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).

Acknowledgment.—We are grateful to the Office of Ordnance Research for the support of this work and to the Institute of Atomic Research for infrared services.

AMES, IOWA

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

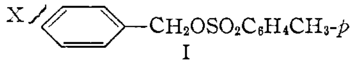
The Solvolysis of Benzyl Tosylates. V. Some Solvent Effects

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

RECEIVED AUGUST 14, 1957

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]



I

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).

function of rate for acetone–water mixtures.[1] The fit to a linear relationship is only approximate and the complete lack of correlation between the two series of solvents is demonstrated by Fig. 1. One of the reasons for choosing the particular solvent mixtures was the availability of complete data for the total and partial vapor pressures of the mixtures of both acetone and dioxane with water. The fugacities of water in the dioxane–water mixtures were calculated from the data of Herz and Lorenz,[8] and the fugacities of the acetone–water system were calculated from the data of Beare, McVicar and Fergusen.[9] No corrections were made for gas imperfections in either case. All available data for log k for benzyl tosylate is plotted against the partial pressure of water in Fig. 2. The form of the plot was chosen in preference to others (such as log–log) in order to make the data manageable since the values of k diverge much more rapidly than those of p. The data show that it will not be possible to develop any empirical function of the water activity which will correlate the data for the series of solvents. Furthermore, *the rates for the water-acetone series rise monotonously through a region of solvent composition in which the partial pressure of water passes through a maximum.*

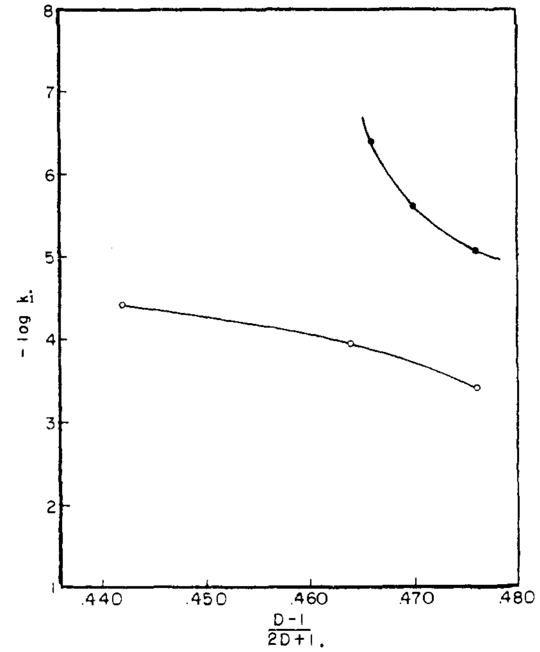

Fig. 1.—Rate of benzyl tosylate solvolysis as a function of dielectric constant: open circles, acetone–water; solid circles, dioxane–water.

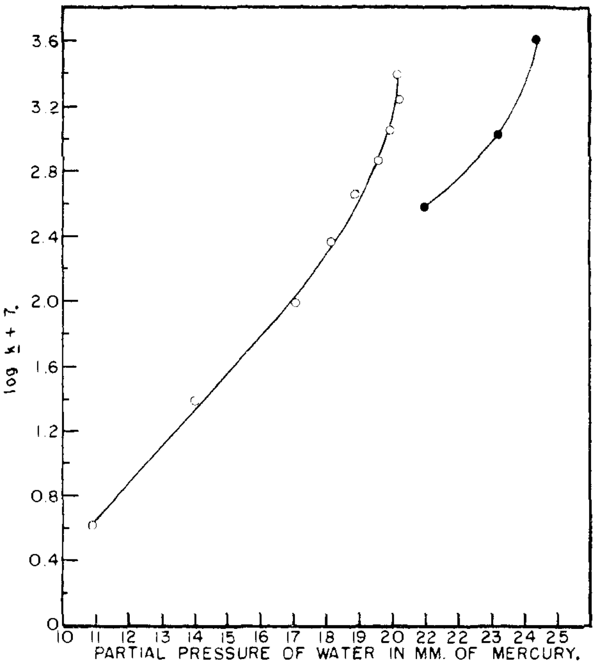

Fig. 2.—Benzyl tosylate solvolysis rates as a function of partial pressure of water: O, acetone–water; ●, dioxane–water.

A similar treatment of the rate data as a function of the mole fraction of water is considerably more promising but the best fit to a single, empirical function is shown by Fig. 3 in which the log k values are plotted against the *molar concentration* of water. The rates in the dioxane–water mixtures are faster by about a factor of two than those observed in acetone solvents containing the same water concentrations. A surprising feature of the correlation is the fact that the rates are faster in the dioxane solvents despite the fact that they have the lower dielectric constants.

Precise interpretation of these data is not easy. The rates cannot be expressed by an integral kinetic order with respect to water concentration. Third-order rate constants, which would be expected on the basis of the treatments by Swain and co-workers,[10] fit no better than fourth order. However, it is worth noting that an average value of a third-order constant would give calculated values of reaction rates with deceptively small error except at the ends of the concentration range studied. The situation is reminiscent of that described by Hughes, Ingold, Mok and Pocker[11] in their report of the kinetics of methanolysis of triphenylmethyl chloride in benzene solution. In the present work the concentrations of the hydroxylic cosolvent (water) are enormously larger than those of the hydroxylic constituent in earlier study. The similarity in the dependence of rate on the concentration of hydroxylic component in the two reactions suggests, but does not prove, a similarity in function. The fact that the rates in acetone and dioxane mixtures are reasonably correlated by a concentration function but not by an activity function implies that the participation of water in the transition states of the tosylate solvolysis does not dislodge the water molecules from their typical involvement in the liquid structure. In other words, the process of withdrawing water molecules from

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(7) 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.

(8) W. Herz and E. Lorenz, *Z. physik. Chem.*, **A140**, 406 (1929).

(9) W. G. Beare, G. A. McVicar and J. B. Ferguson, *J. Phys. Chem.*, **34**, 1310 (1930).

(10) C. G. Swain, R. B. Mosely and D. E. Bown, THIS JOURNAL, **77**, 3731 (1955).

(11) E. D. Hughes, C. K. Ingold, S. F. Mok and Y. Pocker, *J. Chem. Soc.*, 1238 (1957).

the solution to make transition states does not resemble the process of vaporizing water from the solution.

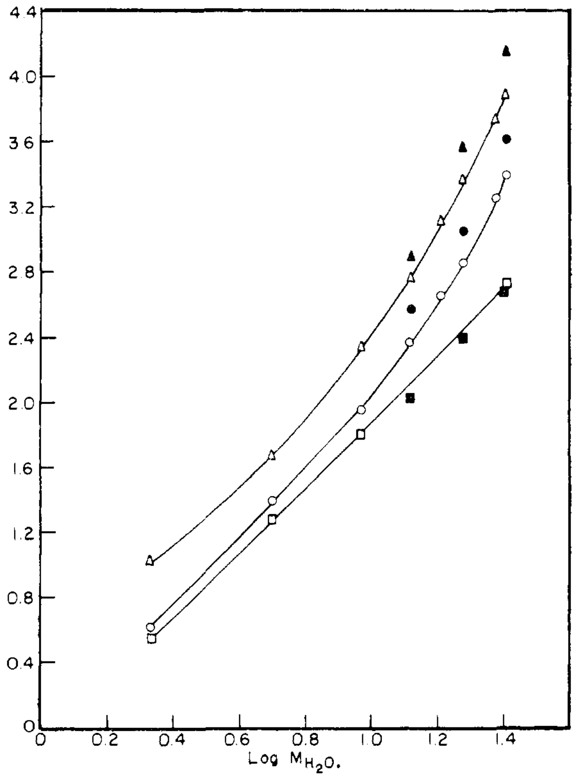
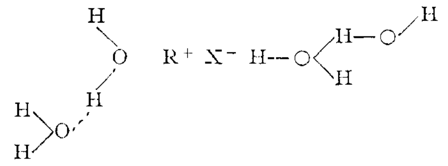


Fig. 3.—Tosylate solvolysis rates as a function of molar concentration of water: open points, acetone–water; solid points, dioxane–water; circles, benzyl tosylate, $a = 7$; triangles, *p*-methylbenzyl tosylate, $a = 6$; squares, *p*-nitrobenzyl tosylate, $a = 8$.

The translation of such generalizations into a description of reaction mechanism must involve some arbitrariness. In one of the solvent mixtures (the fastest of the water–acetone solvents) the diversion of an intermediate, presumably the benzyl cation, by added nitrate and chloride ions was demonstrated.[1] The kinetic form of the effect was that usually considered as a classic proof of the rate-determining formation of carbonium ions. We have found no evidence of any mechanistic discontinuity in any of the work so we would like to describe the influence of water in terms of the so-called "polar cosolvent effect." The superiority of water over acetone and dioxane is clearly demonstrated and there is a strong implication that dielectric effects are not of prime importance. It would be very easy to extend Swain's general formulation to include larger numbers of solvent molecules as has been suggested by Hudson and Saville.[12] The electrophilic reactivity of a hydroxyl group would surely be enhanced by hydrogen bonding of the oxygen to a second hydroxylic molecule and similar coöperative action could increase the necessary polarization of a nucleophilic solvent species. Transition states containing aggregates such as the following would be involved.



Other geometric arrangements can be visualized, but the above seems particularly attractive.

Fine details of timing, such as the arresting of the reaction at an intimate ion pair stage,[13] are "washed out" of the kinetic picture in solvents of high polarity and we can only infer that the conversion of an intimate ion pair to looser, more heavily solvated pairs should be a rapid, and probably irreversible process. It is also reasonable to assume that, especially at low water concentrations, the nucleophilic roles may be assumed by acetone or dioxane. Herein may lie the basis of the superiority of dioxane as cosolvent. The energetic picture presented by Swain remains only slightly modified, but the specific mechanistic implications of the treatment become totally ambiguous.

The data for the rates of *p*-nitrobenzyl tosylate are also plotted in Fig. 3. Again a single function associates the rates for the two sets of solvent mixtures, although the function is different from the one for the unsubstituted compound. In particular, the rate rises more slowly in the mixtures of high water content. The third plot in Fig. 2 shows the behavior of *p*-methylbenzyl tosylate. The rates rise slightly more rapidly than is the case with the parent compound and the spread between the dioxane and acetone mixtures is slightly greater.

There is evidence that the dominant role of water concentration is not a coincidence unique to benzyl tosylates. The data for solvolysis of *t*-butyl bromide in acetone–water and dioxane–water mixtures, which have been gathered by Fainberg and Winstein,[14] show the same effect. In fact, the curves obtained by plotting log *k* *versus* water molarity for benzyl tosylate and *t*-butyl bromide are remarkably close to congruent, especially in the more water-rich mixtures. However, superficial examination is sufficient to show that the relationship does not serve to relate mixtures of water with hydroxylic cosolvents to the acetone and dioxane systems. The values of $\partial \log k/\partial(H_2O)$ are larger with non-hydroxylic cosolvents, reflecting the fact that solvolysis proceeds at a measurable rate in anhydrous hydroxylic compounds.

Substituent Effects.—The variations in temperature and reaction medium effect large variations in the absolute reaction rates. The range of values for benzyl tosylate is approximately 6000; that for *p*-methylbenzyl tosylate is 8300 *within the measurable limits* (the reaction was too fast to follow in the faster dioxane solvents at 45°); and the range for *p*-nitrobenzyl tosylate is 1300. The divergence of the rates as the reactions become faster shows that sensitivity of the reactions to substituent effects increases with rate. In our earlier work we showed that *p*-NO_2 and *meta* substituents gave a very ade-

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[12] R. F. Hudson and B. Saville, *J. Chem Soc.*, 4121 (1955).

[13] A. H. Fainberg and S. Winstein, THIS JOURNAL, **79**, 1609 (1957), and earlier papers in the series.

[14] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957).

quate fit to the Hammett equation.[15] In our present work we have assumed that the same relationship will hold and have taken the value of log $k_{p\text{-}NO_2}$ − log k_H as defining the value of ρ. The values so obtained are summarized in Table I.

TABLE I

HAMMETT ρ CONSTANTS FOR THE SOLVOLYSIS OF BENZYL TOSYLATES IN AQUEOUS SOLVENT MIXTURES

Cosolvent	Volume % of cosolvent	ρ		
		25°	35°	45°
Acetone	96.2	1.36	1.38	1.39
Acetone	90.9	1.48	1.43	1.44
Acetone	83.3	1.60	1.62	1.62
Acetone	55.5[a]	2.20		
Dioxan	76.9	1.99	1.85	1.95
Dioxan	66.7	2.15	2.08	2.11
Dioxan	55.6	2.47	2.33	2.34

[a] Reference 1.

There are no significant trends of ρ as a function of temperature, but at any given temperature ρ *increases with an increase in the absolute values of the reaction rates.*[16] Examination of all the data for halogen substituents on an expanded scale shows that halogen substituents give systematic deviations from the Hammett relationship,[17] but such deviations become insignificant in comparison with the over-all range of effects and points for *p*-chloro fall very close to the line defined by *p*-NO_2 and the parent compound although the rates are always faster than would be predicted by the normal σ-value.

The lack of correlation between benzyl tosylate solvolysis and Brown's σ^+-treatment is shown by a plot of the data for 55.6% acetone solvent against σ^+ as in Fig. 4. Brown[3] has suggested that the curvature in the smooth curve drawn through the points reflects a change in the mechanism of solvolysis within the series. The two solid lines in Fig. 4 represent our best effort to resolve the data into two linear plots. If the line drawn through the faster rates defines a series of compounds which reacts by a carbonium ion mechanism there is some question as to the most appropriate way of treating the rest of the data. Probably the best procedure is to follow the assumption that if σ^+-values are not applicable then the Hammett σ-values must be if, as Brown suggests, only two values of substituent constants are needed to correlate all data. Plots of the relevant data are included in reference 17. A plot such as Fig. 4 of all the data might lead one to believe that a reasonable linear relationships exists among the data for the slower compounds. However, examination of the data on an expanded scale show that the slopes change considerably.[17] Nonetheless, it is interesting to proceed with the assumption that a resolution into two Hammett plots can be accomplished, since the possibility that a sharp change in mechanism can be diagnosed is important as a possible contribution to the general theory of solvolysis.

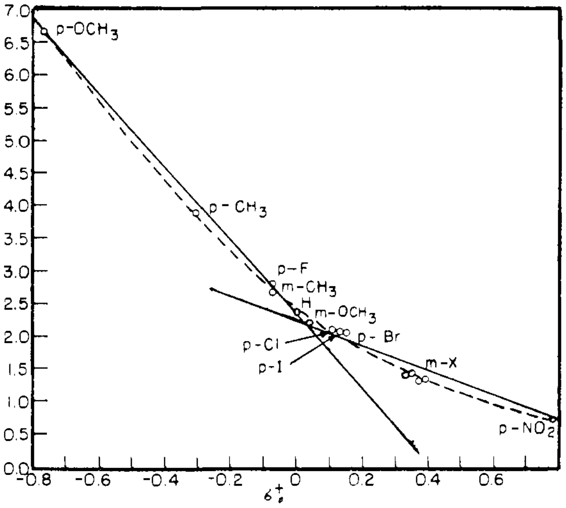

Fig. 4.—Plot of solvolysis rates of benzyl tosylates in 55.6 volume per cent. acetone against σ^+.

If two distinctly different mechanisms were involved in the reactions whose rates are plotted in Fig. 4, we would normally expect that the two reaction types would show different response to changes in the nature of the reaction medium. Specifically, one would expect that the ionization rates would slow down much more than the rates of a direct displacement if the water content of the solvents were reduced. As a symptom of the effect we have looked for an indication that the two straight lines of Fig. 4 intersect farther to the right when the data for slow solvents are plotted. Plots of all the data show no such trend, but we have looked in more detail for a breakdown of the linear relationship between log k and σ^+-constants for benzyl tosylate and the fast, *p*-substituted compounds. Since the point for hydrogen lies just above the intersection in Fig. 4 a change in the relative importance of two mechanisms should be revealed by the transfer of the rate for benzyl tosylate from the line of large slope to the line of small slope. The calculations of Table II show that the linear relationship among *p*-CH_3, *p*-F and the H as substituents remains perfect even in the slowest solvents. Since σ^+ correlates the rates for the three compounds in all the media, and since *p*-fluorobenzyl tosylate is always faster than the unsubstituted compound (Hammett σ is positive for *p*-F), we must conclude that a carbonium ion mechanism persists with these compounds. In order to maintain the view that all of the slower compounds go by a different mechanism, we would have to accept the view that the displacement process is as sensitive (or more so) to medium effects as is the carbonium ion reaction. Changes in reaction type must be more subtle and continuous than are implied by the "two mechanism" analysis.

As a further illustration of the general continuity of substituent effects we have made log–log plots (not included in the text) of all of the data in Table V. If one of the solvents of intermediate ionizing power, such as 83% acetone or 77% dioxane, is

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(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(16) The trends established in this work lead us to believe that the extrapolation procedure used to estimate the solvolysis rate of *p*-methoxybenzyl tosylate in 55.6 volume per cent. acetone[1] must have led us to underestimate the value.

(17) F. T. Fang, J. K. Kochi and G. S. Hammond, THIS JOURNAL, **80**, 563 (1958).

TABLE II

VALUES OF ρ FROM APPLICATION OF MODIFIED HAMMETT EQUATION[3] TO REACTIVE COMPOUNDS

Solvent[a]	ρ: $\dfrac{\log k_{p\text{-CH}_3} - \log k_{p\text{-F}}}{\sigma^+_{p\text{-CH}_3} - \sigma^+_{p\text{-F}}}$	ρ: $\dfrac{\log k_{p\text{-CH}_3} - \log p_{\text{H}}}{\sigma^+_{p\text{-CH}_3}}$
96.2 A	3.6	3.6
90.9 A	3.9	3.8
83.3 A	4.3	4.3
55.6 A	4.8	4.8
76.9 D	4.4	4.3
66.7 D	4.9	4.9
55.6 D	5.1	5.4

[a] A = acetone; D = dioxane.

chosen as a reference medium a series of apparently adequate straight lines is obtained. Systematic trends away from linearity are best demonstrated if the rates are plotted against the the rates in either the fastest or the slowest medium. The over-all results simply show again that the divergence in rates in the faster solvents is greatest with the most reactive compounds and that a series of unique ρ-constants cannot quite keep up with the trend.

If we compare the rate constants for benzyl tosylate solvolysis in 55.6% acetone with those for the solvolysis of phenyldimethylcarbinyl chlorides in 90% acetone (used to define σ^+) we observe that the sensitivity to substituents is greatest among the fastest of the tosylates. However, the lowest sensitivity also comes in the tosylate series among the unreactive compounds. Table III illustrates the comparisons.

TABLE III

COMPARISON OF INDIVIDUAL RATE RATIOS BETWEEN BENZYL TOSYLATE AND PHENYLDIMETHYLCARBINYL CHLORIDE SOLVOLYSES

Substituent	$\log k_x/k_H$: $xC_6H_4CH_2OTs$	$\log k_x/k_H$: $xC_6H_4C(CH_3)_2Cl$
p-CH_3O	4.37	3.53
p-NO_2	−1.66	−3.59

The low sensitivity among the unreactive tosylates must indicate that a considerable fraction of the positive charge left by the departing anion must be dissipated to solvent. Such considerations were the basis of the hypothesis that the slow tosylates react by a direct displacement mechanism.[3] The preceding arguments indicate that the additional involvement of solvent is not easily fitted to a mechanistic discontinuity. As an alternative we may assume that even though the gross reaction mechanism, as indicated by tests for the existence of intermediates or other similar experiments, remains unchanged the transition states can change considerably with respect to such characteristics as free energy of solvation and the number of solvent molecules involved in the first solvation sphere. In short, we believe that all of the benzyl tosylate reactions are S_N1 reactions but that most or all of them may not be limiting in the sense of the discussion by Winstein, *et al.*[18]

Activation Parameters.—Table IV summarizes the data for enthalpy and entropy of activation as a function of solvent for the five compounds for which our data are most complete. The enthalpies vary much less than the entropies. The relative invariance of substituent effects with temperature is, of course, a reflection of the dominance of entropy effects.

We can offer nothing approaching a complete account of these data. Taken in conjunction with the correlation of the rates with the volume concentration of water the dependence on entropy suggests that rate variations might well be considered in terms of the probability that tosylate molecules will encounter water aggregates of an appropriate size. Since the least reactive compounds have very high activation entropies the indication is that a system such as p-nitrobenzyl, which is relatively ineffective in internal charge dispersion, has a relatively strong ordering effect on the solvent envelope. Such a conclusion may seem anomalous in view of the evidence discussed in the first section above which indicates that fewer water molecules are involved in the solvolysis of the p-nitro compound. The ordering effect on the smaller number of solvent molecules must be quite strong. While this is exactly the effect which would be expected if the compound were reacting by an S_N2 mechanism, the qualitative observation apparently cannot be taken as diagnostic for a definite mechanistic switch. All changes in activation parameters are gradual over the entire series of compounds and there is nothing resembling a sharp division into two groups.

Acknowledgment.—We gratefully acknowledge the support of this work by the Office of Ordnance Research.

Experimental

Benzyl Alcohols.—Most of the alcohols were prepared, as previously described,[19] by reduction of the corresponding benzoic acids. p-Fluorobenzyl alcohol was obtained in 78% yield, m.p. 22–23°, b.p. 209° (730 mm.), $n^{20}D$ 1.5080. *Anal.* Calcd.: C, 66.60; H, 5.60. Found: C, 66.02; H, 5.68.

Benzyl Tosylates.—With the exception of p-nitrobenzyl tosylate all of the esters were prepared by the reaction of purified p-toluenesulfonyl chloride (m.p. 68.5–69°) with the sodium benzoxides in dry ether.[19] The esters were recrystallized from either ether or benzene–petroleum ether (Skellysolve B) and were stored in ether or benzene solution. Stored in dry solvents the esters are stable for periods of months. Small portions were crystallized for use as needed. The only new compound in the series, p-fluorobenzyl tosylate melted at 54–55° but was not analyzed because of its instability in the solid form. p-Nitrobenzyl tosylate was prepared by the method of Tipson.[19,20]

Solvents, titrant solutions and lithium perchlorate were prepared as described elsewhere.[1,17]

Kinetic Measurements.—The rates were followed by the intermittent titration method[1,17] using potentiometric titration with Beckman no. 1190–42 glass electrodes and calomel reference electrodes. Brom phenol blue was used in following the slow reactions. Stoichiometric points were located by potentiometric titration of toluenesulfonic acid with triethylamine in the various solvent media. Most of the reactions were carried out in a cell which was fitted with stirrer, thermometer well, and inlets for the buret and electrodes. Because of solvent evaporation the very slow reactions were run in glass stoppered flasks.

Rate Data.—All rate constants were calculated from the integrated first-order rate law. Individual runs showed average deviations of less than 1%. Duplicate runs by

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[18] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

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

[20] J. Tipson, *J. Org. Chem.*, **9**, 239 (1944).

TABLE IV

ACTIVATION PARAMETERS IN TOSYLATE SOLVOLYSIS

Solvent[a]	Substituent p-No$_2$ $\Delta H^\ddagger$	p-No$_2$ $\Delta S^\ddagger$	p-Cl $\Delta H^\ddagger$	p-Cl $\Delta S^\ddagger$	H $\Delta H^\ddagger$	H $\Delta S^\ddagger$	p-F $\Delta H^\ddagger$	p-F $\Delta S^\ddagger$	p-CH$_3$ $\Delta H^\ddagger$	p-CH$_3$ $\Delta S^\ddagger$
96.2 A	19.4	31.2	18.9	21.8	19.1	23.8	18.9	23.2	19.1	18.4
90.9 A	19.6	23.8	18.9	21.5	19.4	19.1	18.3	21.8	19.8	12.4
83.3 A	18.3	22.1	18.9	19.1	19.8	15.1	19.1	16.1	20.0	8.4
76.9 D	18.5	23.8			18.9	15.4	23.1	13.4	18.9	9.4
66.7 D	19.1	20.1	19.1	13.7	18.5	14.4	21.5	16.4	18.3[b]	8.4
55.6 D	20.4	14.4	17.8	15.6	18.3	12.8			17.8[b]	6.7

[a] Numbers refer to volume per cent. of cosolvent; A indicates acetone and D indicates dioxane. [b] Using 45° rate extrapolated from slower solvents.

TABLE V

FIRST-ORDER RATE CONSTANTS FOR SOLVOLYSIS OF BENZYL TOSYLATES IN AQUEOUS SOLVENT MIXTURES

Solvent[a]	$\log k_s + 8$ p-CH$_3$ 25°	p-CH$_3$ 35°	p-CH$_3$ 45°	p-F 25°	p-F 45°	H 25°	H 35°	H 45°	p-Cl 25°	p-Cl 35°	p-Cl 45°	p-NO$_2$ 25°	p-NO$_2$ 35°	p-NO$_2$ 45°
96.2 A	5.26		4.35	1.87	2.77	1.61		3.52	1.50		2.44	0.55		1.42
90.9 A	3.54	4.02	4.48	2.63	3.50	2.39	2.85	3.31	2.24	2.74	3.14	1.24		2.17
83.3 A	4.28	4.78	5.23	3.26	4.17	2.95	3.41	3.89	2.78	3.26	3.68	1.70		2.62
76.9 D	4.88	5.31	5.78	3.85	4.76	3.57	4.02	3.47				2.02		2.90
66.7 D	5.55	5.95		4.40		4.05	4.51	4.93	3.76	4.23	4.67	2.38	2.87	3.39
55.6 D	6.24	6.65		5.04	5.83	4.60	5.03	5.47	4.33	4.76	4.18	2.68	3.21	3.65

[a] Number refers to volume per cent. of cosolvent; A refers to acetone and D to dioxane.

different workers with entirely new preparations and reconstructed apparatus gave rate constants which agreed to 4% or better after correction of a numerical error. All rate constants in reference 1 should be multiplied by a factor of 2.303. Our new data are summarized in Table V.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

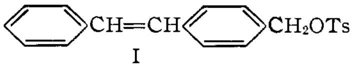
Benzyl Tosylates. VI. The Effects of Phenyl as a Substituent

BY GEORGE S. HAMMOND AND CHARLES E. REEDER

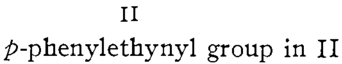
RECEIVED AUGUST 14, 1957

The isomeric *m*- and *p*-biphenylcarbinyl tosylates have been prepared and solvolyzed. The results are compared with those of an earlier study of the influences of β-styryl and phenylethynyl as substituents. There is a strong qualitative similarity between β-styryl and phenyl, although the former provides the greater resonance effects. Phenylethynyl is a unique group in that the values of σ^+ and σ_R apparently have different signs. The entropy of activation in the solvolysis of *p*-biphenylcarbinyl tosylate is less negative than usual.

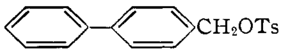
We have continued our application of benzyl tosylate solvolysis rates to the study of the conjugative effects of unsaturated, all-carbon substituents. We previously showed[1] that the *p*-β-styryl substituent in I accelerated the solvolysis rate far more than would have been anticipated by consideration of the Hammett σ-constant for the group. The effect of the *p*-phenylethynyl group in II was qualitatively of the same sort but was quantitatively much reduced. The reactivity of the corresponding *m*-substituted compounds was adequately correlated by the unmodified Hammett equation. The different results were attributed to the firmer binding of electrons by carbon atoms in the sp state of hybridization than by sp^2 carbon atoms. Such considerations lead to the expectation that phenyl as a substituent should resemble β-styryl rather than phenylethynyl. Consequently, we now have made measurements with compounds III and IV.



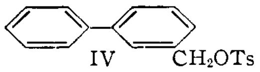
I



II



III



IV

Results and Discussion

The data for the rates of solvolysis of the biphenylcarbinyl tosylates are gathered in Table I. Data for styryl and phenylethynyl as substituents are included for comparative purposes.

The behavior of phenyl as a substituent is intermediate between β-styryl and phenylethynyl. The solvolysis rate of IV is correlated very well by the σ-constant for *m*-phenyl as determined by the ionization constant of *m*-biphenylcarboxylic acid[4] as was the case with the other two substituents.[1] The extra driving forces supplied by the three

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[1] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3454 (1953).

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

[3] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

[4] N. N. Lichtin and H. P. Leftin, *ibid.*, **74**, 4207 (1952).