with this solvent change, solvation at sites acquiring increasing positivity on excitation becomes relatively *more* important than solvation at sites that decrease in positivity on excitation. For the neopentyl compound, by contrast, there is actually a slight blue shift accompanying this solvent change. This indicates that solvation at sites acquiring increased positivity on excitation is becoming relatively somewhat *less* important than solvation at sites that decrease in positivity on excitation. Thus the importance of ring solvation relative to functional group solvation appears to be greater for the hydrogen compound than for the neopentyl compound. A factor in this could be steric hindrance to ring solvation or, alternatively, steric hindrance to hydrogen bonding solvation of the substituent.

The differing solvent shifts for the 1-hydroxypyridinium ions in proceeding from 70% perchloric acid to 9% perchloric acid to acidic methanol could be rationalized similarly. However, a complicating factor is the question of just how solvation at various sites on these ions is affected by the different dispersal of charge induced by the inherent substituent effect. It is clear that considerably more experimental data on the spectra of the ions in various solutions would have to be amassed before a definite pattern allowing clear-cut decisions about solvation effects in such species could emerge.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE IOWA STATE COLLEGE]

Benzyl Tosylates. IV. Halogen Substituent Effects[1]

BY FABIAN T. FANG, JAY K. KOCHI AND GEORGE S. HAMMOND

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All eight *m*- and *p*-halobenzyl tosylates have been prepared. The rates of solvolysis of these compounds have been determined in 55.6% aqueous acetone at 25° and correlation with the Hammett equation has been attempted. The magnitude of deviations of the *p*-halogen substituents from their normal σ-constants follow the order p-F > p-I > p-Cl > p-Br, whereas the *m*-halogen substituents all have negative $\Delta\sigma$-values. These observations are discussed in terms of transition-state resonance and by comparison with similar systems. The unusual rate-enhancing influence of iodine has been further ascertained by solvolysis of the two iodobenzyl tosylates in dioxane–water and acetone–water mixtures of varying composition.

Recent work in this Laboratory showed that the solvolysis of *m*- and *p*-substituted benzyl tosylates gives a limited correlation with the Hammett equation.[2,3] Donor substituents such as methoxyl and methyl in the *p*-position provide exceptionally large driving forces above those to be expected from their normal σ-constants. That these deviations are due to important contributions of transition-state resonance is shown by the relatively normal behavior of *m*-methoxy- and *m*-methylbenzyl tosylates. This is reminiscent of the deviations of acceptor substituents such as *p*-nitro in the reactions of substituted phenols and anilines. These are reactions which involve the freeing of an electron-pair whereas in the solvolysis of benzyl tosylates the vacating of an orbital is important in stabilizing the transition state.

The sensitivity of the solvolysis of benzyl tosylates to substituent effects as indicated by the large negative ρ-values[2,3] has prompted an investigation of the behavior of the *m*- and *p*-halogenated compounds. There has been substantial disagreement in the literature as to the relative effects of halogen substituents. It was felt that the solvolysis of halobenzyl tosylates would make a good case for the evaluation of the polar effects of these substituents. The deviation from the Hammett σ-constant can be taken as a measure of the ability of a substituent to accommodate a positive charge in the transition state regardless of the origin of the stabilizing influence. Since the completion of our work the results of a similar study of halogen substituent effects on the solvolysis of phenyldimethylcarbinyl chlorides has been published.[4]

Previous work in this Laboratory included the solvolysis of *p*-fluoro- and *p*-chloro-,[3] *m*- and *p*-bromobenzyl tosylates[2] in various solvent systems. In order to ensure a fair correlation, all eight *m*- and *p*-halobenzyl tosylates have been prepared and their rates of solvolysis have been determined in the same mixed solvent, namely, 55.6% aqueous acetone. In addition, the rates of solvolysis of the two iodobenzyl tosylates have been measured in five other dioxane–water and acetone–water mixtures of low dielectric constants and varying composition.

Experimental[5]

Preparation and Purification of Materials. Benzyl Alcohol.—The commercial alcohol (Matheson, Coleman and Bell, chlorine-free) was distilled under reduced pressure through a glass helices packed column, b.p. 91.9–92.4° (11.5 mm.).

Halobenzyl Alcohols.—All except *m*-fluorobenzyl alcohol were prepared from the corresponding benzoic acids by reduction with lithium aluminum hydride.[6] Most of the commercial acids were purified by recrystallization from ethanol followed by vacuum sublimation. This procedure was found to increase the ease of purification of the benzyl alcohols. The liquid alcohols were purified by distillation under

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[1] Presented in part before the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[2] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

[3] G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *ibid.*, **80**, 568 (1958).

[4] H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957).

[5] All melting and boiling points are uncorrected.

[6] W. G. Brown, in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 491.

reduced pressure and the solid alcohols were purified by recrystallization from mixtures of benzene and petroleum ether (64–67°, Skellysolve B). The average yields of preparation are given in Table I.

TABLE I

PREPARATION OF HALOBENZYL ALCOHOLS BY $LiAlH_4$ REDUCTION

Alcohol	M.p. or b.p. (mm.), °C.	Yield, %
p-Fluorobenzyl	59-59.5 (1.0)	78
m-Chlorobenzyl	81.5-82.5 (1.1)	84
p-Chlorobenzyl	71.5-72.5	81
m-Bromobenzyl	90.5-92 (0.65)	74
p-Bromobenzyl	78.5-79	78
m-Iodobenzyl	104.5-105 (0.45)	37
p-Iodobenzyl	73.5-74	26

Considerable amounts of benzyl alcohol also were obtained in each of several preparations of *m*- and *p*-iodobenzyl alcohols.

m-Fluorobenzyl alcohol was prepared from *m*-fluorobenzyl bromide *via* the acetate according to the procedure of Melstrom.[7] *m*-Fluorotoluene was brominated by the procedure of Vaughan and co-workers.[8]

***p*-Toluenesulfonyl Chloride.**—The commercial material (Eastman Kodak Co., reagent grade) was melted and taken up in a small amount of benzene. The benzene solution was filtered and treated with low boiling petroleum ether (Skellysolve A) in the cold to recrystallize very pure tosyl chloride, m.p. 69–70°.

Halobenzyl *p*-Toluenesulfonates.—The tosylates of the halobenzyl alcohols were prepared by the method previously described[9] with slight modification. The benzyl alcohol was allowed to react with sodium hydride in ether over a lengthy period of time and the suspension of the sodium benzyloxide was treated at low temperatures (*ca.* −25°) with an ethereal solution of an equimolar amount of tosyl chloride. The reaction mixture was stirred for several hours at room temperature and then filtered under nitrogen through a medium-grade sintered glass funnel. The clear ethereal filtrate was concentrated or evaporated to dryness. The crude tosylate was recrystallized several times from cold mixtures of benzene and petroleum ether. The pure products again were dissolved in anhydrous benzene and stored as such in a desiccator in the dark. The tosylates were characterized by quantitative sulfur analyses and determinations of solvolysis equivalents as previously described.[9] The melting points and analytical data are listed Table II.

TABLE II

HALOBENZYL TOSYLATES

Benzyl tosylate	Melting point, °C.	Mol. weight	Solvolysis equiv.	Sulfur, % Calcd.	Sulfur, % Found
m-Fluoro-	54.2–54.7	280.3	279	11.44	11.39
p-Fluoro-	56.2–56.7 (54–55[a])	280.3	280	11.44	11.50
m-Chloro-	81.5–82.0	296.8	297	10.80	10.83
p-Chloro-	53.0–53.5 (52.8–53.0[a])	296.8	296	10.80	10.85
m-Bromo-	102.3–102.6 (105.2–105.6[b])	341.2	341	9.40	9.36
p-Bromo-	74.8–75.2 (76.8–77.5[b])	341.2	341	9.40	9.38
m-Iodo-	117.0–117.5	388.2	389	8.26	8.25
p-Iodo-	92.5–92.8	388.2	389	8.26	8.30

[a] Ref. 3. [b] Ref. 2.

Acetone.—Commercial acetone (J. T. Baker, analyzed reagent) was refluxed with and distilled from potassium permanganate, dried over anhydrous potassium carbonate and then redistilled through a 60-cm. helices-packed and vacuum-jacketed column. The center fraction, b.p. 55.1° (752 mm.), was collected.

Dioxane.[10]—A mixture of 2.2 l. of commercial dioxane (J. T. Baker, technical grade), 30 ml. of concentrated hydrochloric acid and 220 ml. of water was refluxed for 11 hours, during which time a slow stream of nitrogen was bubbled through the solution to entrain acetaldehyde. The solution was cooled, treated repeatedly with potassium hydroxide pellets to remove adhering aqueous liquor, decanted, refluxed with metallic sodium for 20 hours, and then distilled through the glass helices packed column. The center fraction, b.p. 99.0° (734 mm.), was collected.

Triethylamine.—The commercial amine (Matheson, Coleman and Bell) was refluxed over metallic sodium for 0.5 hour and then distilled through the glass helices packed column. The center fraction, b.p. 86.8° (726 mm.), was collected. The titrant solutions of triethylamine in various solvolytic media were standardized directly with potassium acid phthalate in aqueous solution using phenol red as indicator.

Lithium Perchlorate.—Commercial lithium perchlorate trihydrate (G. F. Smith Chemical Co.) was dehydrated by heating under reduced pressure at about 145° for 10 hours.

Indicators.—A 0.1% solution of brom cresol green was prepared by dissolving 0.0793 g. of the indicator (Harleco) in 100 ml. of acetone. A 0.2% solution of methyl red was prepared by dissolving 0.1988 g. of the indicator (Harleco) in a mixture of 20 ml. of water and 100 ml. of acetone. Equal volumes of the two solutions were mixed and used for runs in 55.6% aqueous acetone. Solutions (0.5%) of brom cresol green and brom phenol blue also were prepared and used for solvolysis of the iodobenzyl tosylates in other media.

Determination of Rates of Solvolysis.—The rates of solvolysis of benzyl and halobenzyl tosylates were determined by the rapid intermittent titration method[11,12] as previously modified.[2,3]

The constant-temperature bath was maintained at 25.07 ± 0.02° and the microburet containing the titrant solution was jacketed and thermostated with water at the same temperature.

For solvolytic runs in 55.6% aqueous acetone, the specially constructed reaction cell was fitted with a Beckman No. 1190-42 glass electrode and a Beckman No. 1170 calomel electrode. The mixed solvent was made up with 50 ml. of acetone and 40 ml. of a 0.479 *M* lithium perchlorate solution. The end-point (*p*H 4.5) of titrations was determined potentiometrically with a Beckman model G *p*H meter supplemented by eight drops of the mixed indicator.

Benzyl tosylate was prepared and solvolyzed at various times during the course of this work as a control standard to ensure reproducible experimental conditions.

The unimolecular rate constants were calculated from the integrated form of the rate equation

$$k_1(t_2 - t_1) = \ln \frac{a - x_1}{a - x_a}$$

A typical run is shown in Table III. The rates of solvolysis of all eight halobenzyl tosylates in 55.6% aqueous acetone follow in Table IV.

The solvolysis of the halobenzyl tosylates was found to be neither acid nor base catalyzed. This was determined by alternately allowing the reaction to proceed in basic and acidic solutions. In no case could any correlation be found between the rate constant and the presence of either acid or base.

The rates of solvolysis of benzyl and *m*- and *p*-iodobenzyl tosylates were also measured in two other acetone–water and three dioxane–water mixtures of low dielectric constants and varying composition. The mixed solvents were made up with 50 ml. of organic component and the calculated amount of a 1.04 *M* lithium perchlorate solution. The faster runs in aqueous dioxane mixtures were followed as above by potentiometric determination of end-point (*p*H 6.0) using brom cresol green as supplementary indicator. The slower runs in aqueous acetone mixtures were carried out in tightly stoppered erlenmeyer flasks to avoid evaporation of the organic solvent. The rates were followed by visual titrations using brom phenol blue as indicator. The first-order rate constants are given in Table V.

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(7) D. S. Melstrom, Doctorate Dissertation, Iowa State College, 1943.

(8) J. R. Vaughan, Jr., G. W. Anderson, R. C. Clapp, J. H. Clark, J. P. English, K. L. Howard, H. W. Marson, L. H. Sutherland and J. J. Denton, *J. Org. Chem.*, **14**, 230 (1949).

(9) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **76**, 3443 (1953).

(10) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 284.

(11) R. A. Peters and E. Walker, *Biochem. J.*, **17**, 260 (1923).

(12) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **71**, 1406 (1949).

TABLE III

SOLVOLYSIS OF *p*-CHLOROBENZYL TOSYLATE IN 55.6% AQUEOUS ACETONE AT 25° AND CONSTANT IONIC STRENGTH

Weight of sample, 276.4 mg. (0.9314 mmole); electrolyte, 0.213 *M* $LiClO_4$; normality of titrant, 0.1429; infinite titer, 6.306 ml.

Volume of titrant, ml.	Time increment, sec.	10^4k_1, sec.$^{-1}$	Reaction, %
0.244			3.9
0.562	459.7	1.17	8.9
1.150	882.7	1.22	18.2
1.564	690.5	1.21	24.8
2.055	896.5	1.22	32.6
2.570	1051.4	1.23	40.8
3.060	1137.0	1.24	48.5
3.498	1151.8	1.26	55.5
3.990	1519.5	1.27	63.3
4.410	1604.1	1.25	69.9
4.820	1937.5	1.25	76.4
5.225	2464.2	1.29	82.9
5.558	2910.1	1.27	88.1
5.869	4189.5	1.28	93.1
6.112	6596.1	1.23	96.9
	Average	1.24	

TABLE IV

RATES OF SOLVOLYSIS OF BENZYL AND HALOBENZYL TOSYLATES IN 55.6% AQUEOUS ACETONE AT 25° AND CONSTANT IONIC STRENGTH

Substituent	10^4k_1, sec.$^{-1}$	Substituent	10^4k_1, sec.$^{-1}$
H	2.31	*m*-F	0.236
p-F	5.96	*m*-Cl	.196
p-Cl	1.24	*m*-Br	.204
p-Br	1.00	*m*-I	.261
p-I	1.14		

TABLE V

RATES OF SOLVOLYSIS OF BENZYL AND IODOBENZYL TOSYLATES AT 25°

Aqueous solvent	First-order rate constants × 10^5, sec.$^{-1}$ Benzyl	*m*-Iodobenzyl	*p*-Iodobenzyl
55.6% dioxane	46.3	....	23.2
66.7% dioxane	13.0	1.51	6.88
76.9% dioxane	3.76	0.595	2.29
55.6% acetone	23.1	2.61	11.4
83.3% acetone	1.06	0.214	0.636
90.9% acetone	0.268	0.0639	0.175

Deviation from first-order kinetics was observed in the hydrolysis of *m*-iodobenzyl tosylate in 55.6% aqueous dioxane. The calculated unimolecular rate "constants" increase as the reaction proceeds, reach a maximum at about 60% reaction, and then fall off. One of several such runs is shown in Table VI.

Results and Discussion

An examination of Table IV reveals that the absolute rate of solvolysis of *p*-fluorobenzyl tosylate in 55.6% aqueous acetone at 25° more than doubles that of the unsubstituted benzyl compound. *p*-Iodobenzyl tosylate is found to solvolyze at a rate higher than that of the *p*-bromo compound and *m*-iodobenzyl tosylate has beyond any doubt the highest absolute rate of solvolysis among the four *m*-substituted compounds.

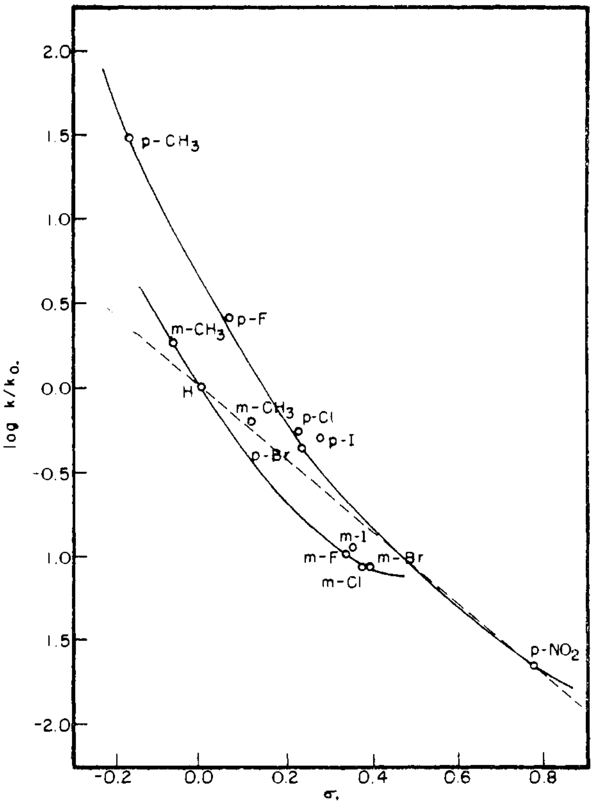

Fig. 1.—Swain–Langsdorf plot for solvolysis of substituted benzyl tosylates in 55.6% aqueous acetone at 25°.

TABLE VI

HYDROLYSIS OF *m*-IODOBENZYL TOSYLATE IN 55.6% AQUEOUS DIOXANE AT 25°

Weight of sample, 282.9 mg. (0.7287 mmole); electrolyte, 0.476 *M* $LiClO_4$; normality of titrant, 0.1471; infinite titer, 4.804 ml.

Volume of titrant, ml.	Time increment, sec.	10^4k_1, sec.$^{-1}$	Reaction, %
0.192			4.0
.329	1590	1.90	6.8
.519	2265	1.92	10.8
.760	2966	1.95	15.8
1.207	5642	2.08	25.1
1.540	4186	2.32	32.1
1.749	2652	2.50	36.4
1.934	2373	2.63	40.3
2.174	3052	2.86	45.3
2.704	6986	3.22	56.3
3.072	5691	3.39	63.9
3.231	2742	3.51	67.3
3.390	3096	3.44	70.6

The logarithms of these rate constants relative to that of the unsubstituted benzyl tosylate are plotted against the Hammett σ-values for the corresponding substituents in Fig. 1. The graph includes also corrected data[13] for *m*- and *p*-methyl-, *m*-methoxy- and *p*-nitrobenzyl tosylates, which were studied previously[2] in this Laboratory. The scatter of the points indicates a rather poor correlation with the Hammett equation. The deviations of the halobenzyl tosylates from a linear relationship can be visualized more clearly in Table VII, which lists for each substituent the Hammett σ-value, the modified σ′-value as calculated from ρ

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[13] The constant factor, ln 10 = 2.303, was neglected in the calculation of all rate constants in ref. 2.

$= -2.20$, and the difference $\Delta\sigma = \sigma - \sigma'$. It is interesting to note that the extraordinary reactivity of *p*-fluorobenzyl tosylate results in a negative σ'-value. The $\Delta\sigma$-values for the *p*-halogen substituents follow the order *p*-F > *p*-I > *p*-Cl > *p*-Br. The *m*-halogen substituents all have negative $\Delta\sigma$-values, which means that the tosylates all solvolyze at rates lower than those to be expected from their "normal" σ-constants. It should be pointed out, however, that *m*-iodo has the least negative deviation in the group.

TABLE VII

σ-VALUES FOR SOLVOLYSIS OF HALOBENZYL TOSYLATES IN 55.6% AQUEOUS ACETONE AT 25°

Substituent	k/k_0	σ	σ'	$\Delta\sigma$
H	1.00	0.000	0.000	0.000
p-F	2.58	.062	− .187	.249
p-Cl	0.537	.226	.123	.103
p-Br	.433	.232	.165	.067
p-I	.494	.276	.139	.137
m-F	.102	.337	.450	− .113
m-Cl	.0849	.373	.487	− .114
m-Br	.0883	.391	.479	− .088
m-I	.113	.352	.430	− .078

Our interpretation of these data is substantially the same as that of Brown[4] with one exception. Even though the electronegativities of the halogens follow the order F > Cl > Br > I, it is known that these substituents often do give rate or equilibrium constants of opposite order to that expected from their inductive effects. This reversal of relative reactivities has been explained on the basis that the halogens can partially donate their outer-orbital, non-bonding electrons to the π-orbitals of an aromatic nucleus or similar systems. The capacity of the halogens for entering into such resonance has been thought to decrease in the order F > Cl > Br > I, with fluorine having a much greater ability to do so than the rest.[14,15] The solvolysis of *p*-fluorobenzyl tosylate thus provides another striking example in which the conjugative effect of the substituent far outweighs its inductive effect.

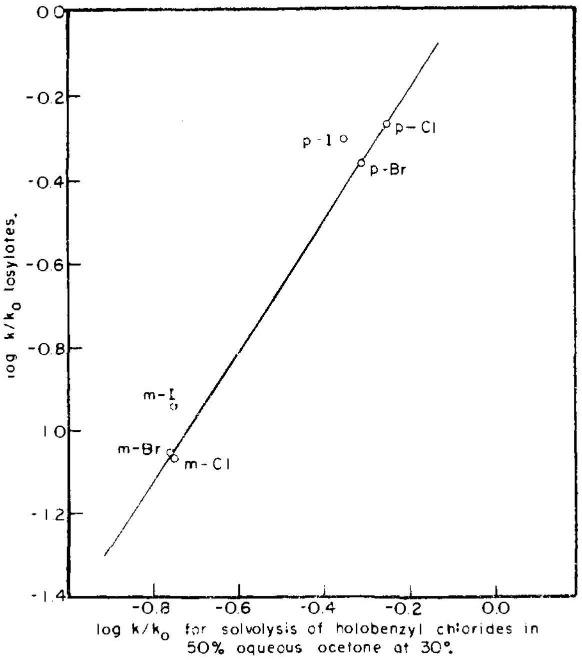

Fig. 2.—Correlation of rates of solvolysis of halobenzyl tosylates and halobenzyl chlorides.

While the behavior of *p*-fluorobenzyl tosylate is readily accounted for in terms of transition-state resonance and may have been predicted, the extra rate-enhancing influence of iodine seems to be rather unusual. In Table VIII are listed the σ-values for solvolysis of *m*- and *p*-iodobenzyl tosylates in three dioxane–water and three acetone–water mixtures of varying composition. The σ'-values are calculated from ρ-values as determined previously in this Laboratory.[2,3] The magnitudes of deviations of *m*- and *p*-iodo from the corresponding Hammett σ-constants are established beyond doubt.

It has been pointed out repeatedly in the literature that displacement and solvolysis reactions on benzylic systems do not give good linear Hammett relationship and that ρ is difficult to define for such systems.[2-4,16-18] Swain and Langsdorf used two curves to correlate the rate of these reactions. One curve accommodates unsubstituted and *m*-substituted compounds and the other accommodates *p*-substituted compounds.[16] The theoretical basis for this treatment is not clear but satisfactory plots can be made for a number of reactions. Figure 2 shows the result of applying such a treatment to the rates of solvolysis of the benzyl tosylates. The broken line is the best straight line excluding the points for *p*-CH_3 and *p*-OCH_3. It can be seen that most of the points fall on the curves while *m*- and *p*-iodo deviate from their respective curves by about the same extent. According to Swain and Langsdorf their curves take into account contributions of transition-state resonance. If the assumption is proper, deviations from the relationship should be due to some effect other than resonance interaction in the transition state. The fact that *m*-iodobenzyl tosylate also deviates significantly supports this view.

TABLE VIII

σ-VALUES FOR SOLVOLYSIS OF IODOBENZYL TOSYLATES AT 25°

Aqueous solvent	ρ	$\sigma'_{m\text{-I}}$	$\Delta\sigma_{m\text{-I}}$	$\sigma'_{p\text{-I}}$	$\Delta\sigma_{p\text{-I}}$
55.6% dioxane	−2.46	...	.....	0.122	0.154
66.7% dioxane	−2.15	0.432	−0.080	.126	.150
76.9% dioxane	−1.91	.424	− .072	.114	.162
55.6% acetone	−2.20	.430	− .078	.139	.137
83.3% acetone	−1.60	.430	− .078	.138	.138
90.9% acetone	−1.43	.434	− .082	.133	.143
		$\sigma_{m\text{-I}}$	.352	$\sigma_{p\text{-I}}$	.276

It has been shown that a linear correspondence exists between the solvolysis of benzyl chlorides and the solvolysis of benzyl tosylates.[2] A straight line is obtained when the rates of solvolysis of the

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(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter II.

(15) J. W. Baker and H. B. Hopkins, *J. Chem. Soc.*, 1089 (1949).

(16) C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

(17) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 646 (1956).

(18) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 185 (1957).

chlorides[19,20] are plotted against those for the tosylates on a logarithmic scale. This treatment provides a convenient way to compare reactions and correlate substituent effects when the applicability of the Hammett equation is in doubt. Such a plot has been made for the halogenated compounds and is shown in Fig. 3. It is obvious that both *m*- and *p*-iodo deviate from the straight line and by about the same magnitude. This again indicates without going through the Hammett relationship that both *m*- and *p*-iodobenzyl tosylates are associated with an unusual enhanced reactivity in solvolysis. It is well known that tosylate is a better departing group than chloride in solvolytic reactions. On the other hand, if logarithms of the relative rates for the solvolysis of *p*-halobenzyl tosylates are plotted against those for the solvolysis of *p*-halobenzhydryl chlorides,[21] a good straight line is obtained as shown in Fig. 3. Whatever extra rate-enhancing influence iodine has in the solvolysis of benzyl tosylates must therefore also exist in the solvolysis of benzhydryl chlorides. The additional stabilization of the transition state provided by the second benzene ring appears to compensate for the relative impotence of chloride as a leaving group.

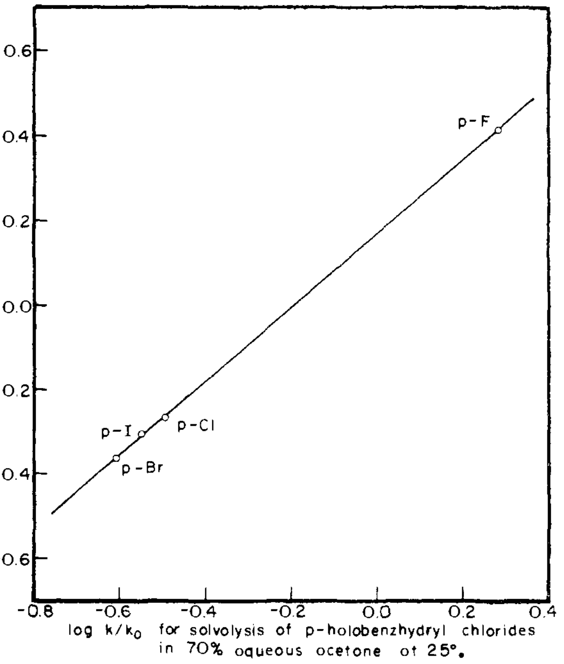

Fig. 3.—Correlation of rates of solvolysis of *p*-halobenzyl tosylates and *p*-halobenzhydryl chlorides.

Okamoto and Brown recently claimed the existence of a linear relationship between the solvolysis of *m*- and *p*-substituted phenyldimethylcarbinyl chlorides and various aromatic substitution and electrophilic reactions.[18] Figure 4 shows a plot of the rates of solvolysis of halobenzyl tosylates against partial rate factors for the nitration of halobenzenes as determined by Roberts and coworkers.[22] *p*-Fluoro is far out of line, possibly because transition-state resonance does not seem to have played as important a role in the nitration of fluorobenzene as it does in the solvolysis of the tosylate.

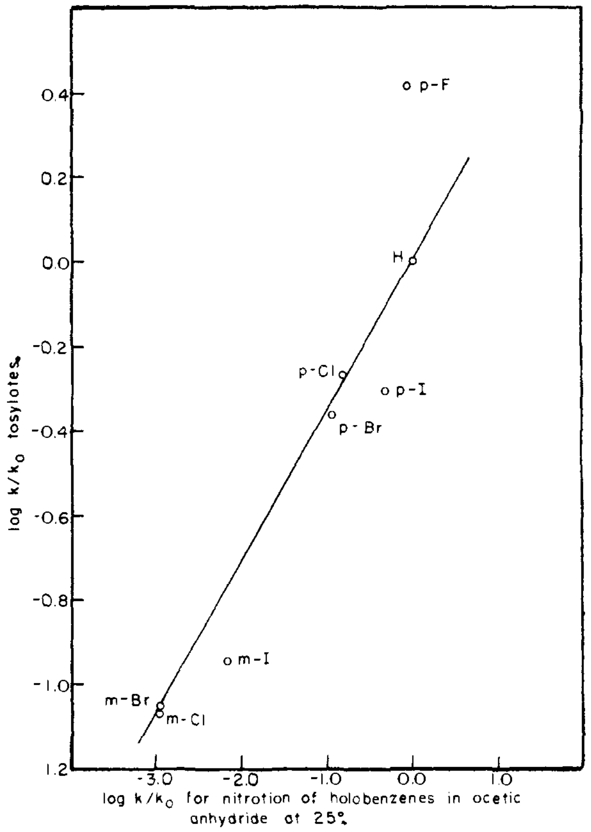

Fig. 4.—Correlation of rates of solvolysis of halobenzyl tosylates and nitration of halobenzenes.

These data show that there is a close association between "deviations" shown by *m*- and *p*-iodo which is not always reflected in the behavior of *p*-fluoro. Purely empirical reasoning leads us to the conclusion that iodine must be responding to long range electrostatic effects because of its high polarizability. Fluorine, on the other hand, shows the specific *para* effect which is associated with resonance interactions.

Adoption of this view, which is compatible with the large magnitude of substituent effects in aromatic nitration, compels some special explanation of the meager influence of *p*-fluoro in nitration. We have no firm convictions as to the nature of the effect, but it is possible that the availability of fluorine non-bonding electrons is decreased by hydrogen bonding to the solvent in the highly acidic nitration medium.

The analysis of halogen substituent effects is partially independent of the fine details of the model chosen to represent the solvolysis process. What is demonstrated is that there are discontinuities in the empirical correlation of substituent effects which show that both *meta* and *para* iodine have exceptional properties. In discussion we

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[19] S. C. J. Olivier, *Rec. trav. chim.*, **49**, 697 (1930); **56**, 247 (1937).

[20] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

[21] E. D. Hughes and G. Kohnstam, personal communication quoted in ref. 14, p. 332.

[22] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, THIS JOURNAL, **76**, 4525 (1954).

have assumed tacitly that solvolysis involves a carbonium ion mechanism, but the observed increase in the iodine effect with increasing electrostatic field strength in transition state would also follow even if considerable emphasis were laid upon nucleophilic attack by solvent. Conversely, the results reported here do not establish limiting character of benzyl solvolysis (see also reference 3).

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AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE IOWA STATE COLLEGE]

The Solvolysis of Benzyl Tosylates. V. Some Solvent Effects

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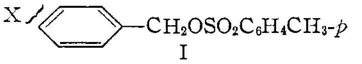
The rates of solvolysis of several benzyl tosylates have been studied at three temperatures in a group of acetone–water and dioxane–water solvents. The correlation of the rates as a function of solvent composition is best accomplished by an empirical function of the molar concentration of water. The substituent effects fit neither the Hammett equation nor Brown's σ^+-treatment. The variations of substituent effects with medium indicate a systematic variation in a single mechanism rather than a clear-cut separation of the reactions into two distinct mechanistic types. Interesting variations in the activation entropies also are noted.

In earlier work we found that the rates of solvolysis of substituted benzyl tosylates I in the solvent "55 volume %" acetone–water (prepared from 55 volumes of acetone and 45 volumes of water) showed interesting and qualitatively understandable deviations from the Hammett ρ–σ relationship.[1]



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Donor substituents in the *p*-position supplied a larger driving force than would have been anticipated by a normal Hammett relationship. The result is attributed to the resonance interaction between the substituent and an electron deficiency created at the benzyl carbon atom during the course of the solvolysis. Many other examples of similar deviations from the original Hammett relationship are known.[2,3]

One might hope to use the solvolysis of benzyl systems as a probe in the study of fine details of solvolytic processes. Variations in the magnitude of substituent effects might well provide a measure of the relative importance of carbonium ion character in the reaction transition states. If all other factors could be maintained constant the absolute magnitude of the reaction constant, ρ, could be expected to increase with increasing concentration of positive charge in the functional group.[4] In actual practice "other factors" can never be held constant and one must proceed semi-empirically while keeping a cautious eye on the importance of factors such as reaction molecularity, specific solvation effects and short range dielectric effects on the interaction between polar substituents and the site of the reaction.

In the present work we have chosen to vary the solvolysis media. Several tosylates were solvolyzed in a series of solvent mixtures at three different temperatures. The mixtures were made up by blending water with dioxane or acetone. Two different cosolvents were used in the hope that additional information could be inferred from the correlation of the rate data obtained from the two sets of media.

An additional feature of the study has arisen subsequent to the completion of the work reported in this paper. Okamoto and Brown[2,3] have suggested that a single set of substituent constants, designated by σ^+, can be used to correlate the partial rate factors for a variety of aromatic substitution reactions with other electrophilic reactions such as the solvolysis of phenyldimethylcarbinyl chlorides[5] and the ionization of triarylcarbinols.[6] Our original data[1] are exceptional in that they do not fit a rather general relationship.[3] Since the existence of a set of unique σ^+-values is surprising in itself, we were particularly interested in reviewing our data.

Results and Discussion

Correlation of Rate with Solvent Composition.—It is a well known fact that solvolysis rates rise rapidly with an increase in the concentration of hydroxylic constituents, especially water, in solvent mixtures. The reason for the increase is not clear since water and related compounds should provide both nucleophilic and electrophilic solvation and will often increase the dielectric constants of solvent mixtures. In an attempt to understand the basis for the observed effects we have sought some function of composition which serves to unify the effects of adding water to both acetone and dioxane. We investigated various functions of composition such as dielectric constant, water activity and mole fraction. In no case were the results encouraging. The familiar dielectric function,[7] $(D - 1)/(2D + 1)$, has been shown to be a near linear

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(1) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445, 3452 (1953).

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

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

(4) C. G. Swain, THIS JOURNAL, **72**, 4583 (1950).

(5) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957); H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); and H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1909 (1957).

(6) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).