter the products of the photochemical chlorination of 2,3-dimethylbutane. Moreover, the magnitude of the solvent effect observed for various aromatic solvents suggests that the solvent effect arises from association of the chlorine atom with the π-electrons of the aromatic nucleus. This association produces a complexed chlorine atom (a π-complex) which has a lower reactivity and hence a greater selectivity than a free chlorine atom.



In the chlorination of 2,3-dimethylbutane in the absence of a solvent chlorine atoms attack a tert.-hydrogen atom about four times as readily as a prim.-hydrogen atom, presumably because of the greater resonance stabilization of a tert.-alkyl radical rela-

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[1] Directive Effects in Aliphatic Substitution. XI. Presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September, 1957. A preliminary Communication appeared in THIS JOURNAL, **79**, 2977 (1957).

[2] J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 237; C. Walling, "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 35.

[3] For a compilation of pertinent data, see W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 1948, p. 47. Large solvent effects have been observed in the thermal decomposition of dibenzoyldiimide and benzoyl peroxide (J. E. Leffler and W. B. Boyd, THIS JOURNAL, **78**, 335 (1956)), but it is difficult to decide if these are true solvent effects or represent a change in the mechanism of decomposition or the actual intervention of the solvent in a chain decomposition. The rate of decomposition of phenylazotriphenylmethanes has been shown to be relatively independent of solvent, although large and compensating changes in entropy and enthalpy of activation have been noted as the solvent is varied (J. E. Leffler and R. A. Hubbard, *J. Org. Chem.*, **19**, 1089 (1954); M. G. Alder and J. E. Leffler, THIS JOURNAL, **76**, 1425 (1954)).

[4] R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 238 (1947).

[5] C. Walling and F. R. Mayo, *J. Polymer Sci.*, **3**, 898 (1948); F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and W. J. Wenisch, THIS JOURNAL, **70**, 1527 (1948); C. C. Price and J. G. Walsh, *J. Polymer Sci.*, **6**, 239 (1951).

[6] Solvent effects in the free radical addition of hydrogen bromide to olefins have been discussed [F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940)] but conclusions are indefinite.

[7] G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4031 (1955). This prediction has been discussed in more general terms by K. L. Nelson and H. C. Brown, "The Chemistry of Petroleum Hydrocarbons," B. T. Brooks, Editor, Reinhold Publishing Corp., New York, N. Y., 1955, Vol. III, p. 549.