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Benzyl Tosylates. II. The Application of the Hammett Equation to the Rates of their Solvolysis

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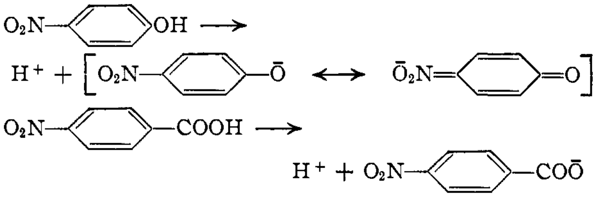
The rates of solvolysis of *m*- and *p*-substituted benzyl tosylates have been studied in acetone–water mixtures. A limited correlation with the Hammett equation is observed. The value of ρ for the solvolysis in 76.6 mole per cent. aqueous acetone is -2.20 ± 0.07. Using this value for ρ apparent values of σ for *p*-methyl and *p*-methoxyl become -0.63 and -2.5, respectively. However, the σ-constants for *m*-methoxyl and *m*-methyl agree well with those derived from the ionization constants of the substituted benzoic acids.

The correlation of the reaction rates and equilibria of meta and para substituted derivatives of benzene has been achieved by use of the Hammett equation.[1] The applicability of this empirical equation in many reaction series is a well-established fact.

There are certain other cases, however, in which the Hammett relationship does not hold. For example, it is necessary to assign two values of the substituent constant (σ) to the *p*-nitro group, one for the reactions of phenols and anilines and another for the reactions of other derivatives. This abnormal behavior of *p*-nitrophenol (and *p*-nitroaniline) has been attributed by Branch and Calvin[2] to the strong resonance interaction of the substituent group, *p*-nitro, with the aromatic ring. In addition, such substituents as *p*-carbalkoxyl, *p*-cyano,[3] *p*-acetyl,[4] *p*-trifluoromethyl,[5] *p*-methylsulfonyl, sulfone and sulfide[6] show this abnormal behavior.

In the case of the phenols, it is believed that one of the more important causes for deviation from the Hammett equation (*i.e.*, assignment of a different σ-constant) is the additional resonance stabilization of the phenolate anion which is not present in the carboxylate anion. *p*-Nitrophenol may be used to typify the case as shown below.



Whereas the values of the σ-constants as measured by the ionization constants of the benzoic acids represent the perturbations of the substituent group on the acids as well as the carboxylate anion, the same sigma constant would not be expected to represent the analogous situation in the phenol and the phenolate anion, unless the extent of the interaction of the substituent group with the ring is the same in both the phenol and the acid. It is clear that the latter condition is not satisfied in the case of the *p*-nitro group. Moreover, the extraordinary resonance stabilization of the phenolate anion is not exhibited, as one would surmise, in the case of *m*-nitrophenol nor with the other well-behaved *p*-substituents.

The difference in the two sigma values ascribable to substituents showing abnormal behavior (in the case of phenols) may yield an indication of the extent of the additional stabilization of the substituted phenolate anion in excess of the substituted benzoate anion. This difference, denoted as $\Delta\sigma$ is listed for several substituents in Table I.

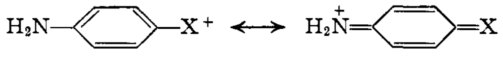
TABLE I

DELTA SIGMA VALUES FOR PHENOLS

Substituent	σ-phenol	σ-acid	$\Delta\sigma$
p-Nitro	1.27	0.78	0.49
p-Cyano	1.00	.66	.34
p-Acetyl	0.87	.43	.44
p-Methylsulfonyl	.98	.72	.26
p-Trifluoromethyl	.73	.53	.20

It is apparent that similar deviations will be observed whenever one deals with a process which involves the *freeing* of an electron-pair in a position conjugated with an unsaturated, acceptor substituent.

A logical extension of this argument would lead one to anticipate that a system in which the vacating of an orbital (formation of an open sextet) is important in stabilizing the product or the transition state would show a correspondingly abnormal behavior in the Hammett relationship. Moreover, those substituents which can donate an electron-pair to the ring (*i.e.*, accommodate a positive charge) would be expected to show deviations. In particular one might expect *p*-amino to show such a behavior because of interactions which may be represented as



Here X represents an atom or a group of atoms.

In order to apply this interpretation, we have sought to investigate the solvolysis of the benzyl system. This system has been used extensively by early workers to study the effects of side chains on reactions of substituted benzene derivatives. In most cases the unimolecular solvolyses[7] were carried out in binary solutions of acetone or alcohol and water. Studies include those by Olivier[8] and

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

[2] G. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 249.

[3] J. D. Roberts and E. McElhill, THIS JOURNAL, **72**, 628 (1950).

[4] F. Bordwell and C. Cooper, *ibid.*, **74**, 1059 (1952).

[5] J. D. Roberts, R. Webb and E. McElhill, *ibid.*, **72**, 409 (1950).

[6] C. C. Price and J. Hydock, *ibid.*, **74**, 1943 (1952); F. Bordwell and C. Cooper, ref. 4; H. Kloosterziel and H. Backer, *Rec. trav. chim.*, **71**, 295 (1952).

[7] E. D. Hughes, *Quart. Revs.*, **5**, 245 (1951); S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

[8] S. Olivier, *Rec. trav. chim.*, **49**, 996 (1930), and earlier papers.

Bennett and Jones[9] of benzyl chlorides in acetone–water solutions, the hydrolysis of benzyl bromides in aqueous alcohol by Shoesmith and Slater,[10] and the alcoholysis of benzhydryl chlorides by Hughes, Ingold and Taher,[11] by Norris and coworkers,[12] and by Altscher, Baltzly and Blackman.[13] An interesting observation was made by Miller and Bernstein[14] who found that the hydrolyses of benzyl fluorides in ethanol–water solutions were acid catalyzed.

A detailed kinetic study of the solvolysis of benzyl chloride and benzyl nitrate in solutions of aqueous dioxane has been made by Hammett and co-workers.[15] They were especially interested in determining the effects of salts on the rates of solvolysis.

We have chosen benzyl tosylates for our study for several reasons. They are all crystalline compounds and the oxygen–carbon cleavage is unambiguous.[16] Most important is the high solvolytic reactivity of tosylates as compared to halides (*e.g.*, EtOTs:EtI:EtBr:EtCl in the ratio 5.5:1.0:0.96:0.048[17]). As was anticipated, this high relative reactivity was reflected in high sensitivity to substituent effects in the benzyl system. Furthermore, the low nucleophilic reactivity of the tosylate ion indicated that the solvolysis kinetics should be relatively free from complications due to the regeneration of the tosylate from carbonium ions and tosylate ion.

Experimental

Materials. Benzyl Tosylates.—The preparation of the benzyl tosylates already has been described in detail.[18]

Acetone.—Stockroom (reagent grade) acetone was treated with potassium permanganate (1 g. per liter) and Drierite (10 g. per liter) for two days at room temperature. The liquid was filtered and then distilled through a five-foot helix-packed, vacuum-jacketed still. A two-hundred milliliter forerun was rejected. Two and a half liters boiling at 55.1° (uncor.) was collected.

Lithium Perchlorate.—Lithium perchlorate ($LiClO_4 \cdot 3H_2O$, G. F. Smith Company) was dehydrated *in vacuo* for 10 hours at 145°. An aqueous solution was made up in a one-liter volumetric flask to 0.479 *M* by dissolving 51.0 g. of the anhydrous salt.

Potassium Nitrate.—Potassium nitrate (Baker and Adamson, reagent grade) was used without further purification.

Triethylamine.—Triethylamine (Eastman Kodak Co., reagent grade) was refluxed over sodium shavings for one-half hour and then distilled through the helix-packed column. From a 100-ml. sample a 25-ml. forerun was separated. Thirty milliliters boiling at 88.0° was collected.

Indicator.—A 0.1% solution of brom cresol green (Harleco) and 0.2% solution of methyl red (Harleco) were prepared in acetone as solvent. A slight amount of water (16% by volume) was necessary to dissolve the methyl red indicator. These two solutions were mixed in equal volumes before use. Eight drops of the mixed indicator was added to each run.

The Kinetics of the Tosylate Solvolysis.—The rate of solvolysis was investigated using the rapid intermittent titration method.[19] The arrangement was modified slightly by the insertion of a glass and a calomel electrode into the cell to supplement the visual indicator. Preliminary comparison studies with visual indicators showed that the response of the glass electrode was sufficiently sensitive in the medium to measure *p*H changes of the order of one-half unit per second. The advantages of the glass electrode over the visual indicator for determining end-points lie in its convenience and in the freedom from personal factors. The *p*H change caused by dilution during a single run can be minimized by adjusting the ratio of the titrant to the solvolyzing solution to a minimum. In most cases the total volume of the titrant added was approximately 4 ml. This represents a dilution of 4% at the end of the run.

The following procedure was used. A weighed amount of tosylate (0.5–1.0 meq.) was transferred to the reaction cell and washed down with 50 ml. (pipet) of anhydrous acetone. The cell was fitted with the electrodes, thermometer, buret and stirrer and then equilibrated in a constant temperature bath maintained at 25 ± 0.03°. In the meantime 40 ml. of 0.479 *M* lithium perchlorate solution was pipetted into a modified fast delivery separatory funnel equipped with a thermometer. This cylinder was immersed in an ice-bath until the temperature of the solution reached 13°, a value which had been calculated to give no temperature rise (due to heat of solution) when the salt solution was added to the acetone solution. The delivery from the cylinder was reproducible to within 0.03 ml. The addition of the lithium perchlorate solution was followed by the addition of eight drops of the indicator solution. The titrant consisted of a solution of triethylamine in the solvolysis medium, 55.6 volume per cent. aqueous acetone, The base maintained its strength for several days after standardization with aqueous hydrochloric acid to the indicator end-point. The remainder of the procedure is similar to the method of Bartlett and Swain, except for the use of the potentiometric determination of the end-points.

Since the majority of the tosylates could not be kept for prolonged periods, it was necessary to prepare and identify the compounds immediately before use. In order to maintain reproducible experimental conditions, benzyl tosylate was used as a control standard. It was solvolyzed at various times to ensure that the conditions were the same in all cases.

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

$$k_1(t_2 - t_1) = \ln(a - x_1)/(a - x_2)$$

A typical run is shown in Table II. In Table III are listed the rates of solvolysis of the benzyl tosylates.

TABLE II

THE SOLVOLYSIS OF BENZYL TOSYLATE IN 76.6 MOLE PER CENT. WATER IN ACETONE AT 25.3° AND CONSTANT IONIC STRENGTH

Vol. titrant added,[a] ml.	Time increment, sec.	$10^6 k_1$, sec.$^{-1}$
1.066	113.5	102.1
1.275	161	105.9
1.480	163	106.6
1.705	184	108.2
1.896	165	106.9
2.094	179	106.6
2.306	198	107.7
2.509	198	108.8
2.704	200	109.7
2.904	216	108.8
3.119	241	111.2
3.301	222	108.1
	av.	108

[a] Weight of sample solvolyzed, 225.2 mg.; normality of triethylamine solution, 0.1351.

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

[10] R. Shoesmith and T. Slater, *ibid.*, 221 (1926).

[11] E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 949 (1940)

[12] J. F. Norris, *et al.*, THIS JOURNAL, **50**, 1795, 1804, 1808 (1928).

[13] S. Altscher, R. Baltzly and S. W. Blackman, *ibid.*, **74**, 3649 (1952).

[14] W. Miller and J. Bernstein, *ibid.*, **70**, 3600 (1948).

[15] G. W. Beste and L. P. Hammett, *ibid.*, **62**, 2481 (1940); G. R. Lucas and L. P. Hammett, *ibid.*, **64**, 1928 (1942).

[16] J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

[17] H. McCleary and L. P. Hammett, THIS JOURNAL, **63**, 2254 (1941).

[18] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3443 (1953).

[19] P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949); W. Peters and S. Walker, *Biochem. J.*, **17**, 260 (1923).

TABLE III

SOLVOLYSIS OF SUBSTITUTED BENZYL TOSYLATES

Tosylate	Wt. used, mg.	$k \times 10^5$, sec.$^{-1}$	Reaction followed, %	Total reaction, %
p-Nitrobenzyl	162.0	0.224	57	95.6
	174.5	0.245	75	97.7
m-Bromobenzyl	174.8	0.880	52	101
	170.7	0.880	67	99.8
	215.4	0.883	77	100
p-Bromobenzyl	201.1	4.30	96	100
	305.3	4.40	97	100
m-Methoxybenzyl	295.1	6.50	63	100
	220.0	6.48	67	99.7
	307.5	6.60	81	97.1
Benzyl	144.2	11.0	66	100
	303.7	10.7	70	100
	315.8	10.3	99	99.1
m-Methylbenzyl	273.9	19.7	91	98.4
	310.0	18.7	84	101
p-Methylbenzyl	266.6	318	97	98.6
	377.7	320	98	99.8
p-Methoxybenzyl	...	480[a]	100	...
	...	450[a]	100	...

[a] Values of the rate constant were determined in 13.5 mole per cent. aqueous acetone.

Rates of solvolysis of the very reactive tosylates in the standard medium (76.6 mole per cent. water in acetone) were much too rapid to measure. In order to measure the rates of these compounds there were two feasible alternatives which could be followed. These two alternatives are: (i) The solvolysis could be carried out at lower temperatures. (ii) The rates could be measured in media of lower water concentration. The latter recourse was chosen. The rates of solvolysis of benzyl and *p*-methylbenzyl tosylates were studied as a function of the water concentration of the medium by the following continuous method.

A weighed amount of tosylate was dissolved in 50 ml. of acetone and an aliquot of aqueous lithium perchlorate was added at the prescribed time in the usual manner. Several kinetic points were then recorded and an aliquot of a second aqueous perchlorate solution was added and the rate was then observed in the new medium. The procedure could be repeated until either the rate became too rapid to measure or the original charge of tosylate was exhausted. In order to maintain constant ionic strength it was, of course, necessary to adjust the perchlorate concentration of the fortifying solution in such a way as to compensate for the change in volume of the solution on addition. The procedure is illustrated by Table IV which shows the actual volume changes resulting from the addition of successive aliquots of a 0.16 *M* perchlorate solution to a solvent which was originally 0.16 *M* perchlorate in 13.5 mole per cent. aqueous acetone. Table V shows the data obtained in a typical run.

TABLE IV

ADJUSTMENTS OF IONIC STRENGTHS

Vol. acetone, ml.	Vol. salt soln. added, ml.	Salt soln., *M*	Total vol. soln., ml.	Total amt. salt, meq.
50	10	1.04	58.5	10.44
50	05	0.16	63.0	11.24
50	10	.16	67.6	12.08
50	15	.16	72.2	12.90
50	20	.16	76.9	13.74
50	25	.16	81.7	14.62
50	30	.16	86.5	15.47

TABLE V

THE SOLVOLYSIS OF *p*-METHYLBENZYL TOSYLATE IN AQUEOUS ACETONE MEDIA OF VARIOUS WATER CONCENTRATIONS AT 25.3°

Vol. titrant[a] added, ml.	Time increment, sec.	Vol. $LiClO_4$[b] soln. added, ml.	$k \times 10^5$, sec.$^{-1}$[c]
0.549	...	10.00	9.17
.650	41.5		9.21
.749	42.0		8.98
.853	44.4		9.02
.950	42.0		8.96
1.073	52.0		9.26
1.149	30.0		10.03
1.201	28.0		9.10
1.607	113.4		9.52
1.771	23.6	5.00	28.9
1.880	17.5		26.4
2.015	22.5		25.7
2.140	21.2		25.5
2.275	24.3		24.4
2.378	18.0		25.4
2.503	22.8		24.6
2.604	20.3		22.8
2.723	19.2		28.6
2.854	25.1		24.3
3.736	86	5.00	50.7
4.416	26.4		55.3
4.594	19.4		52.5
4.716	13.9		51.2
4.987	30.5		53.3
Refill buret			
0.187	...		...
.540	40.4		54.7
.800	31.8		53.6
.913	14.9		51.1
1.059	19.2		52.4
1.224	21.9		53.2
1.789	54	5.00	78.6
2.019	19.0		97.5
2.203	15.8		97.5
2.339	12.2		96.3
2.487	13.6		96.8
2.770	26.1		100.8
3.586	...	5.00	....
4.001	36.8		140.0
4.253	21.8		158.3
4.480	21.0		160.1
4.656	18.6		157.7
Refill buret			
0.308			
0.970			
1.129	27.2		160.5
1.763	...	5.00	....
1.908	34.7		228
2.078	52.0		224
2.195	50.2		205
2.316	66.1		213

[a] Normality of basic titrant, 0.1567. [b] Original 10 ml. was 1.04 *M* $LiClO_4$, fortifying solution was 0.16 *M* $LiClO_4$. [c] Weight of sample solvolyzed, 518.5 mg.

The rates of solvolysis of the reactive tosylates as a function of the water concentration of the solvolysis medium are listed in Table VI. These tosylates include benzyl, *p*-methylbenzyl and *p*-methoxybenzyl. In the case of *p*-methoxybenzyl tosylate the rate constant was obtained in only one medium, 13.5 mole per cent. water in acetone or 2.0 ml. water per 50 ml. of acetone. Even in this medium the rate was much too fast to be followed by one operator. The coördinate efforts of several persons were required. Since the reactivity of *p*-methoxybenzyl tosylate precluded careful techniques, the rate constant for this compound represented in Table VI is reliable only to within 0.005 sec.$^{-1}$.

TABLE VI

RATE CONSTANTS FOR THE SOLVOLYSIS OF SOME SUBSTITUTED BENZYL TOSYLATES AS A FUNCTION OF THE WATER CONCENTRATION

Water, mole per cent.[a]	$k \times 10^5$, sec.$^{-1}$ Benzyl	p-Methylbenzyl	p-Methoxybenzyl
13.5	....	0.541	460
29.0	0.103	1.98	...
44.8	0.415	9.40	...
55.0	1.02	25.1	...
62.0	1.93	54.1	...
67.0	3.05	98.2	...
71.1	4.81	154	...
74.1	7.50	230	...
76.6	10.7	319	...

[a] All runs were made at 25.3° and constant ionic strength (1.83 *M* $LiClO_4$).

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

The effect of added electrolyte on the solvolysis is tabulated in Table VII. In general, it appeared that the rate was rather insensitive to the salt concentration, when the salt was lithium perchlorate. Moreover, very little common-ion effect was evinced. In the case of potassium nitrate and lithium chloride, however, a pronounced salt effect was observed. This effect was retarding rather than accelerating as one might expect in a unimolecular solvolysis. It was noted that in every case in which the abnormal salt effect was operative, the final titer of the base titrant after a suitable length of time did not correspond to complete reaction. This effect can be attributed to the mass effect described by Beste and Hammett.[15] Thus, for a particular potassium nitrate run, the reaction may be formulated as

$$\underset{a-(x+y)}{C_6H_5CH_2OTs} \xrightarrow[\text{slow}]{k_1} C_6H_5CH_2^+ + OTs^- \qquad \text{(a)}$$

$$C_6H_5CH_2^+ + 2H_2O \xrightarrow[\text{fast}]{} \underset{x}{C_6H_5CH_2OH} + H_3O^+ \qquad \text{(b)}$$

$$C_6H_5CH_2^+ + NO_3^- \xrightarrow[\text{fast}]{} \underset{y}{C_6H_5CH_2NO_3} \qquad \text{(c)}$$

$$2C_6H_5CH_2NO_3 + 3H_2O \xrightarrow[\text{v. slow}]{} C_6H_5CHO + C_6H_5CH_2OH + NO_3^- + HNO_2 + H_3O^+ \qquad \text{(d)}$$

For this system

$$dx/dt = k_1[a - (x + y)] \qquad \text{(i)}$$

If we assume step (d) to be negligibly slow as compared to (a), then the relative amounts of benzyl nitrate and benzyl alcohol formed may be approximated by the yields of each after a suitable length of time. Letting α equal the fraction of the tosylate which is converted to acid, then

$$\alpha = x/(x + y) \qquad \text{(ii)}$$

The integration of equation (i) leads to

$$\alpha \ln \frac{(a - x_1)}{(a - x_2)} = k_1(t_2 - t_1) \qquad \text{(iii)}$$

This value of k_1 was found to be in excellent agreement with that obtained in lithium perchlorate solutions, as shown in Table VII.

The activation energies for the hydrolysis of the tosylates in 76.6 mole per cent. aqueous acetone were determined by the standard procedure. The rates were determined at 25.3, 31.4 and 40.1°. These values for benzyl, p-bromobenzyl and m-bromobenzyl tosylates are listed in Table VIII.

TABLE VII

THE EFFECT OF IONIC STRENGTH AND ELECTROLYTE ON THE RATE CONSTANT FOR THE HYDROLYSIS OF BENZYL TOSYLATE AT 25.3°

Water, mole per cent.	Electrolyte, meq./ml.	$k \times 10^4$, sec.$^{-1}$	Reaction, %
76.5	2.21 $LiClO_4$	1.10	100
76.5	1.83 $LiClO_4$	1.07	100
76.5	No salt added	1.02	97.2
76.5	2.21 KNO_3	1.05[a]	85.7

[a] Calculated, see text.

TABLE VIII

THE ACTIVATION ENERGIES OF TOSYLATE SOLVOLYSIS IN 76.6 MOLE PER CENT. AQUEOUS ACETONE

Tosylate	$k \times 10^{-4}$, sec.$^{-1}$ 25.3°	31.4°	40.1°	E, kcal./mole
Benzyl	1.07	1.93	4.61	18.5
p-Bromobenzyl	0.435	..	2.05	19.6
m-Bromobenzyl	0.0881	..	0.395	17.9

Results

Glasstone, Laidler and Eyring[20] have exhibited the existence of a linear relationship between the logarithm of the rate constants for several reactions involving two dipolar species and a function of the dielectric constant, D, of the pure solvent. This relationship is a direct consequence of the theoretical studies by Kirkwood.

$$\ln k = \ln k_0 - \frac{1}{kT} \times \frac{D-1}{2D+1}\left[\frac{\mu_a^2}{r_a^3} - \frac{\mu_b^2}{r_b^3} - \frac{\mu_*^2}{r_*^3}\right] - \frac{\Sigma\phi}{kT}$$

where μ_a, μ_b and μ_* represent the dipole moments of the reactants and the activated complex, respectively, r_a, r_b and r_*, the corresponding values for the molecular radii, and $\Sigma\phi$, a term correcting for non-electrostatic forces. The other symbols have their usual thermodynamic significance.

In Fig. 1, the logarithm of the rate constants for the solvolysis of benzyl tosylate and p-methylbenzyl tosylate have been plotted against $(D - 1)/(2D + 1)$.[21] The expected linear relationship is fair. Moreover, the values of the slopes represented by $(d \ln k)/d\,(D - 1)/(2D + 1)$ are almost the same in both cases. Subsequent studies[22] on p-β-styrylbenzyl tosylate and p-phenylethynylbenzyl tosylate indicate that the near coincidence of the slopes is not entirely fortuitous. This being the case, the rate constant for the solvolysis of p-methoxybenzyl tosylate in 76.6 mole per cent. aqueous acetone was obtained by extrapolating the value obtained in a 13.5 mole per cent. solution. The resulting value for the rate constant, 2.5 sec.$^{-1}$, should be relied on to only within 0.5 sec.$^{-1}$.

Similar types of studies on the correlation of rate constants with the constitution of the medium have been made by Braude[23] who showed a linear relationship of the logarithm of the rate constant for the unimolecular acid-catalyzed rearrangement

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[20] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 419 ff.

[21] H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 118.

[22] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3452 (1953).

[23] E. Braude, *J. Chem. Soc.*, 443 (1944).

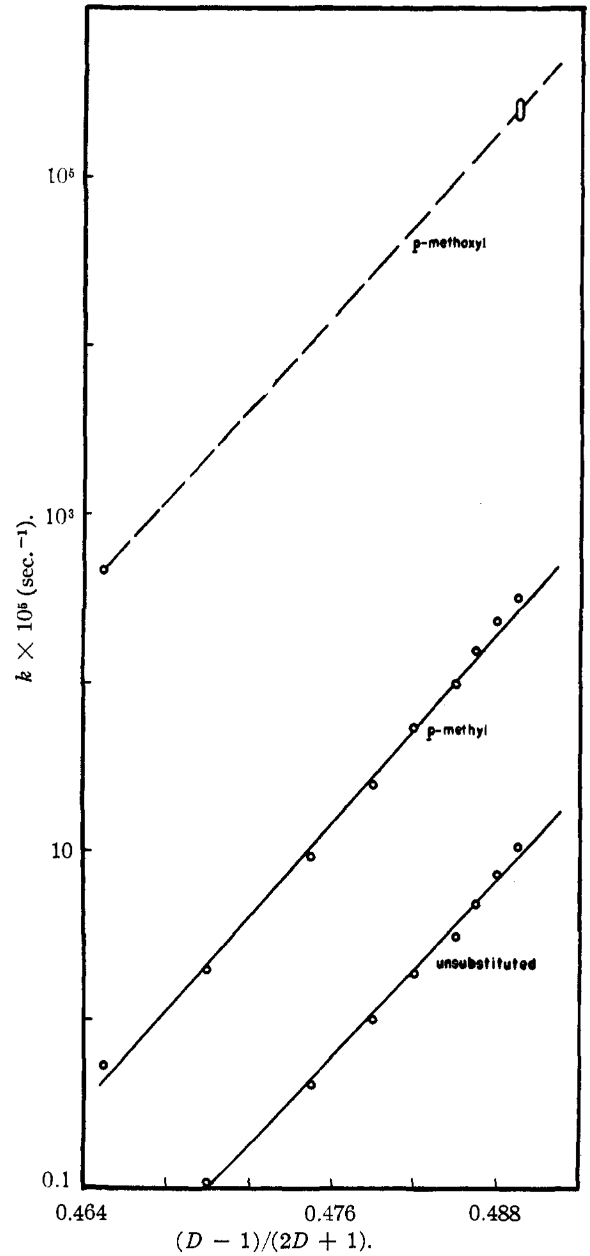

Fig. 1.—Correlation of solvolysis rates of benzyl tosylates with dielectric constant of the medium (rates on log scale).

of unsaturated alcohols with the dielectric constant of the medium.

Winstein and Grunwald[24] have shown that the rate constant, k, for the unimolecular solvolysis of alkyl halides, tosylates and brosylates can be correlated with the constitution of the medium by the equation

$$\log k = mY \quad - \log k_0$$

where Y is a measure of the ionizing power of the solvent. Log k_0 by an arbitary designation is the rate of solvolysis in an 80% ethanol–water solution. The value of m is a function of the particular compound being solvolyzed and is a constant for various solvolyzing media. In the case of several binary solvents there exists a smooth function of the Y-value with the water composition of the medium. This implies a correlation of log k with the water concentration. Solutions of acetone and water, however, showed peculiar anomalies.

The logarithms of the rate constants for the unimolecular solvolysis of the benzyl tosylates have been plotted against the σ-values for the corresponding substituents in Fig. 2. An examination of this graph reveals a rather indefinite linear relationship, an indication of a poor Hammett correlation. A close scrutiny of the data, however, discloses a limited linear relationship. If one excludes from consideration the following points: p-methoxybenzyl tosylate and p-methylbenzyl tosylate, the value of the ρ-constant evaluated by the method of least squares for the six remaining points is -2.20 with a probable error of 0.07.

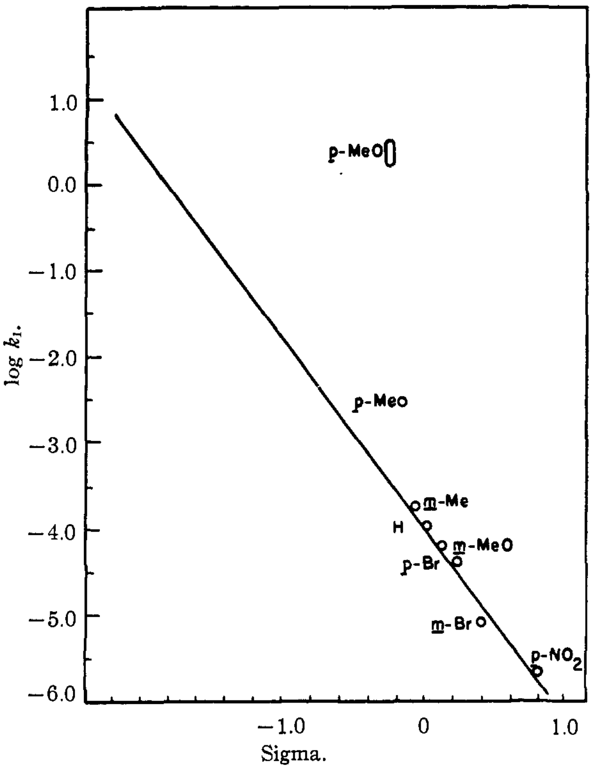

Fig. 2.—Hammett plot of rate constants for solvolysis of substituted benzyl tosylates.

That the value found for ρ is a reasonable one is shown by examining the data of Olivier[25] and Bennett and Jones[9] for the solvolysis of benzyl chlorides. Plots of the logarithm of the rate constants, for the solvolysis of benzyl chlorides from six sets of data available from these investigators, with the corresponding σ-constants have been made. A striking similarity in the disposition of the points around the best straight line in each case is exhibited for all the curves representing benzyl chlorides as well as benzyl tosylates. It is apparent that in all the cases shown, the compound containing the p-methyl substituent deviates from the linear correlation of the logarithm of the rate constant and σ- shown by the others. A more apparent correspondence between the solvolysis of

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[24] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 846 (1948); S. Winstein. E. Grunwald and H. Jones, *ibid.*, **73**, 2700 (1951).

[25] S. Olivier, *Rec. trav. chim.*, **56**, 247 (1937).

benzyl chlorides and the solvolysis of benzyl tosylates is shown in Fig. 3, in which the logarithms of the rates of solvolysis of the chlorides have been plotted against the corresponding values for the tosylates. In the figure the values for the benzyl chlorides have been corrected to 25.3° using the activation energies listed by Olivier. The slight difference in solvent composition in the two series (44 volume per cent. for benzyl tosylates and 50 volume per cent. for benzyl chlorides) should have little or no effect on the complexion of this curve. This expectation is a consequence of the previously discussed uniformity in the effect of variation of the medium on the rates of solvolysis of different tosylates. It would be expected that whatever deviations do exist for the solvolysis of benzyl chlorides should apply to the tosylates as well.

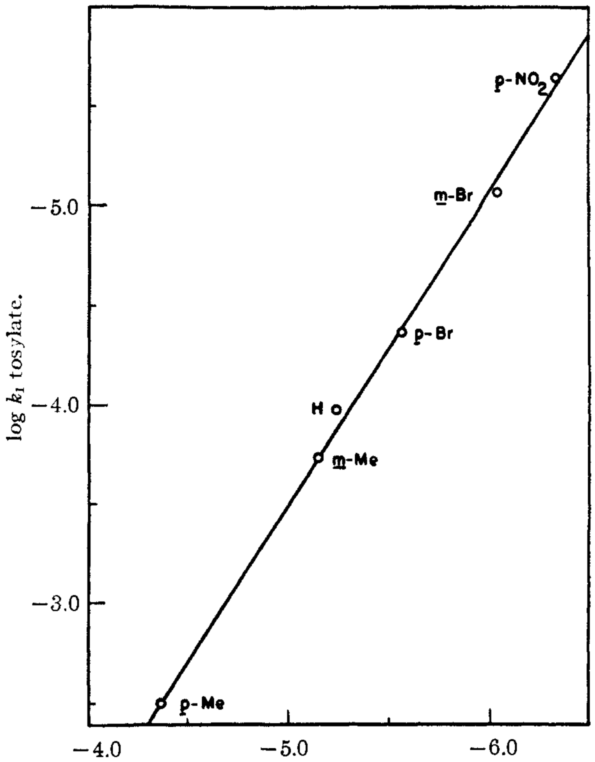


Fig. 3.—Correlation of solvolysis rates of benzyl chlorides and benzyl tosylates.

Discussion

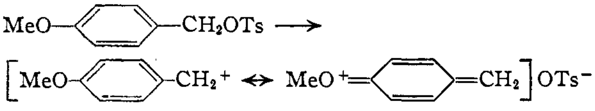
The rate-limiting step

$$ArCH_2OTs \longrightarrow ArCH_2^+ . + OTs^-$$

in the solvolysis of tosylates should be aided by electron-repelling substituents on the aromatic system. The extent of this effect is indicated by the large negative value obtained for ρ ($\rho = -2.20$). As it has been pointed out by Swain and Langsdorf,[26] the large negative value of ρ indicates that in the transition state for the solvolysis, a large formal charge is placed on the aromatic system; that is to say, there is a large amount of ionic character to the old bond.

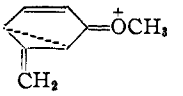
The extent of the bond-breaking in the transition state depends not only on the aromatic system but also on the nature of the departing group. Since the ρ-constant for the solvolysis of benzyl chlorides ($\rho = -1.33$) under similar conditions is found to be less than that of the tosylates ($\rho = -2.20$), the indication is that there is a more complete breaking of the old bond when tosylate is the departing group, and, therefore, a larger formal charge is placed on the aromatic system. The greater sensitivity of the tosylates to the bond breaking process may be partly attributable to the more complete solvation of the tosylate anion.

The deviation of such para-substituents as methoxyl and methyl indicates that in addition to the large mount of ionic character to, and the normal resonance stabilization of, the transition state for the solvolysis of benzyl tosylates there is, perhaps, an additional amount of ionic character and certainly an exceptional increase in resonance stabilization in the case of *p*-methoxy and *p*-methylbenzyl tosylate ascribable to the interaction of these substituent groups with the electron-deficient aromatic system shown below.



The extent of this additional aid to the bond-breaking process (magnitude of ρ) will depend greatly on the ability of the substituent group to form a π-molecular orbital with the aromatic ring. That the driving force over and above that to be expected from the σ-constants is due primarily to the para relationship is shown by the "normal" behavior of *m*-methoxy and *m*-methylbenzyl tosylate.

In this connection it is interesting to note that Overberger and co-workers[27] have concluded that structures such as



may be of importance in stabilizing *m*-methoxyphenylcarbonium ions. This view, which is based upon the high reactivity of *m*-methoxystyrene in ionic copolymerization, is not supported by our results. It seems possible that the anomalous behavior of the styrene should be attributed to the high reactivity of the *aromatic nucleus* toward growing chains. The result of an attack on the nucleus would be alkylation by a growing chain. If this is the case *m*-methoxystyrene should behave as a chain transfer agent rather than as true comonomer.

The "abnormal" behavior of *p*-methoxy and *p*-methylbenzyl tosylate was predicted in part by consideration of the large mesomeric moment of *p*-nitroanisole,[28] the nucleophilic reactivity of anisole (toward bromine, for example[29]) and the

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

(27) C. G. Overberger, *et al.*, THIS JOURNAL, **74**, 4848 (1952).

(28) R. LeFèvre, "Dipole Moments," Methuen Co., Ltd., London, 1948; *Trans. Faraday Soc.*, **30**, Appendix (1934).

(29) E. Huntress and S. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 526.

large overlap integral of the O–C bond.[30] Hyperconjugation had been previously prescribed to account for the electron-releasing properties of the *p*-methyl substituent by Baker and Nathan and others.[31]

This behavior by *p*-methoxyl and *p*-methyl appears to be quite analogous to the behavior of *p*-nitro- and *p*-cyanophenols. The $\Delta\sigma$ values for these two substituents based on the value for $\rho = -2.20$ are listed in Table IX. It is interesting to note the magnitude of these values. Whereas the variation in σ for *p*-nitro is 0.49, the value for *p*-methoxyl is −2.2.

TABLE IX

DELTA SIGMA VALUES FOR BENZYL TOSYLATES

Substituent	σ-tosylate	σ-acid	$\Delta\sigma$
p-Methoxy	−2.5	−0.27	−2.2
p-Methyl	−0.63	− .17	−0.46

In the previous discussions, the variation of the ρ-constant for the solvolysis of benzyl tosylates and chlorides with substituents, such as *p*-methyl and *p*-methoxy, was considered solely on the basis of the lowering of the activation energy. Hammett[32] has shown that one of the necessary conditions for the application of the Hammett equation is that the entropy of activation remains unchanged for the series of reactions. The solvolysis of benzyl chlorides is one of the several reactions which have been reported to show non-constant ΔS^* terms. However, a close examination of the data of Olivier shows that indeed there is a limited linear correlation between the activation energy and log *k*. This indicates a constancy in the entropy term for several members of the series. Since the activation energies were determined at only two temperatures a small discrepancy in their values may be overlooked. A striking exception is apparent in the case of *p*-methylbenzyl chloride, a misbehaver in the Hammett relationship. The large rate constant for the solvolysis of this compound is due not to a decrease in the energy of activation, but to the entropy terms. Thus, according to the basic hypothesis it is not inexplicable to find *p*-methylbenzyl tosylate exhibiting an anomalous behavior. Similar data on *p*-methoxybenzyl chloride are not available.

Since we know that ΔS^* is no longer constant for the reaction of some of these compounds, it is necessary to determine to what extent the ρ-constant can be utilized in the interpretation of the relative solvolytic reactivities of these compounds. It can be shown[33] by making several simplifying assumptions that a necessary condition for the qualitative discussion of the rates on the basis of activation energies alone is that there exists a correspondence between the resonance energy of the $ArCH_2^+$ carbonium ion and the activation entropy for the solvolytic process; *viz.*, a relative increase in the resonance energy of the carbonium ion must correspond to a relative decrease in the activation entropy for a series of benzyl tosylates. That such a relationship may be expected is a consequence of our view that the variation in activation entropies is due almost exclusively to differences in the electrostriction of the solvent. In general, no regular correlation is to be expected when there are important variations in the "internal" activation entropies.

It is this qualitative correspondence between entropy terms and resonance terms that enables us to correlate ρ with the configuration of the transition state in the cases in which the ΔS^* term is not a constant for the series. Since the entropy and resonance energy are modified in a compensating manner by solvation effects, the consideration of relative rates on the basis of one term, usually the resonance energy, is qualitatively valid.

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(30) R. Mulliken, THIS JOURNAL, **72**, 4493 (1950).

(31) V. Crawford, *Quart. Revs.*, **3**, 226 (1949).

(32) L. P. Hammett, ref. 1, p. 194 ff.

(33) J. K. Kochi, Doctorate Dissertation, Iowa State College, Ames, Iowa, 1952.