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ESTIMATION OF LIMITING CHARACTER OF THE HYDROLYSIS

REACTION OF BENZYL TOSYLATES

by

Charles E. Reeder

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INTRODUCTION

A very important reaction in organic chemistry is that
of nucleophilic substitution. A large amount of study has
been carried out on this reaction especially in more recent
years in an effort to gain the secrets of the process by
which the reactants are transformed into products. Although
a fair amount of knowledge has been gained about the macro-
scopic properties of various reactions and this knowledge
has led to many interesting postulates concerning the roles
played by and the changes undergone by individual atoms
involved in a close up view of the reacting species, the
microscopic picture is far from being clear at the present
time for many reactions, especially those where one of the
reactants is a molecule of the solvent. A section of this
general field which is quite rich in speculation is the so
called S_N1 solvolysis reaction, which traditionally is pic-
tured as consisting of a slow, rate-determining ionization
of one of the reactants followed by one of the ions reacting
rapidly with the solvent to give the product of most interest
to the general chemist. It is now generally agreed that
there is no sharp point of separation between these S_N1 re-
actions and those classified as S_N2. The latter consists
of a rate determining attack of solvent or other nucleophiles

with simultaneous departure of the leaving group. Rather, there is a whole spectrum of reaction types between these extreme two views.

Often a question of interest is how closely a given reaction generally classified as S_N1 solvolysis can be represented by the limiting case of complete ionization, or stated in other words, to what extent ion formation has taken place in the transition state for the reaction. A reaction thought by some not to be such a limiting case is the solvolysis of benzyl p-toluenesulfonate, which will be referred to as benzyl tosylate. However, certain of the substituted derivatives of this ester are almost certain to react in a more limiting fashion. As a result of this observation and for other reasons, this system appeared to be a good one in which to detect a change in the amount of ionic character for the various individual reactions if such a phenomenon existed.

The method proposed for detection of such a change in reaction character was an investigation of the effect of change of media upon the rates of solvolysis of the various substituted benzyl tosylates. This could best be accomplished by employing one or more series of mixed solvents of varying composition of which one component only could lead to products. Such a comprehensive study of solvent effects

could also reveal other important information regarding the general subject of S_N1 solvolysis.

HISTORICAL

Changes in Mechanism in Solvolysis Reactions

Solvolysis reactions most often encountered in organic chemistry are a smaller portion of the broad area of nucleophilic substitution. The latter has long been looked upon as consisting of reactions of two distinctly different types. They have been designated as S_N1 and S_N2 and the supposed properties of each have been developed in great detail by Hughes and Ingold.[1,2,3] The point of basic distinction between the two mechanisms was whether the formation of the new bond occurred after the old bond had broken in a rate determining ionization step or whether the bond formation was the driving force which in part caused the rupture of the old bond in a simultaneous bond-making bond-breaking step. However, for solvolysis reactions both mechanisms lead to first order kinetics since the concentration of the solvent remains nearly constant throughout the reaction.

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[1] J. L. Cleave, E. D. Hughes and C. K. Ingold, _J. Chem. Soc._, _1935_, 236.

[2] E. D. Hughes and C. K. Ingold, _ibid._, p. 244.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N. Y., 1953, p. 308.

Therefore the distinction of reaction type must be made on the basis of other properties of the reaction such as steric effects, occurrence of an intermediate or solvent effects.

Quite early it was discovered that certain reactions did not fall into either class too well, but had certain properties of each. This led to the postulate that certain compounds could react by both mechanisms. This postulate has been questioned by a number of workers in the past and has more recently been shown not to account for the changes of rate with change of solvent composition.[4,5]

On the basis of accumulated experimental evidence it is not generally accepted that there is no sharp dividing line between reactions going by the postulated dual mechanisms, but rather that reactions form a whole spectrum of graduately shifting types of which the two originally postulated types are the extremes. The latter have been redesignated as limiting (Lim) and nucleophilic (N) in an excellent discussion of the subject by Winstein and co-workers.[4]

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[4]S. Winstein, E. Grunwald, and H. W. Jones, _J. Am. Chem. Soc._, 73, 2700 (1951).

[5]C. G. Swain and R. B. Mosely, _ibid._, 77, 3727 (1955).

Swain has recently postulated a termolecular mechanism for solvolysis reactions[6,7] b extrapolation from the kinetics in benzene of the reaction of triphenylmethyl chloride with methanol.[8] Reactions of trityl chloride are generally classified as $S_N 1$ or limiting in most solvents, but a question may arise as to whether or not this extrapolation is completely valid.[9] However, the mechanism, which consists of a simultaneous attack of a nucleophilic group and an electrophilic group upon the substrate molecule, in its developed form becomes almost equivalent to that of Winstein and coworkers. A probable improvement would be to include a consideration of other solvent effects than nucleophilic or electrophilic attack on substrate. As emphasized by Swain, this mechanism does provide a single but flexible mechanism for all nucleophilic substitutions.

Since this mechanism appears to provide a very sound basis for further discussion, it seems appropos that it should be further reviewed here. Repeating, the mechanism consists of a simultaneous attack by both an nucleophile
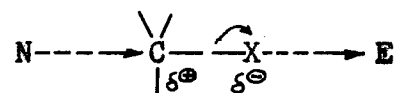
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[6] C. G. Swain, *ibid.*, 72, 4583 (1950).

[7] C. G. Swain and W. P. Langsdorf, *ibid.*, 73, 2813 (1951).

[8] C. G. Swain, *ibid.*, 70, 1119 (1948).

[9] C. K. Ingold, *op. cit.*, p. 356.

and an electrophile upon the substrate molecule in a bond
forming and a bond breaking process.

$$N \text{----} \overset{\diagdown \diagup}{\underset{|_{\delta^\oplus}}{C}} \text{---} \overset{\frown}{\underset{\delta^\ominus}{X}} \text{----} E$$

In the transition state the extent of bond formation to
the nucleophile (N) and the extent of bond breaking by the
leaving group (X) as it is pulled away by the electrophile
(E) in general will not be equal. Other things being equal
the extent of bond formation will depend on the strength of
the nucleophile and the extent of bond breaking will depend
on the strength of the electrophile; both will be dependent
on the ability of the residue of the substrate molecule to
stabilize a positive charge. An examination of this mecha-
nism shows that a loose transition state in which both old
and new bonds are only slightly formed approaches the classi-
cal S_N1 mechanism, with the nucleophile taking the role of
a solvating agent for the cation, while a tight transition
state where both bonds have a large amount of covalent
character leads to the classical S_N2 mechanism. The tight-
ness or looseness of the transition state should depend
directly on the ability of substrate residue to stabilize
a positive charge.

On the basis of this latter mechanism, a sharp dividing
line separating reactions into two classes would not be
expected. Instead one would anticipate the wide range or
spectrum of reaction types observed, the type depending on
the strengths of the nucleophile and the electrophile and
upon the character of the substrate residue and of the leaving
group. One would also expect that the mechanism by which a
given substrate reacted with a given or similar nucleophiles
might vary greatly with the experimental conditions employed
due to a change in the electrophile and other solvent
properties. The role of an electrophile has often not been
considered in past discussions, so that the observation of
apparent changes in mechanism has resulted in a certain amount
of confusion.

Other expected variations of mechanism which are sup-
ported by experimental observations are the changes of reac-
tion mechanism with a change of the nucleophile and with a
change of the substrate. The change of mechanism as one
goes from methyl to tertiary butyl halides in solvolysis
and other substitution reactions is fully recognized.[10]
That the mechanism may also change greatly as one makes
what might appear at first to be minor changes in the

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[10]C. K. Ingold, _op. cit._, p. 316.

substrate, could also be expected if these changes greatly changed the capacity of the substrate residue to accommodate a positive charge and if the reaction were not already a truly limiting case in the direction of the proposed shift. Such a substrate system might be found in the substituted benzyl chlorides or similar compounds.

To what extent reactions which in the past have been considered as definitely proceeding by the S_N1 mechanism actually do so in the limiting sense is still an open question. The Grunwald-Winstein correlation of solvolysis rates with ionizing power of the solvent (Y) by means of the equation

$$\log k = mY + \log k_o \qquad (1)$$

was based on the assumption that this compound is a limiting case[11,4], however with some reservation. The m values obtained for various compounds appear to be somewhat indicative of the position of the compound in the mechanistic spectrum. Another recent correlation of solvolysis rates by Swain[12,13]

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[11] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846 (1948).

[12] C. G. Swain, R. B. Mosely and D. E. Brown, *ibid.*, 77, 3731 (1955).

[13] C. G. Swain and C. B. Scott, *ibid.*, 75, 141 (1953).

based on his termolecular mechanism makes use of the four
parameter equation

$$\log (k/k_o) = c_1 d_1 + c_2 d_2 \qquad (2)$$

where c_1 and c_2 are related to the sensitivity of the com-
pound to nucleophilic and electrophilic attach respectively
and where d_1 and d_2 are related to the capacity of the sol-
vent to act as either a nucleophile or an electrophile. The
relative mechanistic type of the substrate seems to be indi-
cated by the ratio, c_1/c_2. This correlation is based on
the assumption that t-butyl chloride is far from limiting
in respect to solvolysis of triphenylmethyl fluoride in
a wide range of solvents. On the basis of both of these
correlations as well as an early statement by Hughes and
Ingold[14], the solvolysis of benzyl chloride is far from
limiting with respect to that of t-butyl chloride and has
been classified as a borderline reaction. Thus the mecha-
nism for the solvolysis of this system should be quite
sensitive to changes in the ionizing power or electrophilic
character of the solvent and to the change of substituents
on the substrate molecule. A similar series of compounds,

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[14]E. D. Hughes and C. K. Ingold, op. cit., p. 248.

the benzyl tosylates, were indicated to be slightly less and slightly more limiting than the corresponding benzyl chlorides by the above correlations. However, on the basis of the Hammett ρ value obtained by Kochi and Hammond[15], a criterion used by Swain and Langsdorf for reaction type[7] (see following section), the solvolysis of benzyl tosylates ($\rho = -2.20$) are much more limiting than the benzyl chlorides ($\rho = -1.33$) and might be approaching that of triphenyl methyl chloride ($\rho = -2.90$[16]). In the work on the solvolysis of benzyl tosylates it seemed certain that the p-methyl and p-methoxyl compounds underwent solvolysis by a mechanism comparable to that of t-butyl chloride. At the time it was thought that perhaps the solvolysis of the whole system of compounds might be nearly limiting in character; but if it were not, this would be a convenient system in which to demonstrate an increased amount of ionic character of the old bond in the transition state, indicative of a shift to a more limiting mechanism, as the ionizing power or electrophilic character of the solvent increased.

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[15]J. K. Kochi and G. S. Hammond, J. Am. Chem. Soc., 75, 3445 (1953).

[16]H. H. Jaffe, Chem. Rev., 53, 205 (1953).

Significance of ρ and σ Values of the Hammett Equation

One of the most successful and widely applicable corre-
lations of organic reactions is the Hammett equation

$$\log k/k_0 = \rho\sigma \tag{3}$$

which relates chemical reactivity to structural changes in-
volving substituents in _meta_ and _para_ positions on a benzene
nucleus. As is well known, σ is a measure of the change in
electron density produced by a substituent and ρ is a measure
of the sensitivity of the reaction under the conditions em-
ployed to such a change in electron density[17]. The applica-
bility, significance, and precision of this equation have
been extensively reviewed recently by Jaffe [16].

The significance of ρ and the factors which influence
its magnitude in nucleophilic substitution have also been
discussed by Swain and Langsdorf in relation to and as
evidence for their concerted termolecular mechanism in dis-
placement reactions[7]. ρ is said to be a measure of the
difference between the magnitudes of the charge on the

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[17]L. P. Hammett, "Physical Organic Chemistry", McGraw-
Hill Book Co., New York, N. Y., 1940, p. 184.

central carbon atom in the ground state and in the transition
state. This difference depends on the relative amounts of
bond making and bond breaking in the transition state and
hence is a measure of the relative limiting character of the
mechanism for the reaction. The factors therefore which
will influence the magnitude of ρ are those that influence
the amount of bond making and bond breaking in the transition
state. Those factors which should increase the magnitude of
a negative ρ would be electron donating substituents which
would increase the capacity of the substrate residue to
stabilize a positive charge, stronger electrophilic agents
which would increase the amount of bond breaking, and weaker
or more hindered nucleophilic reagents which would decrease
the amount of bond making. Other solvent effects are said
to have almost negligible second order effects.

Since σ is a measure of the effect of the substrate
on the electron density at the reaction site, it will be made
up of contributions from both inductive effects and resonance
effects. One should not therefore expect σ to have a
constant value for all reactions if the amount of resonance
differs greatly in the transition states. From the beginning,
it has been observed that the ionization of p-nitrophenol
and p-nitroanilinum ion required a second and much higher
value of σ for the nitro group than that for most other

reactions.[16,17] In both of these reactions the amount of resonance contribution of the nitro group is much greater in the products than in the reactants. It has been more recently postulated and experimentally verified that electron donating substituents also require much more negative substituent constants for reactions where the transition state would be expected to contain a much greater amount of resonance stabilization than the ground state.[18] Since magnitude of σ does increase for reactions where the possibility of resonance increases because of the structure of the molecule, σ should also increase in numerical value for reactions in which the capacity for resonance increases for other reasons and cannot be properly regarded as a constant at all. In the termolecular mechanism postulated for nucleophilic substitution, such an increase in σ capacity would be expected if the nucleophile were weakened or the electrophile were strengthened.

Recast in the approach of Winstein and Grunwald one would expect the numerical value of σ to increase with an increase in the ionizing power of the solvent for solvolysis reactions if the reaction were not already limiting.

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[18] J. K. Kochi and G. S. Hammond, J. Am. Chem. Soc., 75, 3445 (1953).

Another solvent effect which may be expected to alter
the values of σ for some substituents in varying amounts,
would be differences in hydrogen bonding of solvent to the
substituent itself[16], especially in the reactants.

Variations in Entropy of Activation of Reaction

Since the Hammett equation is a linear free energy
relationship and since the contribution of substituents to
the free energy of the reaction is effected through a change
in the internal potential energy of the molecule, this
equation was originally thought to be applicable to those
reactions in which the change in entropy was constant and
therefore independent of the substituent[17]. However, it is now
known that the entropy of activation is not constant for many
reactions, but is the important factor determining the rate.
For the reaction of benzyl chloride with pyridine the Arrhenius
energy of activation is nearly constant while the entropy
changes greatly.[19] The same seems to be true also of many
solvolysis reactions, since again the Arrhenius activation
energy has a nearly constant value.[20] However, at least one

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[19]J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, *1935*,
1840.

[20]G. M. Bennett and B. Jones, *ibid.*, p. 1815.

case has been reported where entropy of activation appears
to vary inversely as the activation energy. This was for
an elimination reaction for which a mechanism similar to
that for the limiting case of nucleophilic substitution has
been postulated.[21]

It does appear to be true that a linear free energy
relationship is obtained only for those compounds for which
the internal entropy changes would be expected to be constant
and is deviated from in series of compounds for which the
internal entropy changes would be expected not to be constant,
such as in most ortho substituted substrates.[17]

Since the internal entropy changes of the reacting
molecules must be nearly constant, the large changes in
entropy of activation must be due to large changes in the
entropy of solvation between the reactants and the transition
state complex. This solvation entropy would be largely due
to the amount of orientation of solvent molecules involved
in the reaction and would depend on the size of the ion being
formed and its charge.[22]

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[21]S. J. Cristol, et al., J. Am. Chem. Soc., 74, 3333
(1952).

[22]A. A. Frost and R. G. Pearson, "Kinetics and
Mechanism", John Wiley and Sons, Inc., New York, N. Y.,
1953, p. 123.

For changes in solvent, Leffler has postulated that the change in entropy of activation of many reactions is a linear function of the enthalpy.[23] Thus the effect of entropy and enthalpy changes upon the rate tend to cancel each other out with solvent changes.[24]

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[23]M. D. Cohen, J. E. Leffler and L. M. Beubato, *J. Am. Chem. Soc.*, **76**, 4169 (1954).

[24]M. G. Alder and J. E. Leffler, *ibid.*, p. 1425.

EXPERIMENTAL

Preparation and Purification of Compounds

Biphenylcarboxylic acids

4-Biphenylcarboxylic acid. This acid was synthesized by a modification of the method used by Fieser[1] which consists of the Friedel-Craft acetylation of biphenyl and the hypochlorite oxidation of the resulting ketone. Tetrachloroethane was used as a solvent for the Friedel-Craft reaction instead of the highly inflammable carbon disulfide used in the procedure of Long and Henze[2]. An attempt to use nitrobenzene was unsuccessful.

Sixty six grams (0.5 mole) anhydrous aluminum chloride (Baker and Adamson, reagent grade) was suspended in 75 milliliters of tetrachloroethane in a 500-milliliter, 3-necked flask equipped with dropping funnel, reflux condenser, and "true bore" stirrer. A solution of 54 grams (0.35 mole) biphenyl (Eastman Kodak, practical grade) and 27.4 milliliters

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[1]L. F. Fieser, et al., J. Am. Chem. Soc., 70, 3186 (1948).

[2]L. M. Long and H. R. Henze, ibid., 63, 1939 (1941).

(0.385 mole) of acetyl chloride (Matheson, reagent grade)
in 150 milliliters of tetrachloroethane was added over a
one hour period, the liberated hydrogen chloride being ab-
sorbed by soda lime. The reaction mixture was stirred at
room temperature for one hour, at 80° for one hour, overnight
without additional heat, and at 105° for one hour. The
mixture was cooled and was poured into dilute hydrochloric
acid and ice after being stirred for one hour. The aqueous
layer was separated from the non-aqueous layer and was
further extracted with small portions of additional tetra-
chloroethane. After being washed with dilute sodium hydroxide
and water, the non-aqueous solution was dried over "Drierite".
Removal of the solvent by vacuum distillation gave more than
the theoretical amount of dark crude material. The latter
was recrystallized from Skelly "D", in which the dark tarry
portion of the crude material did not readily dissolve, to
yield 43.5 grams (63.5%) of 4-acetylbiphenyl, melting at
115°-117°[*] (cf. 121°[2]). The nonsoluble portion could be
further purified by recrystallization from ethanol-ethyl
acetate solution to yield a material melting at 203-205°
which appeared to be the diacetylated compound by its I.R.
spectra.

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[*]All melting points are uncorrected centigrade tempera-
tures unless otherwise noted.

The oxidation of the 4-acetylbiphenyl was attempted using commercial "chlorox" solution, but this failed completely, apparently due to sensitivity of the reaction to the pH of the medium. The use of the sodium hypochlorite solution of Newman and Holmes[3], prepared from sodium hydroxide and chlorine, resulted in almost 100 percent yield of the crude acid. This crude acid was further purified by sublimation to yield clear needle like crystals, melting at $226.0-226.5^{\circ}$ (cf. $224-226^{\circ}$[1]). The yield of purified acid was 76 percent based on the ketone.

3-Biphenylcarboxylic acid. This acid was prepared by the carbonation of the Grignard of 3-bromobiphenyl[4], prepared by a modification of the method of Huber[5]. The latter synthesis consists of brominating acetylated 2-aminobiphenyl, hydrolyzing the amide and removing the amino group by reduction of the diazonium salt.

The first three steps of Huber's synthesis were used with very good yields, although somewhat lower than those

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[3]M. S. Newman and H. L. Holmes, "Organic Syntheses", Coll. Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

[4]G. F. Woods and F. T. Reed, J. Am. Chem. Soc., 71, 1348 (1949).

[5]F. W. Huber, et al., ibid., 68, 1109 (1946).

originally reported. Since the diamination procedure with
a yield of 58 percent was by far the most limiting step of
the above preparation, the method of Kornblum[6] employing
hypophosphorous acid for the reduction of diazonium salts
was used with the expectation of greatly increasing the
yield of the bromide.

The diamination was carried out in the following manner.
Fifty milliliters of concentrated hydrochloric acid and 250
milliliters of water were placed in a one liter 3-necked
flask equipped with dropping funnel, thermometer, and "true
bore" stirrer. This solution was heated to 60° and 48.6 grams
(0.196 mole) of 2-amino-5-bromobiphenyl was added, forming
a heavy precipitate which dissolved on heating to 100° but
started reprecipitating on cooling below 85°. The flask
and contents were cooled to -5° and 15.0 grams (0.211 mole)
of sodium nitrite dissolved in 36 milliliters of water was
added dropwise over a period of approximately 50 minutes,
the temperature being kept at -3° to -8°. After stirring
for a further 20 minutes, 130 milliliters of 50 percent
hypophosphorous acid was added dropwise over a period of
40 minutes, the temperature being maintained at -2° to -5°.
The stirring was continued for approximately three hours

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[6]N. Kornblum, "Organic Reactions", Vol. II, John Wiley
and Sons, New York, N. Y., 1944, p. 294.

at this temperature after which the reaction flask was transferred to the ice box for 40 hours.

A dark brown non-aqueous layer separated, from which the aqueous layer was decanted. The latter was extracted with benzene. The extracts and the crude product mixture were combined in a separatory funnel with enough additional benzene to bring the volume to about 300 milliliters. This solution was washed twice with both 20 percent sodium hydroxide, water, and warm 1:1 sulfuric acid. This was followed by a small portion of 5:1 concentrated sulfuric acid which caused the formation of a black residue in an otherwise homogeneous solution. Addition of water produced two layers which separated. The benzene solution was thoroughly washed with distilled water and dried over anhydrous potassium carbonate.

The benzene was removed at reduced pressure. The dark residual liquid was transferred in two portions to a small fractionation apparatus. Most of the product distilled as a colorless liquid at 177° at 4 mm. pressure. The yield of 3-bromobiphenyl was 40.7 grams (89%).

The preparation of the Grignard of 3-bromobiphenyl was carried out in the usual manner using the procedure of

Vogel.[7] A nitrogen atmosphere was maintained during the preparation and with additional pressure was used to force the prepared Grignard through a double capillary tipped delivery tube from the reaction flask into the dry ice ether slurry. The light tan solid suspension formed, collected into a gummy mass on warming to room temperature, and was hydrolyzed very slowly with dilute hydrochloric acid. The acid was extracted with 10 percent sodium hydroxide from the ether extracts of the hydrolysis mixture and reprecipitated with hydrochloric acid. This crude acid was recrystallized from acetone-Skelly "B" mixture to give white leaflets, melting at 166.5-166.8° (cf. 150-153°[4], 162°[8]). The yield was approximately 60 percent on three preparations.

Benzyl alcohols

Most of the benzyl alcohols used were prepared by the lithium aluminum hydride reduction of the corresponding benzoic acids as previously employed by Kochi[9]. The

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[7]A. I. Vogel, "Practical Organic Chemistry", 2nd ed., Longmans, Green, and Co., London, 1951, p. 725.

[8]F. Mayer, Ber., 46, 2587 (1913).

[9]J. Kochi and G. S. Hammond, J. Am. Chem. Soc., 75, 3443 (1953).

commercially available benzoic acids were first purified
by recrystallization from ethanol followed by vacuum sub-
limation. This procedure was found to increase greatly the
ease of purification of the corresponding benzyl alcohols,
as the latter otherwise had a much greater tendency to oil
out during recrystallizations.

The general procedure of reduction was to add the acid,
which was usually quite insoluble in ether, either directly
or by means of a Soxhlet extractor to a suspension of a fair
excess of lithium aluminum hydride in anhydrous ether as
given in "Organic Reactions".[10] After careful hydrolysis
of the reaction mixture, the crude alcohol was obtained by
evaporation of the dried ether extracts.

The crude alcohols were purified by the following
methods.

p-Phenylbenzyl alcohol (4-biphenylcarbinol). The
crude alcohol from the reduction of 4-biphenylcarboxylic
acid was recrystallized twice by dissolving in acetone and
precipitating with Skelly "A" to give a product which melted
at $100.5\text{-}101.0^{\circ}$ (cf. $101\text{-}102^{\circ}$[11]). Two preparations gave
yields of 54 and 86 percent.

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[10] "Organic Reactions", Vol. VI, John Wiley and Sons,
Inc., New York, N. Y., 1951, p. 491, 492.

[11] J. V. Braun and H. Engel, Ann., 436, 309 (1924).

m-Phenylbenzyl alcohol (3-biphenylcarbinol). The crude alcohol from the reduction of 3-biphenylcarboxylic acid was recrystallized twice from Skelly "D" solution obtained by decantation from the oil which separated first on cooling. The white crystalline product obtained in 44 percent yield melted at $51.2-51.5°$[12]. Analysis: C, 84.67%; H, 6.45%[*] (Calculated: C, 84.76; H, 6.56).

p-Methylbenzyl alcohol. The crude alcohol from the reduction of purified p-toluic acid (Matheson, reagent grade) was recrystallized twice from Skelly "B" to give a product melting at $59-60°$ (cf. $61-62°$[9]). Yields of two preparations were 62 and 78 percent.

p-Chlorobenzyl alcohol. The crude alcohol from the reduction of purified p-chlorobenzoic acid (Eastman Kodak, reagent grade) was recrystallized first from benzene-Skelly "B" mixture and then from aqueous ethanol to give a product melting at $71-72.5°$ (cf. $71-72.5°$[13]). Approximately 75 percent yields were obtained in each of three preparations.

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[12]Adam reports this compound as an oil which slowly solidified. Ann. Chem. et Phys. 15, 243 (1888).

[13]W. H. Carothers and R. Adams, J. Am. Chem. Soc., 46, 1681 (1924).

*Analysis done by W. Manser, Laboratorium für Organische Chemie, Zürich, Switzerland.

p-Fluorobenzyl alcohol. The crude alcohol from the reduction of p-fluorobenzoic acid (Eastman Kodak, reagent grade) was fractionally distilled at 1 mm. pressure, boiling point: 69-71°. The resulting colorless liquid, obtained in 78 percent yield, had a melting point of 22-23° and a boiling point of 209° (730 mm.). $N_D^{20} = 1.5080$.[*] Analysis: C, 66.02%; H, 5.68%[**] (Calculated: C, 66.60; H, 5.60).

p-Nitrobenzyl alcohol. This alcohol (Eastman Kodak, reagent grade) was used without further purification after attempts to recrystallize the alcohol were not too successful in improving the melting point, 92-93° (cf. 96-97°[9]). This was thought not to be too serious since the resulting tosylate ester is stable enough to allow extensive recrystallization.

Benzyl alcohol. This alcohol (Eastman Kodak, reagent grade) was purified by vacuum fractional distillation in a three foot column at 3-4 mm., pressure, boiling point 72.5-73.5^{o}.

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[*]A search of the literature revealed no references that this compound has been previously prepared and isolated, although the corresponding benzyl halides have been subjected to hydrolysis in rate studies.

[**]Analysis by W. Manser, Switzerland.

p-Toluenesulfonyl chloride

p-Toluenesulfonyl chloride (Eastman Kodak, reagent grade) was vacuum distilled through a 4 inch vigreaux column with a heated side arm at approximately 2-4 mm. pressure using a capillary ebulator supplied with nitrogen. Boiling point: 118-122°. A small amount of low boiling for run was discarded. The solidified distillate was remelted and poured into glass jars for storage in order to cut down hydrolysis. The chloride kept extremely well in this form.

Before use in preparing benzyl esters, the melted chloride was added to a small amount of benzene and cooled. A small amount of dark crystals precipitated and was removed by filtration. Skelly "A" was then added slowly and cooled to 0° to precipitate the p-toluenesulfonyl chloride in the form of very fine crystals and in high yield. The crystals melted at 68.5-69°.

Substituted benzyl tosylates

With the exception of the p-nitro compound, the benzyl tosylate esters were prepared by the method of Kochi[9], which consists of reacting the benzyl alcohol with sodium hydride in ether solution and then adding p-toluenesulfonyl chloride

dissolved in ether to the resulting suspension of the sodium benzylate. The precipitated sodium chloride was removed by pressure filtration in a specially constructed, medium grade, sintered glass filter funnel, the filtration being carried out under an atmosphere of nitrogen.

The esters were further purified by one of two methods or by a combination of the two. In one, a part of the ether was evaporated under reduced pressure and the more concentrated solution was cooled in a dry ice bath to precipitate the ester. The ether solution was separated by means of a filter stick in such a way as to protect the contents of the flask from atmospheric moisture. The precipitate was quickly returned to room temperature, fresh ether was added, the solution was recooled, and the solvent was removed from the precipitated crystals as before. After three crystallizations the ester was dissolved in ether for storage until ready for use. In the second method, employed for the benzyl and chlorobenzyl tosylates, the ether was removed completely and the resulting oil or solid was dissolved in benzene. The product was then crystallized by the addition of Skelly "B" and cooled to $0°$. The crystals were separated by filtration on a sintered glass filter and washed with Skelly "A". Care was taken to prevent the benzyl tosylate crystals from becoming too warm or coming in contact with too much

atmospheric moisture in the process. After two or three crystallizations the esters were dissolved in benzene for storage until use.

Although great care was necessary in the handling of the crystalline benzyl and p-methyl benzyl tosylates to prevent rapid autocatalyzed polymerization, a long recognized characteristic of these esters[9,14], the recrystallized compounds appeared to be quite stable dissolved in anhydrous benzene or ether solution. A solution of p-methylbenzyl tosylate in ether showed no decomposition after a period of four months and a solution of benzyl tosylate in benzene showed no decomposition after a period of eight months. By storing the prepared compounds in solution, these esters could be synthesized in relatively large quantities and used as needed.

To prepare the solid ester from these solutions for weighing in the preparation of the samples for the hydrolysis reactions, those dissolved in benzene solution were subjected to a final recrystallization. A small portion of the benzene solution was taken for use and the crystals after washing with Skelly "A" were dried on the filter under a

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[14] C. M. Suter, "The Organic Chemistry of Sulfur", J. Wiley and Sons Inc., New York, N. Y., 1944, p. 525, 528.

rubber dam by the application of aspirator vacuum. This procedure worked well for the unstable benzyl tosylate if the crystals were not allowed to stand too long at room temperature after the cooling effect of the evaporating solvent had vanished. Those esters dissolved in ether solution were usually more reactive and were obtained in a solid form by evaporation of the ether from a suitable sized sample at 0° with a vacuum of one millimeter pressure. The solid p-methylbenzyl tosylate obtained could be kept for a number of hours without apparent decomposition if moisture was rigidly excluded and the temperature was kept at 0°. At room temperature the decomposition is apparently initiated by a small amount of water vapor, and once started proceeds with extreme rapidity in a highly exothermic reaction.

The samples were weighed as rapidly as possible and re-dissolved in the organic solvent to be used in the hydrolysis reaction. This could usually be accomplished without any noticeable decomposition.

The nitrobenzyl tosylate was prepared[*] by the method of Tipson[9,15] by reacting the p-toluenesulfonyl chloride

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[15] J. Tipson, _J. Org. Chem._, 2, 239 (1944).

[*] The nitro compound was prepared and purified by Mr. R. Schlott of this laboratory.

with the alcohol in pyridine solution. The crude product
was recrystallized five or six times from Skelly "D" and
dried under vacuum. Five grams of this ester was dissolved
in 500 milliliters of purified acetone and 4.00 grams were
dissolved in 500 milliliters of purified dioxane. Samples
for the hydrolysis reactions were obtained by taking 25 or
50 milliliter portions of these solutions.

The melting points of the prepared benzyl tosylates are
listed in Table 1.

Table 1. Melting points of the benzyl tosylate esters

Tosylate	Observed m.p.	Literature m.p.[a]
Benzyl	57.8-58.8	58.5-58.8
p-Methylbenzyl	51-52	57.9-58.5
p-Chlorobenzyl	52.8-53.0	---
p-Fluorobenzyl	54-55	---
p-Phenylbenzyl	114	---
m-Phenylbenzyl	76-78	---
p-Nitrobenzyl	99-100	105.0-105.5

[a] J. Kochi and G. S. Hammond, op. cit.

Triethylamine

Approximately 250 milliliters of triethylamine (Matheson) was refluxed with sodium metal for one half hour and then distilled through a three foot "Heli-Pak" fractionating column at atmospheric pressure, 739 mm. After taking off a 25 milliliter forerun an approximately 215 milliliter center fraction boiling at 88.5 to 88.8^o was collected for use and stored in a glass stoppered flask.

Lithium perchlorate

Lithium perchlorate ($LiClO_4 \cdot 3H_2O$, G. F. Smith, Co) was dehydrated by heating the hydrate in a 500 ml. round bottom flask connected to a vacuum pump. Sulfuric acid was used as a bath around the flask. The bath was heated to approximately 100° where the first two molecules of water are lost and then the temperature was increased to 150-160° for 6 hours. The dehydration could be carried out in this manner without the fusion of the hydrate. The resulting anhydride was highly porous and easy to remove from the flask. An attempt to use a vacuum oven resulted in reaction with the vapor of the silicon grease used as a sealant on the door, and in rupture of the hydrate crystals throwing

the perchlorate over the interior of the oven. The anhydrous lithium perchlorate was stored in glass stoppered bottles in a desiccator over anhydrous magnesium perchlorate, and was used to prepare the 1.04 M. aqueous salt solutions used in all hydrolysis rate determinations.

Acetone

Stockroom grade acetone was refluxed with potassium permanganate with very little decoloration. The acetone was distilled from the solution and dried over anhydrous potassium carbonate. The dried acetone was then fractionally distilled through 70 plate Oldershaw column which was protected from atmospheric moisture. The purified acetone was stored in a tightly capped four liter bottle and transferred to a one liter glass stoppered bottle for use. Boiling point: 55.0° at 749 mm.

Dioxane

Commercial grade dioxane (Carbide and Carbon) was refluxed over sodium metal for 3 days and distilled through an 18 inch vigreaux column. The major center fraction was collected. Boiling point: 99.0° at 741 mm. $N_D^{20} = 1.4218$.

Determination of the Rates of Hydrolysis

Apparatus

The rates of hydrolysis were determined by the rapid intermittent titration method[16,17] using glass electrodes to determine the equivalence point as previously employed[18]. The main apparatus consisted of Beckman Model G pH meter and a large sixteen inch thermostated glass water bath (Precision Instrument Co.) on the support rods of which were mounted two reaction cell assemblies. The reaction cell assembly consisted of a five milliliter microburet with attached reservior for titrant storage, a stirring motor, and a glass reaction cell, all rigidly mounted on a common support which could be raised and lowered on the thermostat supports. This allowed the reaction cell to be mounted in position and then lowered into the thermostat.

Because of the large coefficient of expansion of the titrant solutions, the microburets were fitted with water

[16]P. Bartlett and C. Swain, *J. Amer. Chem. Soc.*, *71*, 1406 (1949).

[17]W. Peters and S. Walker, *Biochem. J.*, *17*, 260 (1923).

[18]J. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, *75*, 3445 (1953).

jackets and thermostated at 25° at all times by means of a
small second thermostat and circulating pump. This pre-
caution was especially necessary for the slower rate deter-
minations due to variations in room temperature during the
run. It also made the necessity for standardization of the
titrant solution less frequent.

The reaction cell was constructed with three side arms
into which a thermometer and the two electrodes would just
pass, giving a minimum of dead space for the solution in
these parts of the cell (see Figure 1). The electrode arms
were fitted with tight rubber collars to prevent the escape
or evaporation of the solvent from the cell during the
slower reactions. The thermometer was usually removed after
checking the initial temperature and this arm was corked to
prevent further evaporation. Evaporation was some problem
especially in the reactions employing aqueous acetone at the
higher temperatures.

A 105° thermometer with 0.1° divisions was used for
checking the temperature of the reaction cell and the bath.
It was calibrated at 0° and at the three bath temperatures
employed, using a National Bureau of Standards calibrated
thermometer.

A fair amount of difficulty was encountered in finding
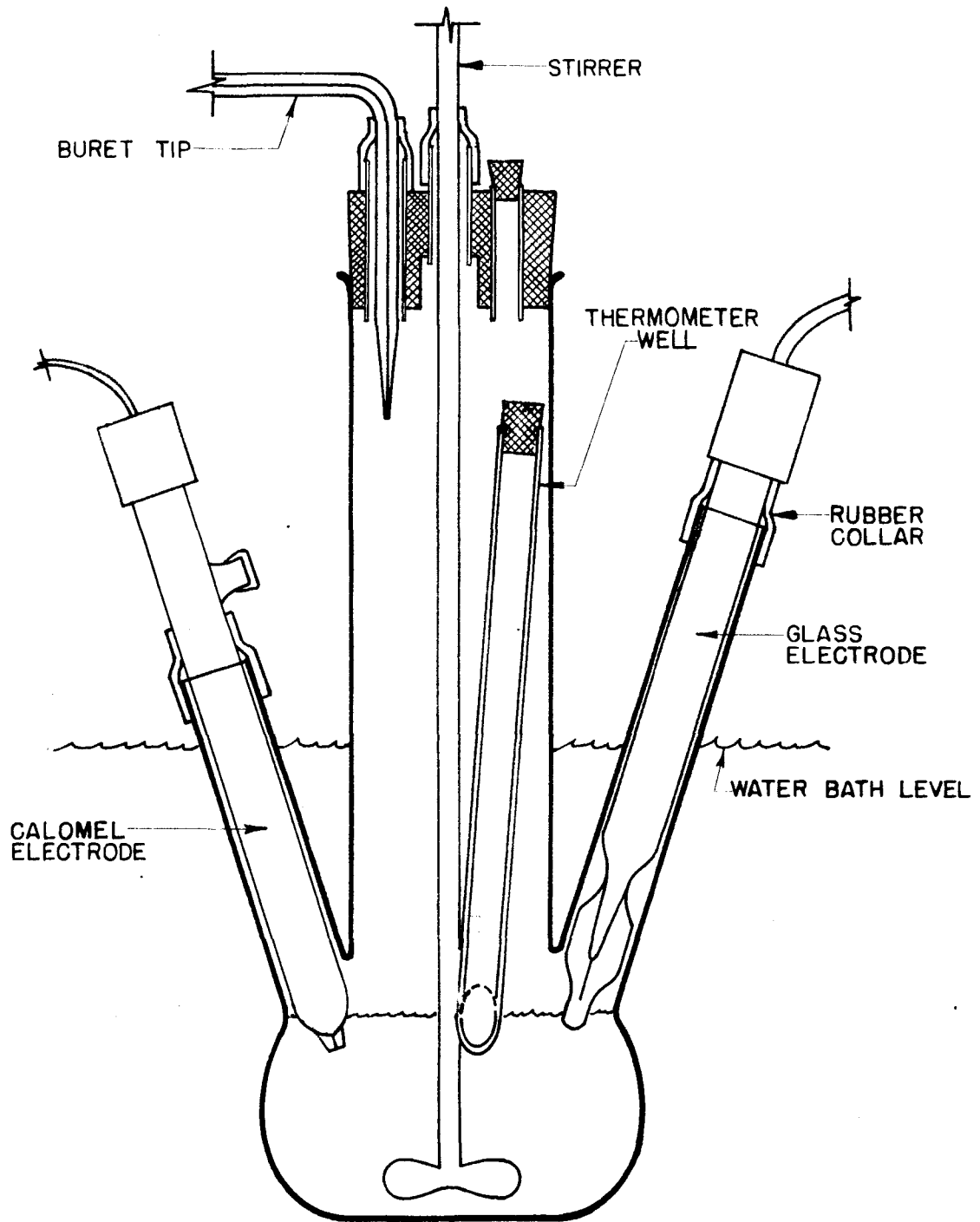a suitable stopcock lubricant for the burets, since the

FIG. I   REACTION CELL

titrants were solutions consisting largely of acetone and dioxane, both very good solvents. Apiezon N lubricant proved to be by far the most satisfactory of the lubricants tried. Silicone grease dissolved quite slowly, but was deposited as a film on the buret walls causing the titrant not to drain properly. A rubber base lubricant was also found to be insoluble in the titrants, but would not stick to the stopcock surfaces in the presence of the titrant. It soon rolled up and came out, allowing the titrant to leak past the stopcock.

Three thermoregulators were carefully set originally and these settings were never altered during the course of the experimental work. They were set at 24.99°, 35.00° and 45.10° respectively. There appeared to be a slight increase in the setting of the 45° regulator during the work, perhaps as much as 0.05°. The variation in the temperature of the bath was usually less than 0.02°.

Beckman number 1190-42 glass electrodes were chosen for use in these solvents of high organic content since they had previously been found to be superior in their performance in aqueous ethanol solutions[19]. They were stored in distilled water when not in actual use. The reference electrodes were Beckman calomel electrodes, number 1170.

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[19] B. Gutbezahl and E. Grunwald, ibid., 560.

It was found necessary to ground the water of the water
bath to the water system to obtain good electrode sensitivity.
This in turn required that the meter be grounded in order to
obtain a steady null point. It was also necessary to use
distilled water in the thermostat and to change it from time
to time as it absorbed ions from various sources.

Preparation of titrants

Triethylamine was used to titrate the p-toluenesulfonic
acid liberated during the course of the hydrolysis, since
this highly sterically hindered base would reduce to a mini-
mum the formation of the benzyl ammonium salt as a side
reaction. The titrants were prepared by dissolving 5.2
milliliters of triethylamine in sufficient amount of the
aqueous-organic solvent mixture of the same volume ratio as
the reaction mixture being titrated, to make 500 milliliters
of approximately 0.15 N solution. These solutions were
stored in the glass stoppered 500 milliliter volumetric
flasks to prevent evaporation of the triethylamine or
acetone. They showed little tendency to change their
strength during the course of the work. All hydrolysis
reactions were followed with a titrant of the same solvent
composition as the reaction mixture, with the exception of

the 23.1 percent aqueous dioxane reactions which were
followed with 33.3 percent aqueous dioxane titrant.

The titrants tended to weaken slowly during storage in
the burets, apparently due to some evaporation of the tri-
ethylamine from solution. For this reason the burets were
kept stoppered with rubber caps except during actual titra-
tions, and the solutions were standardized from time to time.
The strength of the triethylamine solutions originally was
determined by titration with approximately 0.24 N hydrochloric
acid solution[18] which had to be standardized indirectly with
sodium hydroxide solutions. This long procedure was not too
reproducible and quite time consuming. However, it was found
quite early that the triethylamine solutions could be stand-
ardized directly with potassium acid phthalate as a primary
standard using phenol red as an indicator in aqueous solu-
tion, and this method used thereafter.

Titration curves were plotted for the titration of p-
toluenesulfonic acid with triethylamine in 83.3 and 96.2
percent aqueous acetone solutions. These curves are given
in Figure 2. The sharp colorless endpoint of bromophenol
blue in these solvents was found to coincide almost exactly
with the center of the sharp break in the titration curve.
Nevertheless a mixture of bromocresol green and methyl red,
as used in previous work, was employed in most of the

Fig. 2. Titration of p-toluenesulfonic acid with 0.15 N
triethylamine in aqueous acetone

Curve 1 - Titration curve in 96.2% acetone

Curve 2 - Titration curve in 83.3% acetone

Shaded area - Range of color change for bromo-
phenol blue in 83.3% acetone

List of colors - Colors given by methyl red
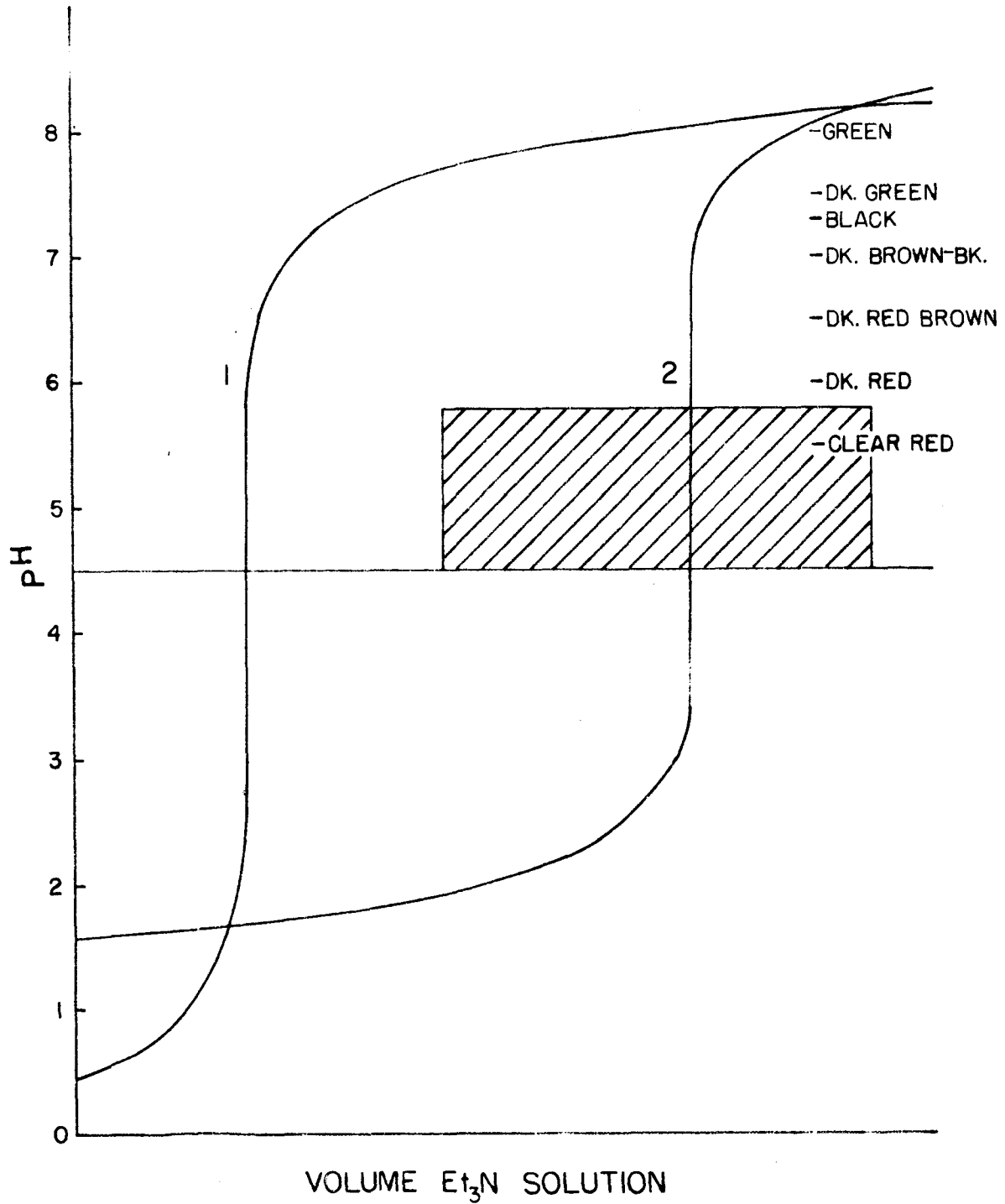bromocresol green indicator mixture
in 83.3% acetone

FIG. 2 TITRATION OF P-TOLUENESULFONIC ACID WITH 0.15 N
TRIETHYLAMINE IN AQUEOUS ACETONE

hydrolysis, since it gave a wide range of color changes before the equivalence point was reached from the basic side and thus produced an indication of the closeness of approach to this point. The bromophenol blue was used, however, in the very slow aqueous acetone hydrolysis, in which the pH meter was not used.

In the aqueous dioxane solutions employed, the stoichiometric points were found to occur at approximately pH 6.0 and this pH was used for timing the rate of the hydrolysis reactions in these solutions. Bromocresol green alone gave a good indication of this approaching equivalence point.

General procedure of hydrolysis

The general procedure of the intermittent titration method is to follow the course of hydrolysis of the benzyl ester by the titration of the liberated acid directly in the reaction cell as it is formed. This method of determination of the kinetics is applicable to this reaction since the latter is neither acid nor base catalyzed in contrast to the hydrolysis of ordinary esters.

The solid tosylate ester, prepared from its benzene or ether solution, was rapidly weighed, transferred directly to the reaction cell, and dissolved immediately in fifty

milliliters of the organic solvent to be used in the hydrolysis reaction. By means of one run on a sample that had decomposed to a fairly deep red color during the weighing process, it was found that any prepolymerization of the solid did not appear to affect the value of the rate constant obtained. However, polymerization was avoided quite successfully. The size of the sample varied from 0.2 to 1.7 mole (60 to 500 mg.). Check runs showed that rates were truly independent of sample size. The prepared sample solutions were usually used immediately. However, some of the dioxane solutions were prepared a day or two in advance and stored in the corked reaction cells.

The reaction cell containing the sample solution was mounted in the thermostat, one drop of 0.5 percent bromocresol green indicator in acetone solution was added, a second drop of 0.6 percent methyl red in aqueous acetone was added in the case of the reactions in aqueous acetone solution, and the contents were brought to the thermostat temperature. The required amount of 1.04 molar aqueous lithium perchlorate solution was then added. In the slower reactions this was done directly from the pipet, and the resulting solution was allowed to return to the temperature of the bath before timing of the reaction was started. In the faster reactions in which it was necessary to start

timing the reaction almost immediately, the aqueous solution
was cooled or heated sufficiently to just correct for the
heat of mixing so that the resulting reaction mixture would
be at the bath temperature. The adjustment of the tempera-
ture of the aqueous solution was carried out in a specially
constructed delivery funnel equipped with a water jacket,
through which water of the approximate temperature was
circulated.

After the cell contents had reached the temperature of
the thermostat, an initial titration was made by adding a
slight excess of the triethylamine titrant as shown by the
color change of the indicator. The time was observed at
the point where the pH of the reaction mixture became equal
to that of the equivalence point of the titration curve of
the p-toluenesulfonic acid in the corresponding solvent.
The reaction was allowed to proceed in the acid medium until,
when convenient, approximately ten to fifteen percent of the
remaining benzyl ester had hydrolyzed. Another titration
was then carried out as before. In a few instances the
reaction medium was kept basic during a period of the
hydrolysis to check for base catalysis, but none was observed.
The absence of acid catalysis was shown by the independence
of the rate constant on the time interval since the acidity
of the media increases with the length of time of reaction,

other things being equal. In the very fast reactions with pk values much less 3.0, the aid of a second person was required to read and record the buret values.*

Infinite titers were determined by adding excess water to the reaction cell and heating to 45 to 80° for a time sufficient to hydrolyze the remaining benzyl ester. The solution was then titrated.

Exceptions to the above general procedure were made in the preparation of the samples of the p-nitrobenzyl tosylates and in the carrying out the slower rate determinations in aqueous acetone solvents. The nitro benzyl tosylate samples were obtained by taking twenty-five or fifty milliliter aliquots from the prepared stock solution of the ester in the correct organic solvent. It was found difficult to completely hydrolyze the samples of the p-nitrobenzyl ester for determination of infinite titers. Since some of the more carefully hydrolyzed samples gave 100 percent titers, this value was assumed for all p-nitrobenzyl tosylate samples.

In order that a number of the very slow reactions in aqueous acetone could be carried out simultaneously, these reactions were carried out in stoppered 125 milliliter Erlenmeyer flasks partially submerged in the thermostat.

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*This aid was generously given by Dr. J. Sen, M. J. Tanaka, and Mr. R. Schlott.

Even though evaporation of acetone was a problem at 45°, it
was probably less than it would have been in the regularly
used reaction cell. Bromophenol blue was used to determine
the equivalence points since the glass electrodes could not
be used in these flasks. The end point was very sharp,
however. The indicator was slowly destroyed in the n-nitro-
benzyl tosylate reactions, but the concentration of indicator
is extremely small and should not have affected the rate con-
stant even if the ester is the agent destroying the indicator.

Experimental data

A summary of the physical properties of the six sol-
vents employed in the course of the present work is given in
Table 2. These particular solvent compositions were chosen
because of their similar low range of dielectric property,
and relative ease with which they could be employed in the
hydrolysis reactions carried out. The dielectric constant
as given in the table is that for the pure two component
aqueous solvent system.

An example of typical data obtained during the course
of a hydrolysis reaction is given in Table 3. There is
little significant trend in the rate constants as determined
for the individual time periods, and the true value is taken

Table 2. Physical properties of the solvents employed

| Properties | Solvent composition[a] | | | | | |
| | Acetone | | | Dioxane | | |
	83.3%	90.9%	96.2%	55.6%	66.7%	76.9%
Volume ratio[b]	10-50	5-50	2-50	40-50	25-50	15-50
Volume percent water	16.7	9.1	3.8	44.4	33.3	23.1
Weight percent water	20.2	11.0	4.7	44.7	33.4	23.0
Mole percent water	45.2	29.2	14.2	79.8	70.8	58.8
Molar conc. water	9.25	5.04	2.14	24.7	18.5	12.8
Molar conc. $LiClO_4$	.173	.095	.040	.463	.347	.240
Dielectric constant[c], 25°	30.0	24.5	21.3	31.2	20.2	12.5
Dielectric constant[c], 45°	27.0	22.0	19.3	28.2	18.0	11.5
Hammett acidity function[d]	2.4	2.3	1.9	2.1	2.3	2.3

[a]Volume percent for ideal solution at 25°.

[b]Volume ratio of water to organic constituent for volumes before mixing at 25°.

[c]Obtained by interpolation from plots of values for the two component solvent system given by G. Akerlof, J. Am. Chem. Soc., 54, 4125 (1932); 58, 1241 (1936).

[d]Estimated from plot given by E. A. Brande and E. Stern, J. Chem. Soc., 1948, 1976.

Table 3. Hydrolysis of benzyl tosylate in 66.7 percent aqueous dioxane at 35.0° and constant ionic strength

Vol. titrant[a] (ml.)	Time increment (10^3 sec.)	Percent reaction	$10^4 k$ (sec.$^{-1}$)
0.		0.	
.393		7.4	
1.765	1.007	33.1	3.26
2.364	.577	44.4	3.21
2.878	.603	54.0	3.20
3.471	.864	65.0	3.25
4.067	1.209	76.3	3.23
4.460	1.245	83.7	3.01
4.760	1.359	89.4	3.23
Rate over entire period			3.20

[a]Wt. of sample: 209.9 mg. (0.803 mmol.).
Normality of titrant: 0.1475.
Infinite titer: 5.30 ml.
Sample purity by infinite titer: 97.4%.

as that for the entire timed period. The unimolecular rate
constants were calculated by use of the integrated form of
the rate equation

$$\ln \frac{a - x_1}{a - x_2} = k(t_2 - t_1) . \qquad (4)$$

Many reactions showed a small tendency to fall off in rate
after fifty to seventy-five percent reaction, probably due
to small inaccuracies in determining the infinite titers.
However, this should have little effect on the values up
to the point where such a tendency became observable.
Errors in reading a buret or determining the time of the
equivalence point for an individual time period cancel out
usually for the longer periods.

In Table 4 is an example of a relatively slow reaction
in which there is a definite increase in the rate constant
as the reaction proceeded. This is believed due to an in-
crease in the water concentration resulting from evaporation
of the acetone from the reaction mixture. The latter was
known to be occurring for some of the reactions of this
group. Here the value of the rate constant is taken as
that of the initial time period.

The pk values for the hydrolysis reactions in aqueous
acetone are given in Table 5, and those for the reactions

Table 4. Hydrolysis of p-chlorobenzyl tosylate in 96.2
          percent aqueous acetone at 25.0° and constant
          ionic strength

Vol. titrant[a] (ml.)	Time increment $(10^5$ sec.)	Percent reaction	$10^7 k$ (sec.$^{-1}$)
0.		0.	
.368	3.433	10.4	3.20^b
.611	2.430	17.3	3.32
1.013	4.319	28.7	3.42
1.390	4.509	39.4	3.60
Rate for entire period			3.41

[a]Wt. of sample: 155.4 mg. (0.524 mmol.).
   Normality of titrant: 0.1445.
   Infinite titer: 3.533 ml.
   Sample purity by infinite titer: 97.3%.

[b]Assumed to be the best value since reactions known to
be losing acetone during these determinations.

in aqueous dioxane are given in Table 6. The precision of
the pk values varies greatly, as might be expected for a
group of reactions whose rates cover a range of 10^6. The
precision of most of the rate constants obtained was greater
than that given in the tables. However, for the extremely
slow and fast reactions, it is slightly less.

Table 5. pk Values for hydrolysis of benzyl tosylates in aqueous acetone

Subst.[a]	Temp. °C	Solvent composition[b]		
		83.3%	90.9%	96.2%
H	25	5.05	5.61	6.39
	35	4.59	5.15	----
	45	4.11	4.69	5.48
NO$_2$	25	6.30	6.76	7.45
	45	5.38	5.83	6.58
Cl	25	5.22	5.76	6.50
	35	4.74	5.26	----
	45	4.32	4.86	5.56
F	25	4.74	5.37	6.13
	45	3.83	4.50	5.23
Me	25	3.72	4.46	5.26
	35	3.22	3.98	----
	45	2.77	3.52	4.35
C$_6$H$_5$	25	4.12		
	45	3.10		
m-C$_6$H$_5$	25	5.21		
	45	4.30		

[a]Substituents in para position except m-C$_6$H$_5$.
[b]Volume percent for ideal solution at 25°.

Table 6.   pk Values for hydrolysis of benzyl tosylates in aqueous dioxane

Subst.[a]	Temp. °C	Solvent composition[b]		
		55.6%	66.7%	76.9%
H	25	3.40	3.95	4.43
	35	2.97	3.49	3.98
	45	2.53	3.07	3.53
NO$_2$	25	5.32	5.62	5.98
	35	4.79	5.13	----
	45	4.35	4.71	5.10
Cl	25	3.67	4.24	----
	35	3.24	3.77	----
	45	2.82	3.33	----
F	25	2.96	3.60	4.15
	45	2.17	----	3.24
Me	25	1.76	2.45	3.12
	35	1.35	2.05	2.69
	45	----	----	2.22
C$_6$H$_5$	25	2.29	2.98	----
m-C$_6$H$_5$	25	3.72	4.22	----

[a]Substituents in para position except m-C$_6$H$_5$.

[b]Volume percent for ideal solution at 25°.

The Arrhenius energies of activation were calculated by using the integrated equation

$$pk_2 - pk_1 = \frac{Ea}{R} (1/T_1 - 1/T_2) \qquad (5)$$

and are given in Table 7. The values given for p-methyl benzyl tosylate in 55.6 and 66.7 percent dioxane were obtained by using extrapolated values for the rate constants

Table 7. Arrhenius activation energies for benzyl tosylate hydrolysis

Subst.[a]	Acetone			Dioxane		
	83.3	90.9	96.15	44.4	33.3	23.1
Me	20.6	20.4	19.7	(18.4)[b]	(18.9)[b]	19.5
H	20.4	20.0	19.7	18.9	19.1	19.5
Cl	19.5	19.5	20.4	18.4	19.7	
NO_2	20.0	20.2	18.9	21.0	19.7	19.1
F	19.7	18.9	19.5	17.2		19.7
C_6H_5	22.1					
$m-C_6H_5$	19.7					

[a]Substituents in para position except $m-C_6H_5$.

[b]Extrapolated values of pk for reaction at $45°$ used.

at 45°. Plots of pk vs. 1/T were completely linear for
the three temperatures employed except for three or four
of the fastest reactions.

DISCUSSION AND CONCLUSIONS

The pk values from Table 5 for the hydrolysis of the benzyl tosylates in aqueous acetone at most of the different temperatures employed, have been plotted in Figure 3 against the pk values of the reactions for a single solvent and temperature, 83.3 percent acetone at 25°. Similar graphs are given in Figure 4 for the hydrolysis reactions in aqueous dioxane. Such graphs are equivalent to Hammett σ curves, but with redefined values of ρ and σ.

Since the definition of σ by Hammett was arbitrary[1,2] being in terms of the equilibrium constants for the ionization of the benzoic acids, a different σ can just as well be defined in terms of equilibrium constants or rate constants of any other reaction. Such redefined values are related however to the values of Hammett. If one defines σ' in terms of the rates of hydrolysis of benzyl tosylates for a given solvent and temperature as

$$\sigma' = \log k'/k'_0 = \rho_0 \sigma^*$$ (6)

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[1] L. P. Hammett, J. Am. Chem. Soc., 59, 96 (1937).

[2] H. H. Jaffe, Chem. Rev., 53, 191 (1953).

Fig. 3. Rates of hydrolysis of benzyl tosylates in aqueous acetone

Curve 1 - Hydrolysis in 96.2% acetone at 25° C

Curve 2 - Hydrolysis in 90.9% acetone at 25° C

Curve 3 - Hydrolysis in 96.2% acetone at 45° C

Curve 4 - Hydrolysis in 90.9% acetone at 35° C*

Curve 5 - Hydrolysis in 83.3% acetone at 25° C**

Curve 6 - Hydrolysis in 90.9% acetone at 45° C

Curve 7 - Hydrolysis in 83.3% acetone at 35° C*

Curve 8 - Hydrolysis in 83.3% acetone at 45° C

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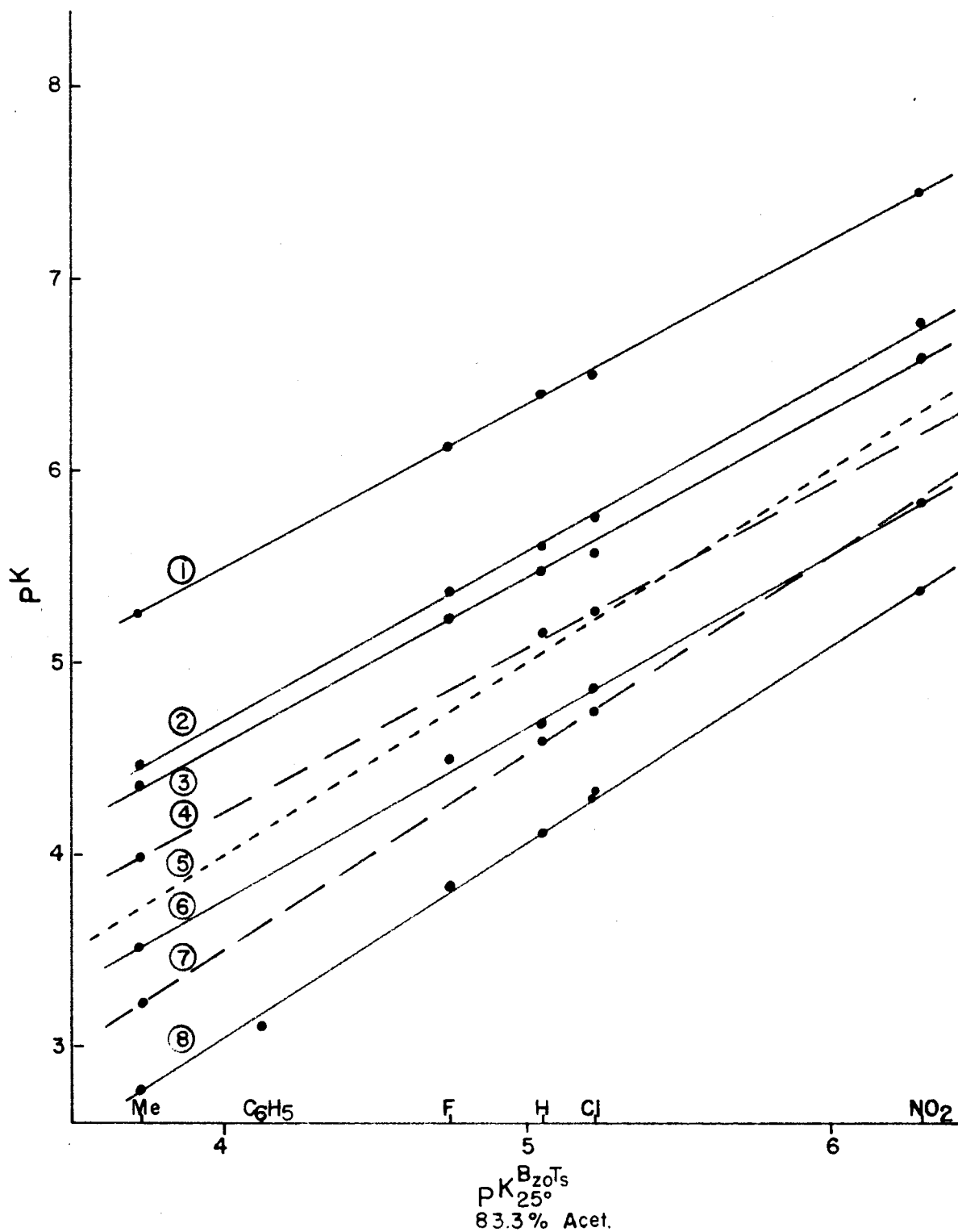*No value of pk for nitro substituent.

**Unit slope line.

FIG. 3 RATES OF HYDROLYSIS OF BENZYL TOSYLATES
IN AQUEOUS ACETONE

Fig. 4.   Rates of hydrolysis of benzyl tosylates in
aqueous dioxane

Curve 1 - Hydrolysis in 76.9% dioxane at 25° C

Curve 2 - Hydrolysis in 66.7% dioxane at 25° C[*]

Curve 3 - Hydrolysis in 76.9% dioxane at 45° C

Curve 4 - Hydrolysis in 66.7% dioxane at 35° C

Curve 5 - Hydrolysis in 55.6% dioxane at 25° C

Curve 6 - Hydrolysis in 55.6% dioxane at 35° C

Curve 7 - Hydrolysis in 55.6% dioxane at 45° C[**]

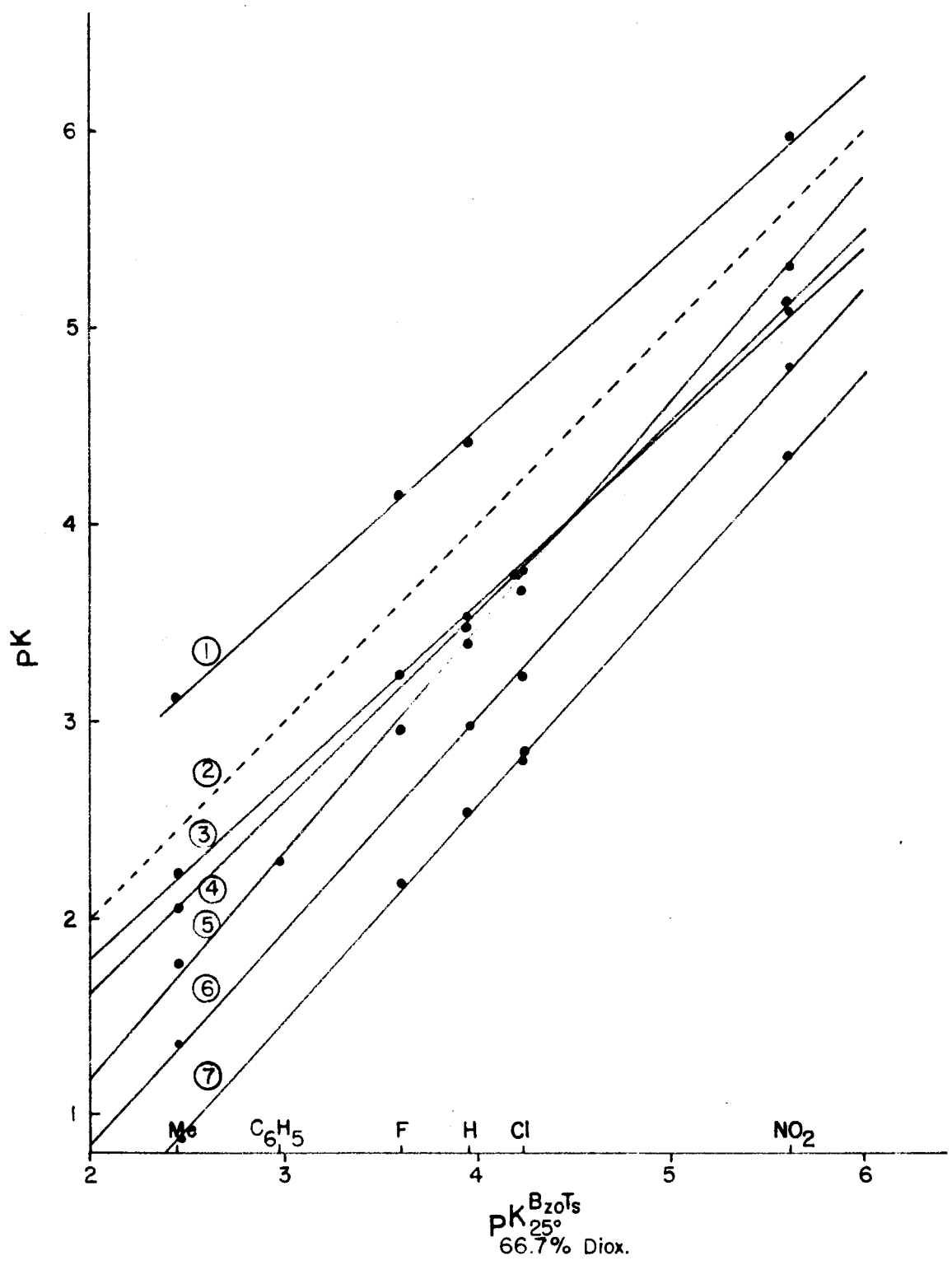[*]Unit slope line.

[**]No pk value for p-methyl substituent.

FIG. 4   RATES OF HYDROLYSIS OF BENZYL
TOSYLATES IN AQUEOUS DIOXANE

where k' is the rate for the substituted benzyl tosylate, k'_o is the rate for the unsubstituted compound, ρ_o is the usual Hammett ρ value for this reaction for the given solvent and temperature, and σ^* (using the symbolism of Jaffe[2]) is the corrected Hammett σ used for those reactions involving additional resonance effects for which the originally defined σ fails. The difference between these latter two values may be designated $\Delta\sigma$. Using this redefined σ'

$$\log k/k_o = \rho' \sigma' \tag{7}$$

which is related to the regular Hammett values by

$$\rho = \rho' \rho_o \tag{8}$$

$$\sigma^* = \sigma'/\rho_o . \tag{9}$$

Rearrangement gives

$$\log k = \rho' \log k' + (\log k_o + \rho' \log k'_o) \tag{10}$$

from which it is seen that the slopes of the lines in Figures 3 and 4 are the ρ' values for the reaction for the solvent and temperature plotted.

An examination of Figures 3 and 4 shows that within a given solvent system, the hydrolysis reactions of benzyl tosylates do obey this redefined Hammett correlation with excellent precision. This means that within such a solvent system a constant σ^* value can be defined. The excellent linearity of the curves is an additional evidence of the internal consistency and precision of the experimental data.

Assuming that the values of σ for the unsubstituted and the p-nitro substituted compounds will not differ from the values given by Hammett, since these substituents cannot enter into resonance with the reaction site in the transition state, the values of ρ_0 for each of the reactions used as bases for the above correlations were calculated. These values of ρ_0 were then used to calculate the Hammett σ^* and ρ values from the σ' and ρ' values. The former values are given in Tables 8 and 9.

It is immediately seen that many of the para substituents which enter into resonance with the reaction site have large increases in the value of $-\sigma$ as indicated by the size of $\Delta\sigma$ and the increase is somewhat greater for the acetone systems than for the dioxane systems. It is also seen that ρ increases with water concentration of the solvent system and that the values of ρ are greater for the dioxane than the acetone solvents.

Table 8. Hammett σ values for benzyl tosylate hydrolysis

Subst.[a]	σ^a	$\sigma^*_{acet.}$	$\sigma^*_{diox.}$	$\Delta\sigma_{acet.}$	$\Delta\sigma_{diox.}$
H	0				
p-CH$_3$	-.170	-.822	-.698	.65	.53
p-C$_6$H$_5$	.009	-.592	-.456	.60	.46
p-F	.062	-.187	-.163	.24	.22
m-C$_6$H$_5$	.218	.097	.121	.12	.10
p-Cl	.227	.106	.126	.12	.10
p-NO$_2$	.778				

[a]L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N. Y., 1940, p. 188.

Table 9. Hammett ρ values for benzyl tosylate hydrolysis

Solvent	25°	35°	45°
83.3% acetone	1.60	1.62	1.62
90.9% acetone	1.43	1.43	1.44
96.2% acetone	1.36	1.38	1.39
44.4% dioxane	2.46	2.33	2.34
33.3% dioxane	2.15	2.08	2.11
23.1% dioxane	1.91	1.85	1.95

On the basis that σ increases with increased capacity for resonance participation between the substituent and the reaction site, the mechanism proposed by Swain[3] for the hydrolysis of benzyl tosylates
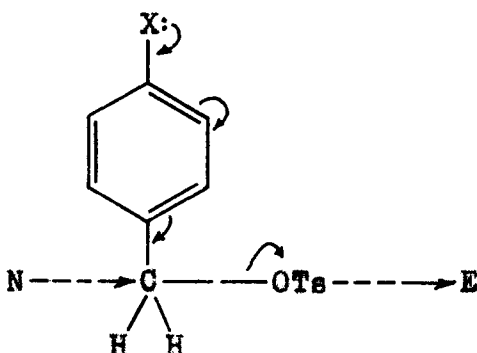
would lead to increasing values of σ^* if the old C-O bond becomes more completely broken or the N-C bond is less well formed, has less covalent character. Since σ^* is constant in a given solvent system, the reaction must be limiting, that is the old C-O bond is almost completely broken for all reactions and therefore cannot further increase in ionic character, or the increase in bond breaking is exactly offset by an increase in covalent character of the N-C bond. The latter is very unlikely for such a wide range of solvent and temperature variation. The amount of covalent character of the N-C must be small and does not

[3]C. G. Swain, J. Am. Chem. Soc., 72, 4583 (1950).

increase greatly with water concentration. Thus the nucleophile possesses only weak "solvation" bonding to the substrate residue. The slightly larger $-\sigma^*$ value for the acetone solvent system must result from its weaker nucleophilic character and therefore decreased power to solvate the positive ion. That the change in the covalent character of the bond between the benzyl carbon and the solvent molecule does not increase much as the water concentration of the solvent increases is quite reasonable if this bond is as yet extremely long in the transition state.

Since the ionizing power of acetone solvents is less than that of dioxane solvents, one would have expected σ^* to have changed in the opposite direction with the change from acetone to dioxane if the reaction were not already limiting. Thus the values of σ^* strongly support the limiting character of this reaction.

However this support is countered by the Swain hypothesis that ρ is a measure of the charge on the substrate residue[4] and therefore of the amount of bond breaking of the old bond, since the value of ρ increases as the water concentration and ionizing power of the solvent

[4] C. G. Swain and W. P. Langsdorf, J. Am. Chem. Soc., 73, 2813 (1951).

increases. It is also greater for the dioxane solvents than for the acetone solvents.

As ρ is a measure of sensitivity to substituent effects, it should increase greatly with an increase in the ionic character of the old bond. However, since ρ is a constant that is a function of all other variables of a reaction other than the effect of changes in substituent, other solvent effects on ρ could easily outweigh the effect of a change of ionic character as one made large changes in the solvent. This would be especially true if the change of ionic character is very small as proposed above.

That the parameters of the Swain[5] and the Grunwald-Winstein[6] equations for the correction of solvolysis rates are probably poor criteria of the ionic or limiting character of this reaction is supported by the fact that these parameters fail to give the proper rate constants for these solvents by a factor greater than ten. This lack of correlation could conceivably be due to large effects of the lithium

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[5]C. G. Swain, R. B. Mosely and D. W. Brown, ibid., 77, 3731 (1955).

[6]S. Winstein, E. Grunwald, and H. W. Jones, ibid., 73, 2701 (1951).

perchlorate salt used in these reactions, but no salt effect was observed by Kochi[7] in the aqueous acetone solvents of higher water concentration.

The pk values of benzyl, p-nitrobenzyl and p-methyl benzyl tosylates at 25° are plotted in Figure 5 against the dielectric function, $(D - 1)/(2D + 1)$.[8] The lack of linearity is quite evident.

The thermodynamic properties, $\Delta F^{\pm}$, $\Delta H^{\pm}$, $\Delta F^{\pm}$ $\Delta H^{\pm}$, and $- \Delta S^{\pm}$, for the hydrolysis of the benzyl tosylates in the solvents used were calculated and are tabulated in Tables 10 and 11. The data upon examination shows some very interesting and unexpected trends. $\Delta S^{\pm}$, in accord with the usual change of ΔS of ionization is mixed solvents[9], decreases with decrease in the water concentration of the solvent for all reactions except those of p-fluoro and p-chloro compounds in aqueous dioxane. This reversal for fluoro and chloro compounds could be due to a fair amount of hydrogen bonding to water molecules by the substituent in the reactants except that one would then expect a lower value for $- \Delta S^{\pm}$, for these compounds, since the change in amount of solvation should be less, and that such solvation

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

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

[9] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions", 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 514.

Fig. 5. Correlation of solvolysis rates of benzyl
       tosylates with dielectric constant of the medium
       at 25° C

       Curve 1 - p-Nitrobenzyl tosylate in aqueous acetone

       Curve 2 - Benzyl tosylate in aqueous acetone

       Curve 3 - p-Methylbenzyl tosylate in aqueous acetone

       Curve 4 - p-Nitrobenzyl tosylate in aqueous dioxane

       Curve 5 - Benzyl tosylate in aqueous dioxane

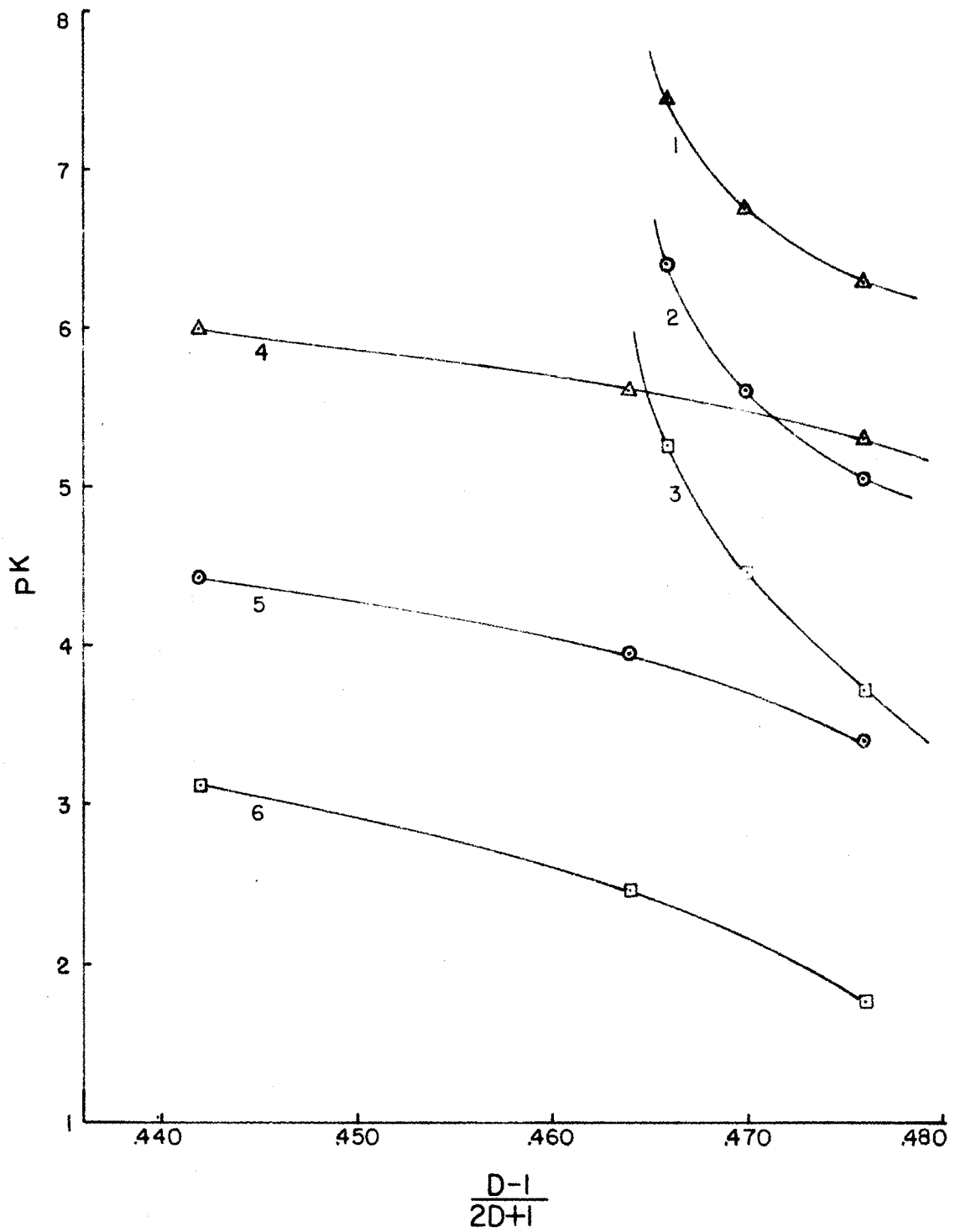   Curve 6 - p-Methylbenzyl tosylate in aqueous dioxane

FIG. 5 CORRELATION OF SOLVOLYSIS RATES OF
BENZYL TOSYLATES WITH DIELECTRIC
CONSTANT OF THE MEDIUM AT 25°C.

Table 10. Thermodynamic properties of activation for
benzyl tosylate hydrolysis in aqueous acetone

Subst.	% Acetone	$\Delta F^{\ddagger}_{25^{\circ}}$ kcal.	$\Delta H^{\ddagger}$ kcal.	$\Delta F^{\ddagger} - \Delta H^{\ddagger}$ kcal.	$- \Delta S^{\ddagger}$ $\frac{cal.}{deg.}$
H	83.3	24.33	19.8	4.5	15.1
	90.9	25.10	19.4	5.7	19.1
	96.2	26.17	19.1	7.1	23.8
NO_2	83.3	26.04	19.4	6.6	22.1
	90.9	26.67	19.6	7.1	23.8
	96.2	27.60	18.3	9.3	31.2
Cl	83.3	24.57	18.9	5.7	19.1
	90.9	25.30	18.9	6.4	21.5
	96.2	26.31	19.8	6.5	21.8
F	83.3	23.92	19.1	4.8	16.1
	90.9	24.78	18.3	6.5	21.8
	96.2	25.80	18.9	6.9	23.2
Me	83.3	22.52	20.0	2.5	8.4
	90.9	23.52	19.8	3.7	12.4
	96.2	24.62	19.1	5.5	18.4
C_6H_5	83.3	23.07	21.5	1.6	5.4
$m\text{-}C_6H_5$	83.3	24.54	19.1	5.4	18.1

Table 11. Thermodynamic properties of activation for benzyl tosylate hydrolysis in aqueous dioxane

Subst.	% Dioxane	$\Delta F^{\pm}_{25^{\circ}}$ kcal.	$\Delta H^{\ddagger}$ kcal.	$\Delta F^{\ddagger} - \Delta H^{\ddagger}$ kcal.	$-\Delta S^{\ddagger}$ $\frac{cal.}{deg.}$
H	55.6	22.08	18.3	3.8	12.8
	66.7	22.83	18.5	4.3	14.4
	76.9	23.49	18.9	4.6	15.4
NO_2	55.6	24.70	20.4	4.3	14.4
	66.7	25.11	19.1	6.0	20.1
	76.9	25.60	18.5	7.1	23.8
Cl	55.6	22.45	17.8	4.6	15.6
	66.7	23.22	19.1	4.1	13.7
F	55.6	21.48	16.6	4.9	16.4
	76.9	23.10	19.1	4.0	13.4
Me	55.6	19.85	(17.8)[a]	(2.0)[a]	(6.7)[a]
	66.7	20.78	(18.3)[a]	(2.5)[a]	(8.4)[a]
	76.9	21.70	18.9	2.8	9.4

[a]Obtained by using extrapolated values of pk at 45°.

of the substituent would change, causing a variation in σ^* with increased water concentration.

Using the criterion that the ΔS of solvation of ions decreases as the size of the ion decreases[10], the changes of ΔS with change of substituent except for p-fluoro are those to be expected for delocalization of the charge on the substrate residue by the varying amounts of resonance expected for the various groups. By its $\Delta \sigma$, p-phenyl-benzylcarbonium ion has less resonance contribution than the p-methyl ion but the charge is spread out over a larger area.

That there is no linear relation between $\Delta H^{\pm}$ and $\Delta S^{\pm}$, contrary to certain findings of Leffler[11], is immediately obvious since with solvent changes, the two terms may vary in the same or opposite directions. However the two must compensate one another in such a way that there is a linear free energy relationship with changes of substituents in various solvents. It would appear that the amount of solvation depends upon the size of the ion and localization of charge and that in the process of solvation, a part of

[10] I. M. Klotz, "Chemical Thermodynamics", Prentice-Hall, Inc., New York, N. Y., 1950, p. 355.

[11] M. D. Cohen, J. E. Leffler and L. M. Barbata, J. Am. Chem. Soc., 76, 4169 (1954).

the ΔH of the ions is exchanged for solvation energy in the form of $T \Delta S$, in such a way as to cause the ratios of the ΔF terms to remain more nearly constant.

Although the ΔS^* values are not strong evidence for the limiting character of the above reaction, until more is known about the thermodynamic properties of activation for reactions, the support is in that direction.

During the course of this work two additional points of interest which correlate well with a limiting mechanism for the hydrolysis of benzyl tosylates were noted. These points are concerned with the σ values for p-phenyl and p-fluoro substituents.

Simplified molecular orbital calculations of the π-electron delocalization energies for the biphenylmethylcarbonium ions and for biphenyl, as well as for phenylmethyl carbonium ion and benzene, were carried out. The calculated values agreed with those of Wheland[12] and gave differences in energy between the carbonium ion and the parent compound which agreed qualitatively with σ values of the corresponding substituent. Following are the additional delocation energies of the carbonium ions in terms of β: phenyl methyl, 0.720, m-biphenylmethyl, 0.718, and o-biphenylmethyl,

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[12]G. W. Wheland, J. Chem. Phys., 2, 478 (1934).

0.756. This gives energy differences due to substituent effects of -.002β for m-phenyl and .036β for p-phenyl in comparison to values of .12 and .60 for corresponding $\Delta\sigma$'s.

Previous work has indicated that even though the electronegativities of the halogens are in the order of F > Cl > Br > I, these substituents often give rate and equilibrium constants of opposite order to that expected from inductive effects. This reversal has been explained on the basis that the halogens can partially donate their outer orbital, nonbonding electrons along the _sigma_ bond to the _pi_ orbitals of the aromatic nucleus, or stated in other words, these electrons can enter into resonance with the benzene ring. The capacity of the halogens for entering into such resonance decreases in the order F > Cl > Br > I with fluoro having a much greater ability to do so than the rest.[13] This view is borne out in the above results of .24 for the value of $\Delta\sigma$ for p-fluoro as compared to .12 for p-chloro.

Before more definite conclusions can be drawn, it is felt that an investigation of the effect of concentration of salt on the reaction in these solvents is needed as well as a further investigation of the factors which influence

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[13]J. W. Baker and H. B. Hopkins, _J. Chem. Soc._, _1949_, 1089.

value of ρ . However, the above evidence seems to definitely support a limiting mechanism for the solvolysis of benzyl tosylates.

SUMMARY

The hydrolysis of methyl, chloro, fluoro, nitro, and phenyl para substituted benzyl and the unsubstituted benzyl tosylates were carried out in two series of aqueous mixed solvents at 25, 35, and 45°. The solvents employed were a series of three aqueous acetone mixtures of low but widely differing water content and a series of three aqueous dioxane mixtures having comparable dielectric constants. The rate constants covered a range of values of 10^{6}.

The pk values obtained can be correlated using a modified Hammett equation in which new values of σ must be assigned to those groups which can enter into resonance with the reaction site. A constant value of σ^{*} supports the postulate that the hydrolysis of benzyl tosylates is limiting in character, contrary to the evidence of other proposed solvolysis correlations.

Although ΔF^{*} is a linear function of substituent effects, there appears to be a definite lack of correlation between ΔH^{*} and ΔS^{*} with change of substituent or change of solvent. However, ΔS^{*} seems to be a function of the amount of delocalization of charge on the substrate residue.

The greater ability of the outer orbital electrons of a fluorine substituent to enter into resonance with the

benzene ring than those for chlorine is supported by the much larger $\Delta\sigma$ value for fluorine.

Molecular orbital calculations of the resonance energies of benzyl, p-phenylbenzyl, and m-phenylbenzyl carbonium ions gives differences in resonance energies which correlate qualitatively with the $\Delta\sigma$ values of the compounds.

ACKNOWLEDGMENTS