it was observed that the products were crystalline solids: p-carboxy-t-cumyl chloride, m.p. (dec.) 138°; m-carboxy-t-cumyl chloride, m.p. (dec.) 114–115°.

Kinetic Measurements.—The procedures were similar to those used for the related compounds previously described.[5] The 90% acetone used as solvent was adjusted to yield a rate of solvolysis identical within the experimental uncertainty of ±3% with that previously observed for t-cumyl chloride.[5a] Typical rate data are summarized in Table III.

TABLE III
RATE DATA FOR THE SOLVOLYSIS OF SUBSTITUTED t-CUMYL CHLORIDES IN 90% AQUEOUS ACETONE

Time, hr.	x, ml.	a − x, ml.	k_1, hr.$^{-1}$
A.	m-Carboethoxy-t-cumyl chloride at 25.0°		
0	0.068	8.357	
2.42	0.262	8.163	0.00974
13.42	1.062	7.363	.00944
20.00	1.525	6.900	.00958
27.67	2.028	6.397	.00966
38.58	2.670	5.755	.00967
43.83	2.990	5.435	.00982
53.25	3.470	4.955	.00982
∞	8.425		
		Average	0.00968 ± 0.000095
B.	p-Carboxy-t-cumyl chloride at 35.0°		
0	4.470	2.940	
2.92	4.640	2.770	0.0204
8.25	4.880	2.530	.0182
21.25	5.360	2.050	.0170
33.75	5.750	1.660	.0169
44.75	6.090	1.320	.0179
57.08	6.300	1.110	.0171
76.75	6.550	0.860	.0160
∞	7.410		
		Average	0.0176 ± 0.00085
C.	m-Trifluoromethyl-t-cumyl chloride at 25.0°		
0	0.112	8.512	
138.7	2.113	6.511	0.00193
138.8	2.154	6.470	.00198
192.0	2.822	5.802	.00200
193.2	2.820	5.804	.00198
211.6	3.306	5.588	.00199
215.6	3.079	5.545	.00198
∞	8.624		
		Average	0.00198 ± 0.00002

LAFAYETTE, IND.

Rates of Solvolysis of Substituted Phenyldimethylcarbinyl Chlorides in Methyl, Ethyl and Isopropyl Alcohols. Influence of the Solvent on the Value of the Electrophilic Substituent Constant[1,2]

By Y. OKAMOTO,[3] T. INUKAI[4] AND HERBERT C. BROWN

Rates of solvolysis at 25.0° have been determined for a number of representative substituted t-cumyl chlorides in methyl, ethyl and isopropyl alcohol. With previous data in 90% acetone, the results make available rate data for eighteen different t-cumyl chlorides in two to four solvents. Good linear free energy relationships are exhibited between these new rate data and the rate constants obtained previously in 90% acetone. The reaction constant ρ, −4.54 in 90% acetone, is −4.82 in methanol, −4.67 in ethanol and −4.43 in 2-propanol. In the case of some groups, the relative rates, k/k_H, exhibit a significant change with change in solvent. However, k_m/k_p is far more constant. It is suggested that varying solvation of the substituent in the different solvents are responsible for the relatively minor changes in the k/k_H ratios. Since the substituent in the meta and para position will be similarly solvated, the k_m/k_p ratios exhibit relatively little change with solvent. It is concluded that the alcoholic solvents can be utilized to obtain values of the electrophilic substituent constants within the precision with which these constants are normally used.

Electrophilic substituent constants, σ^+, have been derived from the rates of solvolysis of substituted t-cumyl chlorides at 25° in 90% aqueous acetone.[5] Considerable promise has been observed in the correlation of aromatic substitution data[6] and electrophilic side reactions[7] with the aid of these constants.

(5) (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, T. Inukai and H. C. Brown, ibid., 80, 4969 (1958).

(6) H. C. Brown and Y. Okamoto, ibid., 79, 1913 (1957).

(7) Y. Okamoto and H. C. Brown, J. Org. Chem., 22, 485 (1957).

In the course of further work, certain disadvantages of the 90% aqueous acetone solvent have become apparent. The solvent contains one volatile component and relatively frequent testing with the parent compound, t-cumyl chloride, and adjusting of the composition are required to obtain good values for the relative rates. Moreover, the volatility of the acetone introduces difficulties in attempting to evaluate relatively inert derivatives by carrying out the solvolysis at higher temperatures.[5f] Finally, in attempting to determine the substituent constant for the carboxylate group, we observed separation into two phases in our attempts to neutralize the carboxyl group in the carboxyl-t-cumyl chloride in this solvent.[5f]

For these reasons we decided to undertake a survey of other solvents, restricting our attention to single component systems. Methyl, ethyl and isopropyl alcohol were selected. In addition to their possible utility in the practical aspects of the determination of electrophilic substituent constants, the study made possible a careful examination of the

TABLE I

FIRST-ORDER RATE CONSTANTS AND RELATIVE RATES FOR THE SOLVOLYSIS AT 25.0° OF SUBSTITUTED t-CUMYL CHLORIDES IN VARIOUS SOLVENTS

| | 90% Acetone | | Methanol | | Ethanol | | 2-Propanol | |
| | $k_1 \times 10^5$, sec.$^{-1}$ | k/k_H | $k_1 \times 10^5$, sec.$^{-1}$ | k/k_H | $k_1 \times 10^5$, sec.$^{-1}$ | k/k_H | $k_1 \times 10^5$, sec.$^{-1}$ | k/k_H |
Substituent								
p-Phenyl	80.8	6.52			411	10.5	44.2	8.59
m-Phenyl	3.97	0.320			21.6	0.549	2.81	0.544
p-Fluoro	26.5	2.14			80.8	2.05	10.3	2.00
m-Methyl	24.8	2.00	1175	2.30	90.0	2.28	10.6	2.05
m-t-Butyl	23.0	1.86	1217	2.33	97.5	2.47	10.7	2.08
Hydrogen	12.4	1.00	511	1.00	39.4	1.00	5.14	1.00
m-Methylthio	2.38	0.192			10.4	0.262	1.29	0.250
p-Chloro	3.78	.305	149	0.291	12.4	.314	1.79	.348
m-Chloro	0.194	.0156	8.00	.0157	0.686	.0174	0.0953	.0185
m-Bromo	.178	.0144	8.11	.0159	0.650	.0165	0.0917	.0178
m-Iodo	.289	.0233	12.6	.0246	1.10	.0280		
m-Carboxy	.428	.0345			1.74	.0440		
p-Carboxy	.154	.0124			0.542	.0137		
p-Carbomethoxy	.0750	.00605	3.03	.00592	.261	.00663		
m-Trifluoromethyl	.0550	.00441	1.97	.00386	.153	.00387		
p-Trifluoromethyl	.0206	.00166	0.664	.00130	.0650	.00165		
m-Nitro	.0108	.000871	.292	.000571				
p-Nitro	.00319	.000257	.0722	.000141				

extent to which such solvent changes might influence the observed values of the constants.

Results

The various substituted t-cumyl chlorides used were samples prepared from carbinols and olefins available from earlier studies.[5] The methods used for following the rates were identical with those utilized in the related studies in 90% acetone. The rate data are summarized in Table I, together with the corresponding values in 90% acetone.

Although the values of k/k_H showed a reasonably good correlation in the various solvents, minor variations appeared. For example, in 90% acetone k/k_H is 2.00 for m-Me and 2.14 for p-F, whereas in ethanol k/k_H becomes 2.28 for m-Me and 2.05 for p-F. In other words the relative order changes from p-F > m-Me > H in 90% acetone to m-Me > p-F > H in both ethyl and isopropyl alcohol. Similar small variations of this kind are observed for the m-t-butyl group.

The reactivities in 90% acetone had been measured by a number of different investigators at different times using different batches of solvents. We were concerned over the possibility that these variations might be the result of differences in the techniques, changes in the solvents, or variations in the purity of the t-cumyl chlorides. Accordingly it was decided to repeat the measurements in freshly prepared solvents (90% acetone, ethyl alcohol and isopropyl alcohol) and identical samples of t-cumyl chlorides. The results are summarized in Table II.

The agreement with the values reported in Table I is quite good, well within the limits of our estimated accuracy ($\pm 3\%$ in each value of k_1). Consequently, it appears that the minor variations observed in the different solvents are real and not the result of experimental inaccuracies. Possible explanations for these and other variations in the k/k_H ratios are considered later in the paper.

TABLE II

FIRST-ORDER RATE CONSTANTS AND RELATIVE RATES FOR THE SOLVOLYSIS AT 25.0° OF t-CUMYL, p-FLUORO-t-CUMYL AND m-METHYL-t-CUMYL CHLORIDE IN VARIOUS SOLVENTS

| | 90% Acetone[a] | | Ethanol | | 2-Propanol | |
Substituent	$k_1 \times 10^5$, sec.$^{-1}$	k/k_H	$k_1 \times 10^5$, sec.$^{-1}$	k/k_H	$k_1 \times 10^5$, sec.$^{-1}$	k/k_H
Hydrogen	13.8	1.00	39.4	1.00	5.03	1.00
m-Methyl	27.1	1.97	89.7	2.27	10.4	2.06
p-Fluoro	28.9	2.10	77.8	1.97	9.72	1.93

[a] Solvent not adjusted to the usual 12.4 $\times$ 10^{-5} sec.$^{-1}$ value for t-cumyl chloride.

Discussion

The rate of solvolysis of t-cumyl chloride decreases markedly with increasing molecular weight of the alcohol. The relative rates are: 90% acetone, 1.00; methyl alcohol, 41.2; ethyl alcohol, 3.19; isopropyl alcohol, 0.415. Moreover, the effect of the solvent on the solvolysis rate remains essentially constant throughout the various substituted t-cumyl chlorides. Consequently, this variation in rate should be highly useful in selecting a solvent which will give the most convenient rate, providing that the solvent itself does not influence significantly the absolute value of the σ^+-constant.

In Figs. 1-3, the values of log (k/k_H) observed in methyl, ethyl and isopropyl alcohol at 25.0° are plotted against the corresponding values for acetone at the same temperatures. Reasonably good linear relationships are defined by the experimental data, although deviations do exist which are clearly beyond the possible experimental uncertainty. One such case is provided by m- and p-phenyl; another by p-fluoro.

Least squares treatment of the data in Figs. 1-3, yields a slope of 1.063 for methanol, 1.029 for ethanol and 0.975 for 2-propanol. The reaction constant for the solvolysis of the t-cumyl chlorides in 90% acetone is estimated to be -4.54. From these data, the reaction constant for the solvolysis
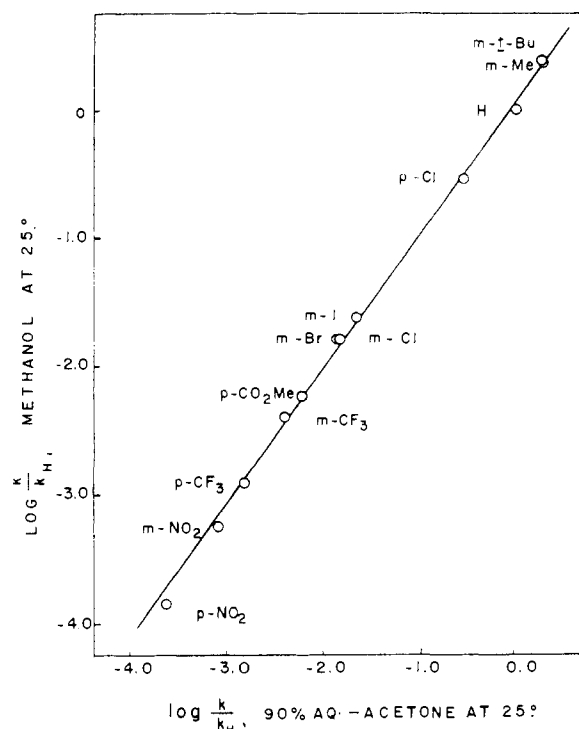
Fig. 1.—Linear free energy relationship between the relative rates of solvolysis of substituted t-cumyl chlorides at 25° in methanol and in 90% aqueous acetone.
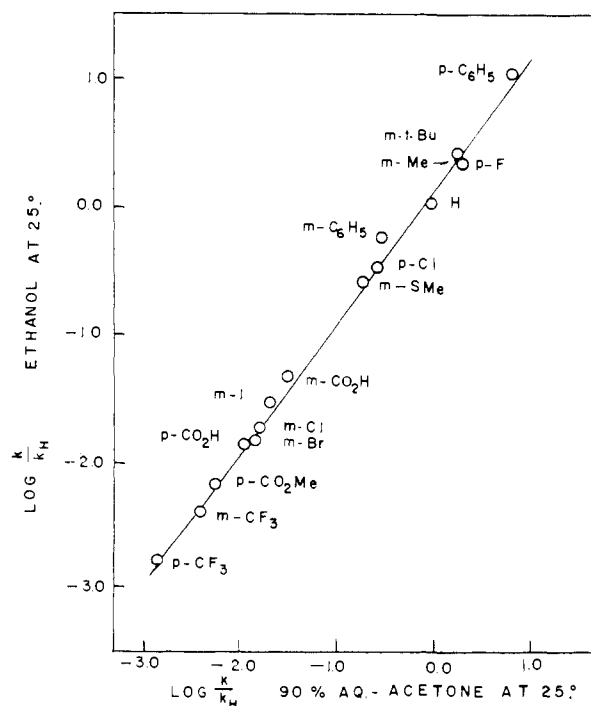

Fig. 2.—Linear free energy relationship between the relative rates of solvolysis of substituted t-cumyl chlorides at 25° in ethanol and in 90% aqueous acetone.

in methanol is calculated as -4.82, in ethanol as -4.67, and in 2-propanol as -4.43.

From these values of ρ and the individual values of log (k/k_H), σ^+ constants have been calculated.

The data are gathered in Table III to permit comparison of the values derived from the solvolysis data in ethanol with the constants based on the solvolysis results in 90% acetone. It is evident that σ^+-constants derived from solvolysis data in alcoholic solvents agree closely with the standard set based on the solvolysis results in 90% acetone.
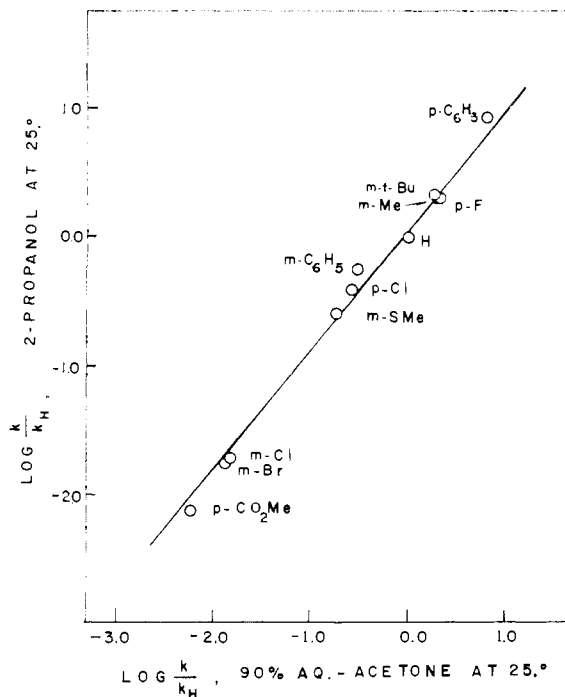

Fig. 3.—Linear free energy relationship between the relative rates of solvolysis of substituted t-cumyl chlorides at 25° in isopropyl alcohol and in 90% aqueous acetone.

In comparing the σ^+-constants derived from the different solvents, it should be recalled that Hammett σ-constants based on thermodynamic dissociation constants of benzoic acids in water have an estimated uncertainty of ±0.02 unit, and such constants calculated from data in non-aqueous solvents have an estimated uncertainty of ±0.05 to ±0.10 unit.[8] In Table III σ^+-constants are given to three significant figures for convenience in calculating deviations. In actual use, both σ- and σ^+-constants should not be considered to be defined to more than two significant figures.

It is pertinent to enquire into possible reasons for the observed variation in the k/k_H values in the different solvents. One reason is that the dielectric constants of the solvents differ considerably. Possibly that portion of the effect of the substituent which is transmitted through the solvent is altered sufficiently by changes in the solvent, so as to result in significant changes in the influence of the substituent.

The precise degree of bond-breaking in the transition state should also vary with the solvent. Depending upon the precise nature of the transition state, the incipient carbonium ion may make greater or lesser electronic demands upon the substituent.

(8) D. H. McDaniel and H. C. Brown, J. Org. Chem., **23**, 420 (1958).

TABLE III

ELECTROPHILIC CONSTANTS DERIVED FROM THE SOLVOLYSIS OF t-CUMYL CHLORIDES IN VARIOUS SOLVENTS

Substituent	90% Acetone[a] $\log(k/k_H)$	σ^+	Methanol[b] $\log(k/k_H)$	σ^+	Ethanol[c] $\log(k/k_H)$	σ^+	2-Propanol[d] $\log(k/k_H)$	σ^+
p-Phenyl	0.814	−0.179	.....	.....	1.021	−0.219	0.934	−0.211
m-Phenyl	− .495	.109	.....	.....	−0.260	.056	− .264	.060
p-Fluoro	.330	− .073	.....	.....	.312	− .067	.306	− .068
m-Methyl	.301	− .066	0.362	−0.075	.358	− .077	.312	− .070
m-t-Butyl	.268	− .059	.367	− .076	.393	− .084	.318	− .072
m-Methylthio	− .717	.158	.....	.....	− .582	.125	.....	.....
p-Chloro	− .516	.114	− .536	.111	− .503	.108	− .458	.103
m-Chloro	−1.811	.399	−1.804	.374	−1.760	.377	−1.733	.391
m-Bromo	−1.842	.405	−1.799	.373	−1.783	.382	−1.750	.395
m-Iodo	−1.633	.359	−1.609	.334	−1.553	.333	.....	.....
m-Carboxy	−1.462	.322	.....	.....	−1.357	.291	.....	.....
p-Carboxy	−1.907	.421	.....	.....	−1.863	.399	.....	.....
p-Carbomethoxy	−2.218	.489	−2.228	.462	−2.178	.466	−2.106	.475
m-Trifluoromethyl	−2.356	.520	−2.413	.501	−2.413	.517	.....	.....
p-Trifluoromethyl	−2.780	.612	−2.886	.599	−2.783	.596	.....	.....
m-Nitro	−3.060	.674	−3.243	.673	.....	.....	.....	.....
p-Nitro	−3.590	.790	−3.851	.799	.....	.....	.....	.....

[a] $\rho = -4.54$.   [b] $\rho = -4.82$.   [c] $\rho = -4.67$.   [d] $\rho = -4.43$.

TABLE IV

EFFECT OF SOLVENT ON THE RELATIVE RATES OF $meta$ AND $para$ ISOMERS IN SOLVOLYSIS OF t-CUMYL CHLORIDES

	90% Acetone k_p/k_m	$\frac{1}{\rho}\log\frac{k_p}{k_m}$	Methanol k_p/k_m	$\frac{1}{\rho}\log\frac{k_p}{k_m}$	Ethanol k_p/k_m	$\frac{1}{\rho}\log\frac{k_p}{k_m}$	2-Propanol k_p/k_m	$\frac{1}{\rho}\log\frac{k_p}{k_m}$
Substituent				Solvent				
Phenyl	20.4	−0.288			19.2	−0.275	15.8	−0.271
Chloro	19.5	− .285	18.6	−0.263	18.1	− .269	18.8	−0.288
Carboxy	.360	.099			.312	.108		
Trifluoromethyl	.377	.092	.377	.098	.425	.079		
Nitro	.295	.116	.247	.126				

Finally, the substituents themselves are presumably solvated in these solutions. Such solvation should be expected to vary from solvent to solvent and thereby alter somewhat the electronic influence of the substituent.

The magnitude of the latter effect might be expected to depend primarily upon the nature of the substituent and only weakly upon its position in the aromatic ring. Consequently, a solvent which strongly influences a given substituent through solvation would be expected to have a similar effect on both the $meta$ and $para$ derivative.

The existence of this factor is strongly indicated by the experimental data (Table I). For example, the k/k_H ratio for p-phenyl increases from 6.52 in 90% acetone to 10.5 in ethanol. At the same time, the k/k_H ratio for m-phenyl increases from 0.320 to 0.549 in the same solvents. Likewise m-nitro exhibits a ratio of 0.000871 in 90% acetone and 0.000571 in methanol, while p-nitro exhibits the values 0.000257 and 0.000141 in the same two solvents.

To test this possibility further, the k_p/k_m ratios have been calculated for the five isomer derivatives (Ph, Cl, CO₂H, CF₃, NO₂) for which rate data are available in two or more solvents. These ratios exhibit a considerably better approach to constancy than do the k/k_H ratios. The data are summarized in Table IV, together with values of $1/\rho \log (k_p/k_m)$ = $\sigma_p^+ - \sigma_m^+$. Consequently, it appears that solvation of substituents does play a role in modifying its electronic contributions from solvent to solvent.

This discussion of the minor deviations which are

TABLE V

RATE DATA FOR THE SOLVOLYSIS OF t-CUMYL CHLORIDE IN ETHANOL AT 25°

Time, hr.	x, ml.	$a - x$, ml.	k, hr.$^{-1}$
0	1.390	12.77	
0.050	2.250	11.91	1.39
.100	3.050	11.11	1.40
.167	4.050	10.11	1.40
.217	4.800	9.36	1.43
.300	5.840	8.31	1.43
.350	6.430	7.73	1.43
.450	7.480	6.68	1.44
∞	14.160		

Average 1.42 ± 0.02

observed in the linear free energy relationship should not permit attention to be distracted from the excellent correlation exhibited by the solvolysis data (Figs. 1–3), as well as from the excellent agreement realized between the electrophilic substituent constants based on solvolysis data in 90% acetone and those calculated from the alcoholic solvents (Table III). Use of ethanol as a solvent to determine the σ^+-constant for the carboxylate group is reported in the following paper.

Experimental Part

Solvents.—The purest available methyl, ethyl and isopropyl alcohol were dried over Drierite and distilled through a fractionating column. The center fractions were used for the rate studies.

t-Cumyl Chlorides.—The t-cumyl chlorides were prepared from the tertiary carbinols and olefins available from earlier studies.[5] The solvolyses proceeded smoothly, utilizing the

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 ($-NMe_3^+$, $-CO_2^-$) 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-$CO_2^-K^+$, solvolyze at rates somewhat faster than that of t-cumyl chloride: k/k_H for m-$K^+$$^-O_2CC_6H_4C(CH_3)_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-

(1) Directive Effects in Aromatic Substitution. XXIX.

(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 said fund.

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

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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-