same techniques previously applied for the rate measurements in 90% acetone. A typical rate study is reported in Table V.

The solvolysis of t-cumyl and m-methyl-t-cumyl chloride in methanol were very fast, with half-lives of approximately 2 and 1 min., respectively. In order to check on the accuracy of the values obtained by direct measurement at 25°,

the rates were determined at 0° and 10°. t-Cumyl chloride exhibited rate constants of 0.918 hr.$^{-1}$ at 0.0° and 3.06 at 10.0°. m-Methyl-t-cumyl chloride exhibited values of 2.43 hr.$^{-1}$ at 0.0° and 7.94 at 10.0°. The linearity of the log k $vs.$ $1/T$ plots were considered to confirm the values at 25°.

LAFAYETTE, IND.

Rates of Solvolysis of Phenyldimethylcarbinyl Chlorides Containing Substituents (-NMe₃⁺, -CO₂⁻) Bearing a Charge[1,2]

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

In contrast to m- and p-carboxy-t-cumyl chloride, which solvolyze in ethanol at 25° at rates 0.0440 and 0.0137 that of the parent compound, the corresponding derivatives containing ionized carboxylate substituents, m- and p-CO₂⁻K⁺, solvolyze at rates somewhat faster than that of t-cumyl chloride: k/k_H for m-K⁺⁻O₂CC₆H₄C(CH₃)₂Cl, 1.35; p-, 1.28. The electrophilic substituent constants for the carboxylate substituent corresponds to the available data in electrophilic aromatic substitution. In 90% aqueous acetone the m-trimethylammonium chloride substituent decreases the rate of solvolysis of t-cumyl chloride by the factor 0.0220; p-, by the factor 0.0131. The relative rates, p- < m- corresponds qualitatively to the orientation observed in electrophilic substitution of trimethylanilinium salts. However, in contrast to the behavior of other $meta$ orienting substituents, there is a major discrepancy between the magnitudes of the σ^+- and the σ-constants. Possible causes for this discrepancy are considered.

The Hammett equation has provided an exceedingly valuable relationship for correlating the effect of substituents on rates and equilibria.[4-6] It has generally been considered that the equation is most successful when the substituents exert their effects primarily through electrostatic interactions[7] with resonance interactions being largely responsible for observed deviations.[6] Thus, the failure of the Hammett equation to correlate directive effects in electrophilic aromatic substitution was attributed to major resonance interactions which were not incorporated into the usual σ-constants.[8,9]

Considerable success has been realized in correlating the available data on electrophilic aromatic substitution[10] by means of a set of σ^+-constants which incorporate a resonance factor.[11] It was of interest to ascertain whether this treatment could be extended to substituents carrying a charge. Accordingly we undertook to determine the rates of solvolysis of t-cumyl chlorides containing the carboxylate group, $-CO_2^-$, and the trimethylam-

monium group, $-N(CH_3)_3^+$, in the $meta$ and $para$ positions.

Results

The Carboxylate Substituent.—m- and p-carboxy-t-cumyl chlorides had been synthesized previously and their rates of hydrolysis determined in 90% aqueous acetone.[11f] We attempted to observe the effect of the carboxylate substituent by adding sufficient potassium hydroxide to convert the carboxy group into the ionized derivative. However, the solvent separated in two phases and all attempts to work in more dilute solution or to use other bases failed to prevent such phase separation.

It proved possible to maintain a homogeneous reaction mixture in ethanol. Having determined the reaction constant for the solvolysis of t-cumyl chlorides in ethanol,[11g] it appeared practical to base the σ^+-constant for the carboxylate group upon rate data obtained in this solvent.

Accordingly, the solvolysis of m- and p-carboxy-t-cumyl chloride was measured at 25.0° in the presence of sufficient potassium ethoxide to ionize the carboxylate group and neutralize the hydrogen chloride formed in the solvolysis. It was established that similar concentrations of potassium ethoxide have a negligible effect on the rate of solvolysis of t-cumyl chloride itself. The results are summarized in Table I.

The Trimethylammonium Substituent.—m-Aminobenzoic acid was converted into methyl m-(dimethylamino)-benzoate and treated with methylmagnesium iodide. The resulting carbinol was treated with methyl iodide to form the trimethylammonium iodide. Treatment with silver chloride exchanged the iodide ion by chloride. The carbinol was transformed into the tertiary chloride by treatment with hydrogen chloride.

p-Bromo-N,N-dimethylaniline was converted into the lithio derivative and treated with acetone. Dehydration of the carbinol occurred, so that p-(di-

(1) Directive Effects in Aromatic Substitution. XXIX.

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

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TABLE I

RATES OF ETHANOLYSIS OF *m*- AND *p*-(POTASSIUM CARBOXYLATE)-*t*-CUMYL CHLORIDES AT 25°

Substituent	Rate constant at 25° k_1, sec.$^{-1}$ × 10⁵	Rate ratio, 25° k/k_H
Hydrogen	39.4	1.00
	38.1^a	0.97
	38.9^a	0.99
m-Carboxy	1.74^b	0.0440
p-Carboxy	0.542^b	0.0137
m-(Potassium carboxylate)	51.7^c	1.35
	54.4^d	
p-(Potassium carboxylate)	50.3^d	1.28

^{a} *t*-Cumyl chloride, 1.00 g., with 0.075 M potassium ethoxide (from 0.300 g. of potassium) in 100 ml. of ethanol. ^{b} Ref. 11g. ^{c} *m*-Carboxy-*t*-cumyl chloride, 1.00 g., with 0.075 M potassium ethoxide (from 0.300 g. of potassium) in 100 ml. of ethanol. ^{d} *m*- or *p*-carboxy-*t*-cumyl chloride, 0.700 g., with 0.060 M potassium ethoxide (from 0.250 g. of potassium) in 100 ml. of ethanol.

methylamino)-α-methylstyrene was isolated and treated with methyl iodide to form the quaternary salt. The iodide ion was exchanged for chloride as in the previous case and hydrogen chloride added to the olefin to form the desired tertiary chloride.

The rates of solvolysis of these chlorides were determined in 90% aqueous acetone at three temperatures. The rate data followed simple first-order kinetics, with no apparent difficulties introduced by the presence of the trimethylammonium chloride substituent. To test further the possible effect of this group on the solvolysis rate, we determined the rate of solvolysis of *m*-carbomethoxy-*t*-cumyl chloride in the presence of trimethylanilinium chloride. A minor increase (15%) in rate was observed, presumably the result of a salt effect. The results are summarized in Table II.

TABLE III

SUBSTITUENT CONSTANTS FOR THE CARBOXYLATE AND TRIMETHYLAMMONIUM GROUPS

Group	Substituent constants			
	σ_m	σ_m^+	σ_p	σ_p^+
Carboxy		0.322^a		0.421^a
Carboethoxy	0.37^a	.366^a	0.45^a	.482^a
Carboxylate (potassium)	− .023 to .197^d	− .028^b	.055 to .232^d	− .023^b
Trimethylammonium (chloride)	.67 to 1.02^d	.359^c	.66 to 1.11^d	.408^c

^{a} Ref. 11f. ^{b} $\sigma^+ = \frac{1}{\rho} \log \frac{k}{k_H}$; $\rho = -4.67$. ^{c} $\rho = -4.54$. ^{d} Ref. 5.

These σ^+-values are qualitatively in agreement with the available data on electrophilic substitution. For example, Smith observed that the chlorination of sodium benzoate with sodium hypochlorite yielded 47% *o*-, 33% *m*- and 20% *p*-chlorobenzoate.[13] Similarly, an almost statistical distribution of the substitution products was realized in the bromination of sodium benzoate by sodium hypobromide.[14]

The trimethylammonium substituent markedly reduced the rates of solvolysis of the *t*-cumyl chlorides. Moreover, the groups exert a larger effect upon the solvolysis rate in the *para* than in the *meta* position. This decreased rate of the *para* derivative as compared to the corresponding *meta* isomer agrees with the preferred *meta* orientation exhibited by electrophilic substitution of trimethylanilinium salts.[15,16]

The explanation proposed by Roberts and his co-workers to account for the preferred *meta* orientation in electrophilic substitutions of trimethylanilinium salts[17] can be extended to account for the relative rates of solvolysis of the *m*- and *p*-(trimethylammonium chloride)-*t*-cumyl chlorides.

TABLE II

RATE CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF *m*- AND *p*-(TRIMETHYLAMMONIUM CHLORIDE)-*t*-CUMYL CHLORIDES IN 90% AQUEOUS ACETONE

Substituent	Rate constant, k_1, sec.$^{-1}$ × 10⁵				Rate ratio. 25°	E_{act}	log A	$\Delta H^\ddagger$	$\Delta S^\ddagger$
	25.0°	35.0°	45.0°	55.0°					
Hydrogen	12.4				1.00	19.5	10.4	18.8	−12.5
m-(Trimethylammonium chloride)	0.273^a	0.917^b	2.19	5.83	0.0220	19.6	8.82	19.0	−20.3
p-(Trimethylammonium chloride)	.161^a	.481	1.36	3.53	.0131	20.1	8.94	19.5	−19.7
m-Carbomethoxy			8.92^c	9.92^d					

^{a} Calculated from values at higher temperatures. ^{b} At 36.0°. ^{c} Chloride, 1.10 g., in 100 ml. of solvent. ^{d} In presence of added 0.60 g. of trimethylanilinium chloride.

Discussion

Both the carboxy and the carboalkoxy groups are strongly electron withdrawing and direct entering substituents strongly to the *meta* position.[12] This directive effect is clearly reflected in the relative values of the σ^+-constants, $\sigma_p^+ > \sigma_m^+$ (Table III).

The presence of a negative charge, such as that present in the carboxylate group, $-CO_2^-$, should operate to oppose this electronic shift. Indeed, the calculated values of the σ^+-constants for the *m*- and *p*-carboxylate groups, $\sigma_m^+ = -0.028$ and $\sigma_p^+ = -0.023$, suggests that the negative pole completely neutralizes the electronic shift normal to the un-ionized carboxy substituent.

Structure II represents a low energy resonance form of the carbonium ion I from the *m*-chloride, which should be stabler than any of the possible resonance forms IV of the *p*-carbonium ion III.

Although there appears to be a qualitative agreement between the relative magnitude of σ_m^+ and σ_p^+ for the trimethylammonium group and the observed directive effects exhibited by this group, there appears to be a quantitative discrepancy. The σ^+-values for the trimethylammonium group based upon the rates of solvolysis are in the neighborhood of 0.4 (Table III), far smaller than the

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.
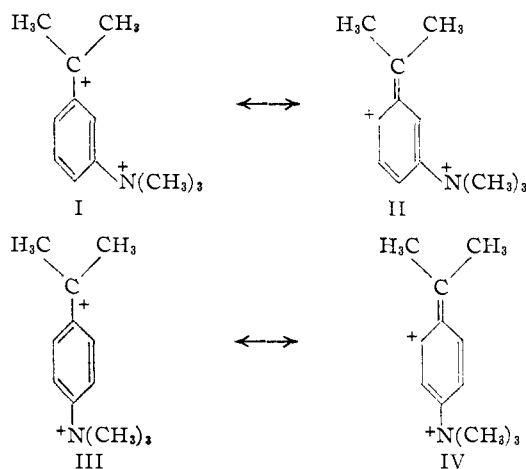
(13) J. C. Smith, *J. Chem. Soc.*, 213 (1934).
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(15) D. Vörlander, *Ber.*, **58**, 1893 (1925).
(16) Reference 12, pp. 231 ff.
(17) J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951).

values determined for the nitro group (σ_m^+, 0.674; σ_p^+, 0.790). Yet the available evidence suggests that the trimethylammonium group is an exceedingly powerful directive group.[15,16]

Moreover, in all cases where comparison is possible between the σ^+-values for *meta* directing groups and the σ-values derived from the dissociation constants of benzoic acid the agreement has been phenomenally close, generally within the limits of uncertainty with which the σ-constants are known.[11f] From the ionization of benzoic acids, substituted in the *meta* and *para* positions, with the trimethylammonium group in 50% aqueous ethanol, Roberts has estimated the σ_m-value as 1.02 and the σ_p-value as 0.88.[17] Not only do these disagree greatly in magnitude with the σ^+-values, but they disagree also in relative value. The σ^+-values exhibit the order $\sigma_p^+ > \sigma_m^+$, corresponding to that anticipated for a *meta* directing substituent, whereas the σ-values exhibit the opposite order, $\sigma_p < \sigma_m$.

It was pointed out earlier that the Hammett relationship has been considered to be most successful when the substituents exert their effects primarily through electrostatic interactions. On this basis one might have concluded that the carboxylate group, with its unit negative charge, and the trimethylammonium group, with its unit positive charge, would have been quite ideal to give precise correlations in the Hammett treatment. However, this appears not to be the case. Thus, Jaffé reports σ-"constants" for *m*-carboxylate range in value from -0.023 to 0.197, and for *p*-carboxylate from 0.055 to 0.206. (In the case of this group there is reasonable agreement between the σ^+-values and the σ-values, within the wide range of uncertainty with which these are defined.)

In the case of the carboxylate group, important resonance interactions are possible, and the wide variations in the σ-value might be due to this cause. However, similar variations are observed in the trimethylammonium group, where resonance interactions are presumed to be impossible. For example, major variations are observed in the σ-values calculated from ionization data from several systems for the trimethylammonium group (Table IV).

These results indicate that the position of groups

carrying a charge in both the usual Hammett treatment and in our proposed extension to electrophilic reactions is quite uncertain, and great caution should be exercised in utilizing these treatments to correlate rates and equilibria involving such groups.

One possible reason why such groups may fail to obey the quantitative treatment may be suggested. The success of the Hammett equation for *meta* and *para* aromatic derivatives is believed to be due to the essentially constant entropy change accompanying reactions in which only the substituent in these positions undergoes variation. However, in the case of the trimethylammonium derivative, there is observed a markedly different entropy change than for the parent compound. Indeed, a large part of the decrease in rate over *t*-cumyl chloride appears to arise from this entropy term. Major entropy changes frequently accompany the formation or disappearance of a unit charge, presumably because of the effect of the charge in organizing solvent molecules. It follows that a substituent change which includes introduction of a unit charge may not be a permissible change allowable in the Hammett treatment.

A critical examination of the possibility of including such charged groups in these quantitative treatments will require an extensive study of the effects of such substituents upon rate and equilibria, and especially of the influences of the reaction medium upon the behavior of charged substituents.

Experimental Part

m- and p-(Potassium carboxylate)-t-cumyl Chlorides.— *m*- and *p*-carboxy-*t*-cumyl chlorides were samples available from earlier studies.[11f] The potassium salts were prepared *in situ* by dissolving the chlorides in ethanol containing excess potassium ethoxide and these solutions were used directly for the rate measurements.

m- and p-(Trimethylammonium chloride)-t-cumyl Chlorides.—m-Aminobenzoic acid was converted into methyl *m*-(dimethylamino)-benzoate by the procedure of Cumming.[18] The product, isolated as the hydrochloride, m.p. 177–178° (lit.[18] m.p. 175–177°), was obtained in 20% over-all yield. The free ester was treated with methylmagnesium iodide. After recrystallization from hexane, the tertiary carbinol, m.p. 73°, was obtained in 50% yield. This product was treated with methyl iodide in benzene solution to form *m*-(trimethylammonium iodide)-phenyldimethylcarbinol, dec. 173°. The salt in aqueous solution was shaken with a suspension of silver chloride to form the corresponding chloride. The salt was dissolved in methanol and precipitated with ethyl ether. The product exhibited m.p. (dec.) 202°.

Anal. Calcd. for $C_{12}H_{20}NOCl$: C, 62.73; H, 8.77; N, 6.10. Found: C, 62.36; H, 8.98; N, 6.09.

p-Bromodimethylaniline was converted into the lithium derivative and treated with acetone. Crude *p*-(dimethyl-

(18) A. C. Cumming, *Proc. Roy. Soc. (London)*, **A78**, 103 (1906).

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.

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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°

Time, hr.	x, ml.	a − x, ml.	k_1, hr.$^{-1}$
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°

Time, hr.	x, ml.	a − x, ml.	k_1, hr.$^{-1}$
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.

Electrophilic Substituent Constants[1,2]

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

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*-NO₂) 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–,

(1) Directive Effects in Aromatic Substitution. XXX.

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(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).

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