STUDIES ON THE RATE OF HYDROLYSIS OF sec-BUTYL p-TOLUENESULFONATE

Thesis by

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TABLE OF CONTENTS

SUMMARY

The rate of hydrolysis of sec-butyl p-toluenesulfonate has been investigated in different solvent mixtures of acetone and water and dioxane and water.

The mechanism of the hydrolysis of this ester, which is similar to the secondary alkyl halides, is situated on the border line between the unimolecular dissociation and the bimolecular displacement.

It has been found that the rate is proportional to a certain function of the dielectric strength of the solvent but that the proportionality factor is much larger when the solvating power of the medium is high.

By studying the ionic strength effect, the so called "mass law effect", and the hydroxyl ion influence on the rate,one has come to the conclusion that both unimolecular and bimolecular mechanisms are involved in this hydrolysis.

For low values of the dielectric constant of the medium, the bimolecular mechanism seems to be present to the larger extent while for high values of this function the unimolecular dissociation is predominant.

I INTRODUCTION

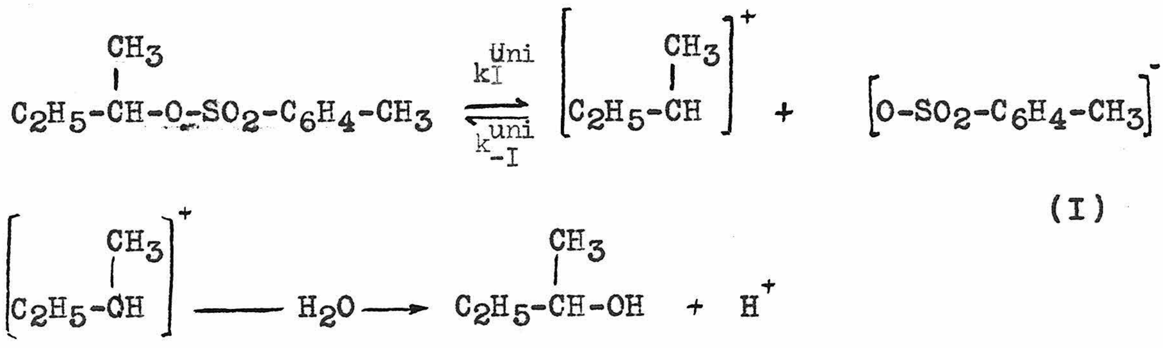
The rates of hydrolysis of alkyl and aryl-alkyl halides have been studied by different authors and especially by Hughes, Ingold and their co-workers (ref. 1), Hammett and his co-workers (ref. 2) and Winstein and his collaborators (ref. 3).

In this paper we have investigated the rate of hydrolysis of *sec*-butyl *p*-toluenesulfonate.

This ester which as far as solvolysis is concerned is very similar to the alkyl halides, presents, like the *iso*-propyl halides the particularity of being probably able to react in usual solvent mixtures by both classical mechanisms of solvolysis. (ref 3^{bis})

Those two mechanisms are the following:

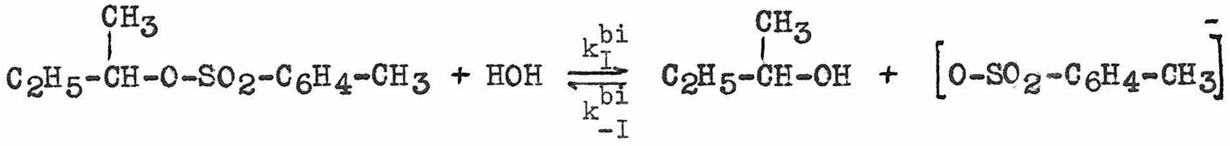
A) The unimolecular dissociation or S_NI:



$$C_2H_5-\overset{\overset{CH_3}{|}}{CH}-O-SO_2-C_6H_4-CH_3 \underset{k_{-I}^{uni}}{\overset{k_I^{Uni}}{\rightleftharpoons}} \left[C_2H_5-\overset{\overset{CH_3}{|}}{CH}\right]^+ + \left[O-SO_2-C_6H_4-CH_3\right]^-$$

$$\left[C_2H_5-\overset{\overset{CH_3}{|}}{OH}\right]^+ \;\text{———}\; H_2O \longrightarrow C_2H_5-\overset{\overset{CH_3}{|}}{CH}-OH + H^+ \tag{I}$$

B) The bimolecular displacement or S_N2:



$$C_2H_5-\overset{\overset{CH_3}{|}}{CH}-O-SO_2-C_6H_4-CH_3 + HOH \underset{k_{-I}^{bi}}{\overset{k_I^{bi}}{\rightleftharpoons}} C_2H_5-\overset{\overset{CH_3}{|}}{CH}-OH + \left[O-SO_2-C_6H_4-CH_3\right]^- + H^+ \tag{2}$$

Since both mechanisms lead as a limit at least to first order kinetics, $\underline{k}_{I}^{uni}$ and $\underline{k}_{I}^{bi}$ are first order specific rate constants. In general both mechanisms being present at the same time, only a resultant first order constant will appear:

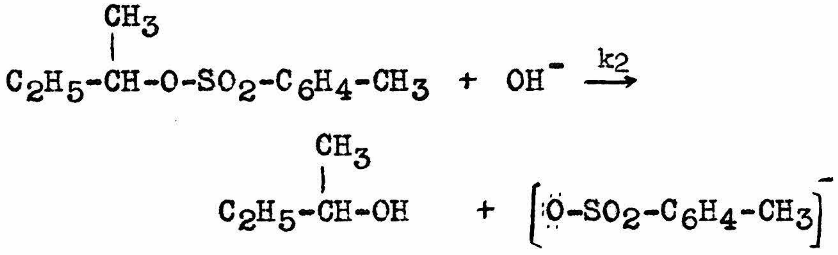
$$\underline{k}_1 = \underline{k}_1^{uni} + \underline{k}_1^{bi}$$

Since in some cases the kinetics are only first order as a limit at initial concentration, all data given here refer to initial first order specific rate constants expressed as:

$$(k_1)_o = (k_1^{uni})_o + (k_1^{bi})_o$$

However the runs where deviations from first order kinetics were found will be mentioned in the text.

We have also investigated the reaction with Hydroxyl ions:



$$C_2H_5\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}O\text{-}SO_2\text{-}C_6H_4\text{-}CH_3 + OH^- \xrightarrow{k_2} C_2H_5\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}OH + \left[\ddot{O}\text{-}SO_2\text{-}C_6H_4\text{-}CH_3\right]^- \tag{3}$$

In this case the total reaction is of course represented by a combination of equations (I), (2) and (3). Here $\underline{k}_2$ is a second order specific rate constant.

II EXPERIMENTAL PART

I) Preparation of sec-butyl p-toluenesulfonate. (4)

This ester was prepared by reacting p-toluenesulfonyl chloride with sec-butyl alcohol in pyridine. After the reaction was over the resulting mixture was diluted with water containing a slight amount of hydrochloric acid. An oily product separated at the bottom of the flask. This was removed with a separatory funnel and the remaining aqueous solution was extracted several times with ether. The oily liquid was added to the ether extract which was dried with anhydrous potassium carbonate. The ether was evaporated leaving a pale yellow oil.

The p-toluenesulfonyl chloride used originally had been carefully washed with a great amount of water, dried and recrystallized from benzene. The sec-butyl alcohol had been redistilled.

2) Purification of sec-butyl p-toluenesulfonate.

Kenyon and Phillips (ref. 4) distilled the product at 92°C. under less than 0.1 mm pressure. H. Gilman and N. Beaber (ref. 5) attempted a distillation at 2 mm pressure and destroyed the liquid. They finally obtained it in a fair state of purity by careful washing and drying. It had a density: $d_4^{20} = 1.140$.

After different attempts, we purify the compound by the following method:

A) An ether solution of the ester was slowly cooled down in dry ice. The sec-butyl p-toluenesulfonate crystallized after scratching of the test tube and the heterogeneous mixture was then poured on a glass-fritted funnel surrounded with packed dry ice. A thermometer inserted in the funnel indicated -50°C. The funnel was stoppered and an inlet tube was provided to permit dry and cold air to be sucked through the filter. When the ether solution was removed by filtration, the solid left in the funnel, still at low temperature, was washed 5 or 6 times with previously cooled ether. Only a very slight aspiration was applied to prevent evaporation of the ether.

Finally by strong suction most of the ether was driven out. The solid was then removed with a spatula and poured in a crystallizing dish, cooled down with dry ice, in a vacuum dessicator. During the slow melting, the ether left and the carbon dioxide were pumped off.

The product obtained was slightly yellow and melted between 10° and 12°C.

B) The ester was put next in the cold room at 4°C. and a small crystal obtained by cooling in dry ice was added in order to induce crystallization. After 4 days the product was separated in two parts: a white solid at the bottom and a yellow liquid at the top. The liquid was poured off and the solid dried on a porous plate maintained at 4°C. Finally the solid was warmed up in a vacuum dessicator. The liquid part was neglected.

A density measurement was made, we found d_4^{25}=1.138, in excellent agreement with Gilman and Beaber's data. The refractive index was found to be n_D^{25}=1.5010. No trace of acidity was present as shown by titration with sodium hydroxide 0.01 normal. The melting point of the final product was found to be 11.5° ± 0.5°.

3) Kinetic experiments

Solvents: The dioxane was purified as recommended by Beste and Hammett (ref. 6). It was first refluxed over sodium hydroxide and, after filtration, refluxed over sodium, then distilled when needed.

The acetone employed was C. P. Merck Acetone containing about 0.5% water. Therefore a slight correction for the total amount of water in the media is necessary.

We also used absolute ethanol and nitromethane (Eastman-Kodak).

The distilled water added was always freshly boiled.

All the solutions were made up by weighing the different constituents. When we refer to % aqueous acetone or dioxane, we mean weight per cents of acetone or dioxane in water.

The 60% aq. dioxane medium however was made up according to Beste and Hammett (ref. 6). We weighed 327.4 g. of water, added them to 1000 g. of dioxane and to each 100 ml of this mixture we added 25 ml of water or aqueous solution of sodium hydroxide, sodium perchlorate, etc.

The exact amount of water in the final medium so obtained is 39.28 wt.%.

The sec-butyl p-toluenesulfonate was weighed out in small "weighing pigs" which were poured open into the solutions.

The sodium hydroxide, sodium perchlorate and sodium p-toluenesulfonate were added as aqueous solutions. A correction was made for the weight of electrolyte contained in the water.

The sodium perchlorate was obtained by carefully neutralizing a standard solution of perchloric acid (C. P. Baker).

The sodium toluenesulfonate was obtained by a similar method from recrystallized p-toluenesulfonic acid.

For these neutralizations we used the same indicator as for the following titrations: bromocresol purple.

The runs were made in sealed ampoules and in 50 and 100 ml volumetric flasks. No difference was observed between the two techniques.

Some irregular results when sodium hydroxide was added made us use for those particular experiments stainless-steel bottles as proposed by Foster and Hammett (ref. 7) who observed similar irregularities.

The ampoules or pipetted samples were broken or poured into a known volume of freshly distilled dioxane and the acidity produced was titrated with 0.02 or 0.01 normal sodium hydroxide.

In some cases we used a solution of sodium hydroxide in 60% aq. dioxane.

For the hydrolysis in the presence of alkali the samples were poured in known amounts of standard hydrochloric acid and dioxane.

The temperature was kept constant at 30.005^{o} C. and 39.970 ± 0.005^{o}.

All burettes and pipettes were calibrated.

The standard sodium hydroxide concentration was checked every other day against standard hydrogen phthalate with phenolphthalein as indicator and against standard hydrochloric acid with bromocresol purple.

III RESULTS

I° Hydrolysis

The study of the rate of hydrolysis of sec-Butyl p-toluenesulfonate has been carried out in a medium containing 40% by weight of water in dioxane (exactly: 39.28%).

This medium has been chosen in order to compare our results with the data obtained by McCleary and Hammett (ref. 8) for the rate of hydrolysis of ethyl toluenesulfonate in the same medium.

About twenty experiments have been performed on the particular point, of the hydrolysis. All of them have been shown to possess simple first-order kinetics.

The rate of hydrolysis has been calculated by the classical formula:

$$k_I = \frac{I}{t} \ln \frac{a}{a - x}$$

Here a is the initial ester concentration and x the portion of ester hydrolyzed.

Most of the time however a graphical determination has shown to be much more accurate. A plot of ln $a/a-x$ v.s. time was in each case a straight line, the slope of which did not change appreciably even after the reaction had proceeded as far as 90%.

It has been observed that the initial rate is decreased when the initial ester concentration is increased.

A similar effect has been recorded for ethyl p-toluenesulfonate by McCleary and Hammett (ref. 8).

In Table I we have reproduced a typical run while in Table II are represented some of the more characteristic results obtained.

The data given here have a maximum error of 3-4%. This is in good agreement with the precision obtained in handling the samples, considering the low concentration of ester.

Diagram I shows the variation of the initial rate of hydrolysis with the initial concentration in the cases of sec-butyl and ethyl p-toluenesulfonate.

Diagram II represents a combined plot of log $a/(a-x)$ vs. time for three typical experiments with sec-butyl p-toluenesulfonate. Since no appreciable decrease of the rate is observed during the first 80% of the course of the reaction, we conclude that the value of k_1 obtained by graphical differentiation is equal to the initial first order rate constant.

Table I

Rate of hydrolysis of *sec*-butyl *p*-toluenesulfonate in 60 % aq. dioxane, at 30° C. - Initial ester concentration : 0.009356 mole/liter. Standard NaOH solution : 0.0I750 n.

Time (sec.)	ml NaOH per 5 ml sple	mole NaOH per liter	mole ester per liter	$\log \frac{a}{a-x}$	$\underline{k}_{I}$ x IO^{6} (sec^{-I})
0	0.00	0	0.009356	0	-
20760	0.43	0.00I230	0.008I26	0.06I2I	6.8I
58260	I.I3	.00397I	.005383	.23990	9.43
64020	I.I4	.004005	.00535I	.24266	8.68
7I340	I.I9	.004I82	.005I74	.25726	8.30
77I60	I.28	.004498	.004858	.28463	8.46
82980	I.33	.004674	.004682	.30066	8.30
85740	I.36	.004780	.004576	.3I060	8.33
I00440	I.54	.0054I2	.003944	.375I5	8.6I
233340	2.24	.007872	.00I484	.79966	7.90
237660	2.25	.007907	.00I449	.8I002	7.85
25I340	2.29	.008046	.00I3I0	.85382	7.83
280560	2.35	.008258	.00I098	.93049	7.65
320520	2.43	.008540	.0008I6	I.05940	7.60
409740	2.46	.008645	.0007II	I.II922	6.28

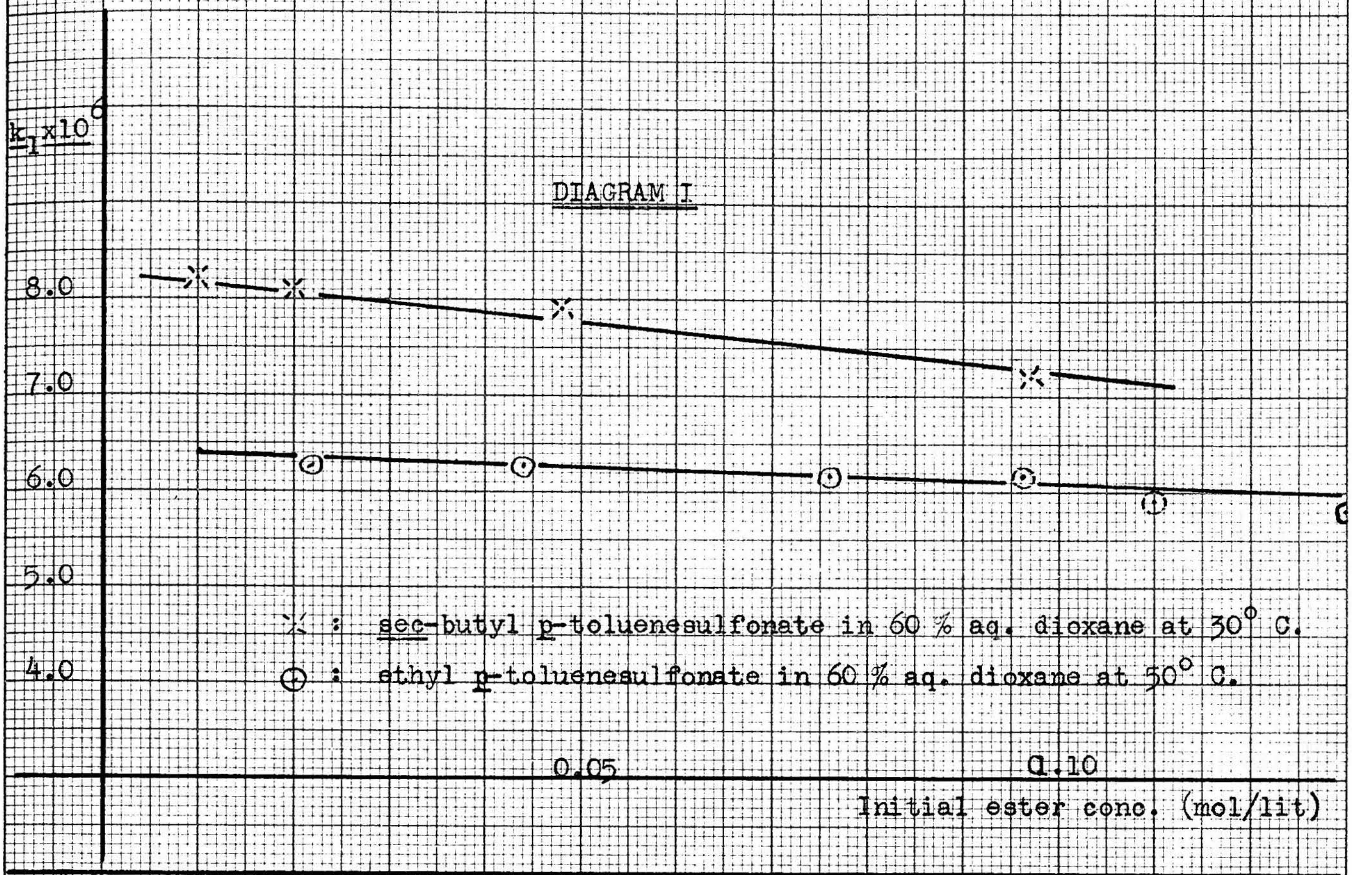
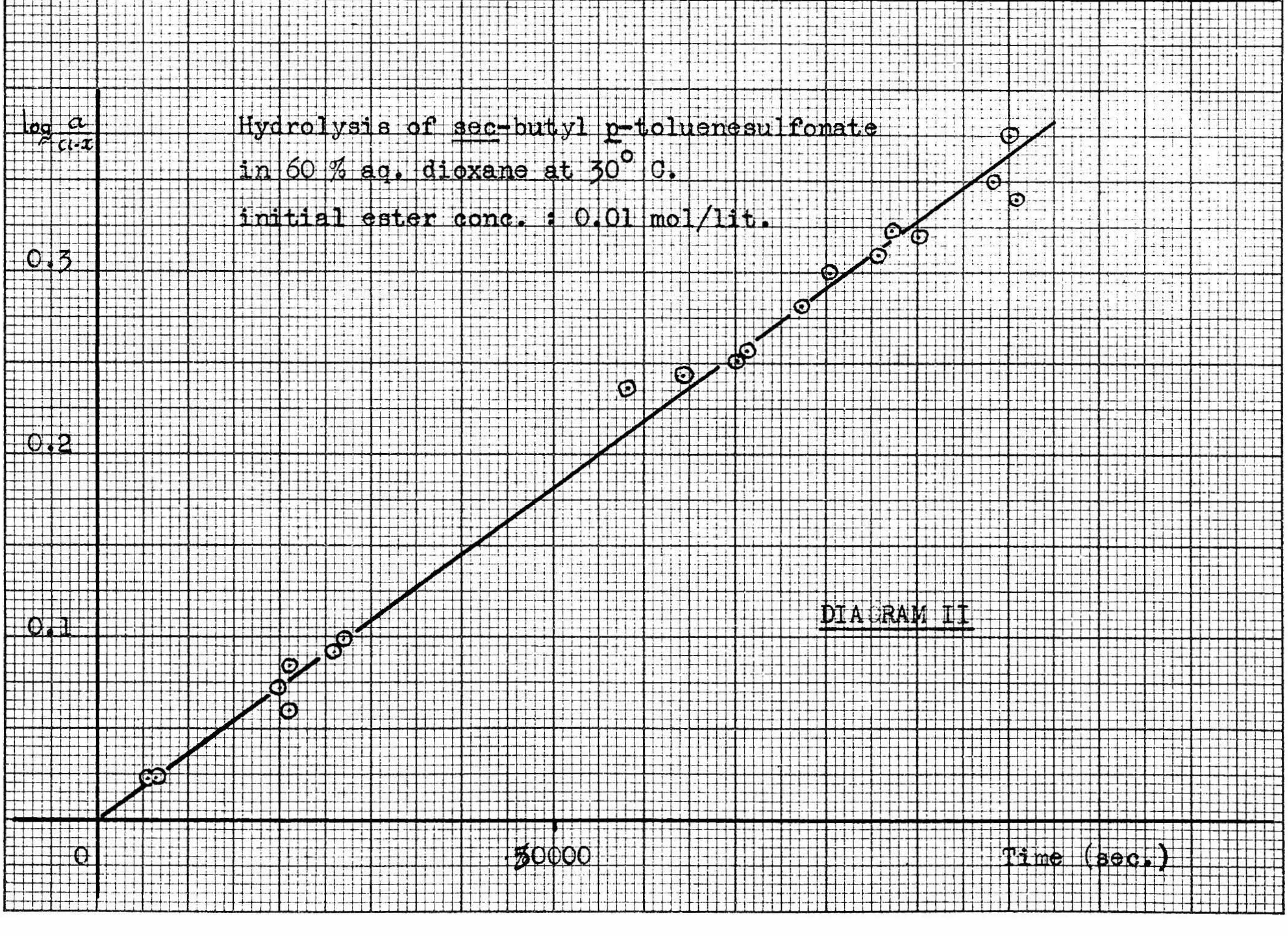


DIAGRAM I



Hydrolysis of sec-butyl p-toluenesulfonate
in 60 % aq. dioxane at 30° C.
initial ester conc. : 0.01 mol/lit.

DIAGRAM II

The first values are of course quite inaccurate due to the small volume of base added.

It is seen that a small decrease of the first order rate constant becomes noticeable only after the reaction has proceeded to about 80 %.

Table II

Rate of hydrolysis of sec-butyl p-toluenesulfonate in 60 % aq. dioxane, at 30° C.

Ester conc. (moles/l.)	k_I x 10^6 sec^{-1}
0.009509	8.08
.009356	8.45
.01059	8.31
.01104	8.15
.01163	8.08
.0202	8.10
.0480	7.93
.09698	7.21

2^o The Solvent Effect

The rate of hydrolysis of such esters like the alkyl halides and the toluenesulfonates are extremely sensible to solvent variations.

In the following section we present the results obtained for the rate of hydrolysis of sec-butyl p-toluenesulfonate in different media.

After the first runs in 60%wt aq. dioxane* we studied the rate in 70, 80, 90 and 50%wt. aq. dioxane. By doing so we decreased together the water content and the dielectric strength of the medium. In order to study the rate in a medium of moderately high dielectric strength but containing only a small amount of water (20%), we added some nitromethane to the solution. The dielectric strength of nitromethane at 30° C. is 38. In a medium containing by weight 60% dioxane, 20% water and 20% nitromethane, the dielectric constant has been calculated by simple proportions.

We also studied the rate in different proportions of water in acetone and in 80%wt. aq. ethanol. For equal water content the acetone-water media have quite higher dielectric strength than the dioxane-water mixtures.

In Table III we give all the results obtained together with the dielectric constant of each medium. Those values have been taken from H. Hartmann (ref. 9) for the dioxane-water mixtures and from Harned and Owen (ref. 10) for the others. We also give the values of the ratio D-1/2D+1 which will be used in the discussion of this effect, in the third part of this paper.

In all experiments, the kinetics were of the first order type; practically no deviation was observed except in 20%wt. aq. acetone where the rate constantly increased during the reaction. However in this medium, the ester concentration was of the order of 0.02 molal while in almost all the others, this concentration was about 0.01 molal. This is very probably the reason why such an effect was not observed in 70 or 80% aq. acetone. In 75% aq. dioxane no similar effect was obtained even with an ester concentration of 0.02 molal.

Table III

Rate of Hydrolysis of sec-butyl p-Toluenesulfonate in different Media at 30° C.

Medium	D	D-1/2D+I	ester conc.	$k_1 \times 10^6$
46.5%aq.dioxane	37	0.4800	0.009791	37.1
50 % aq.dioxane	33	0.4776	0.01203	25.0
60 % aq.dioxane	25.5	0.4711	0.01022	8.21
70 % aq.dioxane	17.0	0.4570	0.01059	3.00
75 % aq.dioxane	13.5	0.4464	0.01120	1.69
80 % aq.dioxane	11.5	0.4375	0.01053	1.026
90 % aq.dioxane	5.5	0.3750	0.01088	0.168
60 % aq.acetone	41.8	0.4822	0.01085	4.95
70 % aq.acetone	35.7	0.4792	0.01233	1.92
75 % aq.acetone	32.5	0.4772	0.02155	0.825
80 % aq.acetone	29.6	0.4750	0.01015	0.587
80 % aq.ethanol	32.8	0.4775	0.01040	5.17
60 % diox. 20% H_2O 20 % CH_3NO_2	18.0	0.4594	0.01109	0.968

3° Ionic Strength Effect on the Rate of Hydrolysis

To investigate this effect, sodium perchlorate has been used. In 60 % aq. dioxane no appreciable effect on the rate has been observed even at concentration of sodium perchlorate as high as 0.05 molal.

Table IV shows some of the results obtained.

Table IV

Rate of hydrolysis of sec-butyl p-toluenesulfonate in 60% aq. dioxane at 30° C.- Influence of addition of $NaClO_4$

ester conc. (mole/lit.)	$NaClO_4$ conc. (mole/lit.)	$k_1 \times 10^6$ (hydrolysis)	$k_1 \times 10^6$ (observed)
0.009509	0.007981	8.50	8.63
0.01671	0.01596	8.26	8.03
0.01017	0.0472	8.26	8.36

No other salt has been employed to determine the ionic strength effect since a similar result obtained by Mc Cleary and Hammett (ref. 8) for ethyl p-toluenesulfonate seems to confirm ours.

In the same paper, those authors show also the influence in the same medium of the addition of chloride, bromide and iodide ions on the rate of solvolysis. We did not repeat such experiments in the case of the sec-butyl ester. Since we will need Mc Cleary and Hammett's results in the discussion below, we show in table V a brief outline of them.

Table V

Rate of Displacement of Et.Tos	I^- >	OH^- >	Br^- >	Cl^-
	I	0.8	0.32	0.14
Rate of Solvolysis	EtTos >	EtI >	EtBr >	EtCl
	5.5	I	0.96	0.048
Stability towards Displacement	EtOH >	EtI >	EtCl >	Et-Tos

The same effect has been noted also in 75%aq. dioxane and 75%aq. acetone media. Here a noticeable increase of the rate has been observed especially in the case of acetone. The data for those experiments are given in Tables IX and X.

4° The Mass Law Effect

To study this effect which, according to Hughes and Ingold (ref.10bis) is one of the six methods for the determination of the mechanism of solvolysis, we have added to the mixture some sodium toluenesulfonate.

Since in 60 % aq. dioxane the ionic strength effect has shown to be not very important, it will not oppose a possible mass law effect. Only a small decrease of the rate of hydrolysis is observed in this medium with concentrations of sodium toluenesulfonate slightly higher than the ester concentrations. With a concentration twice higher, a larger decrease is observed but unfortunately this result is not absolutely certain.

Table VI shows the decrease observed in three cases.

Table VI

Rate of hydrolysis of sec-butyl p-toluenesulfonate in 60 % aq. dioxane medium, at 30° C. Influence of addition of sodium p-toluenesulfonate.

ester conc. (moles/lit.)	$k_1 \times 10^6$ (hydrolysis)	Na-Tos conc. moles/lit.	$k_1 \times 10^6$ (observed)
0.01099	8.23	0.01371	7.93
0.009698	8.26	0.01371	7.93
0.009698	-	0.0246	7.6

In all those experiments it is important to note that the rate of hydrolysis is changed considerably by changing the amount of water in the medium (as shown later.)

Since the 40% water-60% dioxane medium cannot be prepared too long in advance, because of the danger of oxidation of the dioxane in the air, forming peroxides, we had to use different preparations of the solvent.

The maximum error in the weighing of the water and the dioxane is of the order of 0.25%.

We have calculated that such an error on the proportion of water in the mixture must lead to a variation of $\underline{k}_1$ of about 0.25×10^{-6}.

To minimize this important error, we refer whenever possible in the data given in this work to a corresponding value of the specific rate constant of the simple hydrolysis of the ester in the <u>same</u> preparation of the solvent.

In order to permit the comparison of our data with those of McCleary and Hammett (ref. 8) in a similar experiment, we show their results in Table VII.

Table VII

Rate of hydrolysis of ethyl p-toluenesulfonate in 60 % aq. dioxane medium at 50° C. Influence of addition of Na-Tos. Data from Mc Cleary and Hammett, J.A.C.S. 63, 2254, (I94I)

ester conc. (moles/lit.)	$k_I \times IO^6$ (hydrolysis)	Na-Tos conc. (moles/lit.)	$k_I \times IO^6$ (observed)
0.I4597	5.70	0.I0654	5.6I
0.08793	6.08	0.I0766	5.9I

5° Influence of Hydroxyl Ions on the Rate of Hydrolysis

A pure unimolecular mechanism should not be influenced by the presence in the solution of hydroxyl ions.* A bimolecular mechanism should in general be influenced by such a presence.

A longer discussion of this point will be given in the following pages. Here we just want to present the results that we obtained in the case of sec-butyl p-toluenesulfonate

We first added some sodium hydroxide to a solution containing 0.0I mole of ester in a 60 % aq. dioxane medium.

Only a small increase of the rate was observed in six different runs. Since one of these was not absolutely certain, five only are recorded in Table VIII.

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* except by ionic strength effect.

In this table the values for $(k_I)_o$, the observed first order specific rate constant, have been obtained graphically. The plot of log $a/(a-x)$ *v.s.* time was practically a straight line in some cases; in others small deviations were observed. For these last a method of graphical differentiation has been applied and a plot of k_I' (observed first order rate constant) against time, extrapolated to zero.

The value referred to as k_2 are the second order rate constants. They have been calculated by use of the oversimplified equation:

$$(k_I')_o = (k_I)_o + (k_2)_o \, (O\bar{H})_o$$

and leading to:

$$(k_2)_o \qquad \frac{(k_I')_o - (k_I)_o}{(O\bar{H})_o}$$

$(O\bar{H})_o$ is the initial hydroxyl ion concentration.

This expression is derived from the fact that the total reaction rate can be written:

$$v = k_I \text{ (ester)} + k_2 \text{ (ester)}(O\bar{H})$$

or

$$v = k_I' \text{ (ester)}$$

(the parenthesis indicate concentrations)

By taking the values of the constants at initial concentration, one eliminates their eventual variations with changes in concentration.

Table VIII

Rate of hydrolysis of sec-butyl p-toluenesulfonate in the presence of hydroxyl ions in 60 % aq. dioxane, at 30° C.

Ester conc. (moles/lit.)	OH^- conc. (moles/lit.)	$(\underline{k}_1)_o$xIO^6 (hydrolysis)	$(\underline{k}_1)_o$xIO^6 (observed)	$(\underline{k}_2)_o$xIO^5 (calculated
0.01110	0.01792	8.20	8.51	1.72
0.01466	0.02197	8.15	8.5	1.94
0.00971	0.03593	8.2I	9.96	4.86
0.01079	0.03593	8.21	9.78	4.36
0.01033	0.0570	8.21	10.63	4.24

By looking at this table one can see that if the calculated values of $(\underline{k}_2)_o$ fit together in a close range of hydroxyl ion concentrations, they do not fit any better when the concentrations are very different.

The cause of this might be some ionic strength effect which, when the hydroxyl ion concentration is increased, becomes less and less negligible and also a solvent effect since, by addition of OH^- ions, the dielectric constant of the medium is increased.

It is also possible to calculate $\underline{k}_2$ by starting with the experimental value for $\underline{k}_2''$, the observed second order rate constant.

$$v = (\underline{k}_2'') \times (\text{ester})(OH^-)$$

However this method is not applicable here because the values of $\underline{k}_2$ are too small and the determination of $\underline{k}_2''$ quite innacurate.

Since we only wanted to obtain a qualitative picture of this particular effect, we did not try to ameliorate those data.

We will simply consider the fact that a small increase in the overall rate is obtained in 60%"dioxane when some OH^- ions are added. Moreover this increase is proportional to the amount of OH^- ions in the medium.

Our next step was to determine the same effect in a medium having a much smaller ionizing power. We choose a medium containing 75% dioxane and 25% water.

We first run a hydrolysis in the absence of any reagent. The reaction was a perfect first order one but quite slow. Next we study the hydrolysis in the presence of some sodium perchlorate in order to determine the ionic strength effect. Again the reaction was a good first order one and the rate was slightly increased. Finally we add to the solution an equivalent amount of sodium hydroxide. The reaction was still following pretty closely a first order kinetics and the rate was considerably increased. Those results are given in Table IX.

Table IX

Rate of Hydrolysis of sec-Butyl p-toluenesulfonate in 75% aq. Dioxane at 30° C. Addition of $NaClO_4$ and NaOH.

Ester conc, (moles/lit.)	$NaClO_4$ conc. (moles/lit.)	OH^- conc. (moles/lit)	$(k_1)_o \times 10^6$	$(k_2)_o \times 10^5$
0.01120	--	--	1.69	
0.01101	0.04046	--	1.86	
0.01026	--	0.04564	5.32	7.50
0.01994	(0.11)	--	(1.69)*	
0.01994	--	0.01056	2.27	5.27

Here again the same anomaly regarding the calculated value of $(k_2)_o$ appears. This second order constant is higher the higher the concentration of hydroxyl ions in the medium.

A possible explanation for this surprising effect would be that the highly electronegative OH^- ions are strongly attracted by the positive end of the dipole (the butyl part) or by the positive butyl ion, therefore inhibiting the reactivity of the water molecules. The higher the hydroxyl ion concentration, the higher this inhibiting action and consequently, the lower the value of k_1, leading to a constant value for k_2.

Finally we have studied the same effect in 75 % aq. acetone a medium of higher dielectric strength.

The increase of the rate by adding some hydroxyl ions to the system is less important than in the case of 75 % aq. dioxane. As it has been pointed out in the second part of the results, the ionic strength effect is much more important in this medium than in 75 % aq. dioxane.

The figures are given in Table X.

Table X

Rate of Hydrolysis of sec-Butyl p-Toluenesulfonate in 75 % aq. Acetone at 30° C. Addition of $NaClO_4$ and NaOH.

Ester conc. (moles/lit.)	$NaClO_4$ conc. (moles/lit.)	OH^- conc. (moles/lit)	$(\underline{k}_1)_o \times 10^6$	$(\underline{k}_2)_o \times 10^5$
0.02155	--	--	0.825	
0.02202	0.04619	--	1.102	
0.02182	--	0.01320	1.100	1.49
0.02182	(0.013)	--	(0.904)*	

* In Table IX and X the values in parenthesis have been calculated by making use of the reasonable assumption that the ionic strength effect is proportional to the concentration of salt added. In table IX a slight correction has also been made in order to take care of the fact that the initial concentration was slightly higher than for the solvolysis in the absence of salt or sodium hydroxide.

6° Temperature Effect

The rate has been determined also at 39.97° C. in 60 % and 80 % aq. dioxane.

The energy of activation is given in Table XI.

Table XI

Temperature effect on the rate of hydrolysis of *sec*-butyl *p*-toluenesulfonate in 60 % and 80 % aq. dioxane. Temperature 30° C. and 39.97° C.

Ester conc. molal	k_1 at 30.00° C. $\times 10^{-6}$	k_1 at 39.97° C. $\times 10^{-6}$	E_a in cal/mole
60% aq.dioxane:			
0.01022	8-21	--	
0.01107	--	26.6	22.320
80% aq.dioxane:			
0.01053	1.026	--	
0.01117	--	2.87	19.530

IV DISCUSSION

I° Hydrolysis

The kinetics observed during the hydrolysis of *sec*-butyl *p*-toluenesulfonate are definitely of the first order type.

This unfortunately does not give us too much information about the mechanism involved.

We know that a bimolecular mechanism (S_{N2}) or more precisely in this case a double displacement reaction of the type:

$$R\text{-}X + B\text{-}Y \longrightarrow \overset{+}{B}\text{--}\overset{-}{Y}\text{--}\overset{+}{R}\text{--}X^{-} \longrightarrow R\text{-}Y + B\text{-}X$$

leads to pure first order kinetics when the concentration of one of the reactants is so much larger than that of the other, that it can be considered as buffered.

The water in a hydrolysis of this type fulfills these conditions since it plays at the same time the role of a reactant and the role of the solvent.

The unimolecular mechanism of solvolysis (S_{NI}) also called unimolecular dissociation leads to first order kinetics only as a limit from which large deviations of a highly characteristic nature may arise. (Hughes, ref. I)

However the presence of first order kinetics without deviations does not allow us to reject the unimolecular dissociation mechanism.

To explain this point let us first consider briefly the two principal causes of deviation from first order kinetics in an S_NI mechanism.

One of them is due to the ionic strength effect. As the dissociation goes along, the ionic strength of the solution is increased due to the production of ions. We will see later that this increase produces a large acceleration of the rate. (ref. 9, 11)

The second cause of deviation is the mass law effect. During the first stage of the dissociation mechanism,

$$R\text{-}X \longrightarrow \overset{(+)}{R}\text{----}X^{(-)} \underset{k_{-1}}{\xrightarrow{k_1}} R^{+} + X^{-} \underset{k_s}{\xrightarrow{H_2O}} R\text{-}OH + X^{-}$$

the building up of the concentration of the ions and especially of the negative one which does not participate any more in the forward reaction, produces, due to the equilibrium conditions, a progressive backward reaction and therefore a progressive decrease of the observed rate. (ref. 9, 11)

Of course those two effects are never separate from one another and since each of them acts in the opposite direction, it is quite possible that the total effect will be non-existant or at least very small.

This might be the case for our <u>sec</u>-butyl ester. However as Hughes and Ingold pointed out, (ref. 11) when a medium contains a large amount of water and we might say, more generally, when a medium has a large dielectric constant, the ionic strength effect is much diminished and might even not show up.

The media used in our experiments contain always at least 20% wt. water, and no important deviation was observed in any case for ester conc. of the order of 0.01 M. A slight effect however was obtained for an ester conc. of 0.02 M in 25%aq. acetone. The rate was continuously increased. No such effect was observed in the same medium for an ester conc. 0.01 M.

In the "60% aq." dioxane medium (60%wt of dioxane) the absence of any deviation due to increase of ionic strength is very understandable on the preceeding bases ($D = 25.5$)and would therefore lead to the conclusion that the mass law effect is inexistant or extremely small. This is quite possible, for it simply requires that the backward ($\underline{k}_1$) reaction be much slower than the second step forward reaction ($\underline{k}_s$).

When we pass to a medium containing only 20%wt. water, we have strong evidence, as we will show later, that the unimolecular character of the hydrolysis decreases considerably, therefore leading to pure first order kinetics.

One might wonder why we insist, against apparent evidences, to propose a unimolecular dissociation mechanism for the solvolysis of sec-butyl toluenesulfonate in the "60% aq." dioxane medium.

By discussing the results given in the preceeding pages, we will show that this is very probably the case.

Hughes, Ingold and their co-worders who have studied the hydrolysis of alkyl halides, have pointed out (ref. 1) that when one increases the electron release power of the alkyl radical, the hydrolysis has more and more unimolecular character. While methyl and ethyl halides react mainly by S_N2 mechanism, and <u>tert</u>-butyl almost entirely by an S_N1, the isopropyl halides react by both mechanisms simultaneously.

Secondary butyl halides have not been investigated as far as we know to a considerable extent but their similarity with isopropyl halides is evident.

Since the electron release power of an ethyl group is larger than that of a methyl group, (ref. 12) the total electron repulsion effect of the <u>sec</u>-butyl radical will be larger than that of isopropyl and therefore the unimolecular mechanism will be favored.

On the other hand, the presence of a larger ethyl group on the central carbon atom may, by some steric effect, reduce the ease of a displacement attack on the back of this atom, decreasing the possibility of S_N2 mechanism.

About the toluenesulfonate esters, the only reference that we have is the hydrolysis of ethyl toluenesulfonate (ref. 8) the rate of which is about five times as fast as that of ethyl iodide or ethyl bromide and a hundred times faster than that of ethyl chloride (Table V).

It seems that the size of the negative substituent leads to an increase of the rate. Since those three halides are claimed to possess mainly an S_N2 character in their solvolysis, the same thing must probably be true of the tosyl ester. The results obtained by McCleary and Hammett (ref. 8) are in favor of a predominant bimolecular displacement.

Those ethyl esters like the methyl ones and on the opposite side, the tert-butyl, are hydrolyzed almost entirely by one mechanism and even considerable changes in the nature of the solvent are not impotant enough to produce a noticeable amount of the other mechanism.

For esters like isopropyl and sec-butyl however, a change in the solvation power of the medium may have a strong influence on the proportion of each mechanism.

We will come back on this point later on. For the present time we want only to emphasize the fact that it is hardly possible to compare the rates of solvolysis of such esters unless they have been performed in the same solvent even if those rates have been corrected for the difference of solvating power by some empirical function like that one proposed by Grunwald and Winstein (ref. 3).

There is no *a priori* reason why the proportions of both mechanisms should change in the same way for two different esters when passing from one solvent to another.

In order to compare our results with those obtained by McCleary and Hammett for ethyl toluenesulfonate (ref. 8) we decided to run our first experiments in the same medium, "60% aq." dioxane (exactly 39.28% wt. water in dioxane.)

The specific first order rate constant for ethyl tosyl at 50° C. is of the order of 6.4×10^{-6} sec^{-1} for an initial concentration of 0.01 molal (by extrapolation of those authors' curve; diagram (I) while the rate for <u>sec</u>-butyl toluenesulfonate at 30° C. is already 8.21×10^{-6} sec^{-1}, for the same initial concentration.

This is in good agreement with the halides. Hughes (ref. 1) reports the following order for their rate of hydrolysis:

$$\text{Me} > \underline{\text{iso}}\text{Prop.} > \text{Et} > \underline{\text{tert}}\text{-But.}$$

The fact that the first order rate constant of hydrolysis decreases with increase of the initial ester concentration (diagram 1, Table II) has also been observed by Hammett and co-workers for ethyl toluenesulfonate (ref. 8) and benzhydryl chloride (ref. 6, 13) and also for the bimolecular hydrolysis of acetic anhydride by V. Gold (ref. 14). This last author claims that some solvent effect is probably responsible for this decrease.

2° The Solvent Effect

Having observed during some preliminary experiments that the rate of hydrolysis of <u>sec</u>-butyl toluenesulfonate was extremely sensitive to variations in the amount of water in the medium, we decided to investigate this effect quite extensively.

First we decreased continuously the amount of water in dioxane and by doing so the specific first order rate constant becomes smaller and smaller. Those results have already been mentioned and are recorded in Table III.

We tried next to determine whether the smaller proportion of water or the lower value of the dielectric constant was responsible for this decrease of the rate.

We added to a 75% aq. dioxane mixture 20% of nitromethane, a compound which has a very high dielectric constant. Thus we increased the total dielectric strength of the medium from 13.5 up to 18.0. We were surprised to observe that the rate, instead of being increased was slightly decreased. Its value was the same as that of the rate in 80%aq. dioxane with a dielectric strength of only 11.5.

Farinacci and Hammett have obtained a similar surprising effect when adding some nitrobenzene to a solution of benzhydryl chloride in ethyl alcohol (ref. 13,15).

An explanation of this phenomenon, advanced by Professor Kirkwood has been recently mentioned by P. Auer (ref. 16).

A solution can only be considered as a continuous medium when its constituents are comparable in electrostatic properties. When dipole moments and radii of interaction are not of the same order of magnitude for the various constituents, the molecular character of the solvent becomes apparent. The dielectric strength of the solvent is not any more the sum of the dielectric strength of the constituents.

Nitrobenzene has a very high dipole moment and a large radius of interaction in comparison with ethyl alcohol. Their mixing produces large holes in the otherwise continuous pattern of dipoles, resulting in an actual decrease of the dielectric strength in the neighborhood of the reacting benzhydryl chloride molecules.

The dipole moment of nitromethane and its radius of interaction are smaller than those of nitrobenzene but still not in proportion with those of water and dioxane. The introduction of this specie in the dioxane-water solvent decreases the rate probably for the same reason as that proposed for nitrobenzene.

It was therefore impossible to obtain any answer to our problem by using nitromethane. In order to increase the dielectric strength without increasing the amount of water, we tried next a mixture of 80% wt. ethanol and 20% water ($D = 32.8$). The rate was increased considerably but not as much as we expected on the basis of dielectric strength.

We think however that here again another phenomenon came to interfere with the hydrolysis. A displacement mechanism might probably occur between ethanol and *sec*-butyl toluenesulfonate molecules, producing the ethyl ester, the hydrolysis of which is, according to the results of Mc Cleary and Hammett (ref.8) much slower than that of *sec*-butyl toluenesulfonate.

Finally to decide if the dielectric strength effect was really responsible for the change of rate, we performed a number of experiments in different mixtures of water and acetone. Like in the dioxane-water mixtures, the rate was found to be proportional to the amount of water present.

In order to analyze the results obtained we shall use some theoretical formulas derived by P. Auer from Kirkwood's expression for the activity coefficient of a polar specie in solution (ref.16).

Those formulas are claimed to be only valid for medium of dielectric constant around 25 and higher. For lower values some non-electrostatic effects become important and may change the whole picture.

a) unimolecular dissociation:

$$\ln k_1 = \frac{\Delta\mu^\circ}{kT} - \ln\frac{\alpha_{RX}}{\alpha_t}$$

$$\ln k_1 = \frac{\Delta\mu^\circ}{kT} - \frac{1}{kT}\left[\frac{m_{RX}^2}{b_{RX}^3} - \frac{m_t^2}{b_t^3}\right]\frac{D-1}{2D+1}$$

$$\left[\frac{m_{RX}}{a_{RX}} - \frac{m_t}{a_t}\right]\frac{3N^2}{1000(DkT)^2}$$

m : dipole moment, b : radius of sphere containing the polar specie; a : radius of sphere of effective interaction of above polar specie and real ions in solution; $\Delta\mu^{0}$: change in chemical potential from initial state to transition state in standard state of activity; N, D, k, T, μ and the α's have their usual signification.

The second part of this expression is cancelled out if we consider only the initial rate constants in the absence of salt:

$$\ln \underline{k}_1 = \frac{\Delta\mu^{0}}{kT} - \frac{B}{kT} \times \frac{D-1}{2D+1}$$

where B is a function of the dipole moments and radii of the sphere containing the polar species RX and the transition complex.

b) bimolecular displacement: $RX + HOH \longrightarrow ROH + H^{+}$

$$\ln \underline{k}_2 = \frac{\Delta\mu^{0}}{\underline{k}T} - \ln \frac{\alpha_{RX}\,\alpha_{H_2O}}{\alpha_t}$$

$$\ln \underline{k}_2 = \frac{\Delta\mu^{0}}{\underline{k}T} - \frac{1}{\underline{k}T}\left[\frac{m_{RX}^2}{b_{RX}^3} + \frac{m_{H_2O}^2}{b_{H_2O}^3} - \frac{m_t^2}{b_t^3}\right]\frac{D-1}{2D+1} + \begin{matrix}\text{higher terms}\\ \text{in } t\end{matrix}$$

The rate constant here is the second order specific rate constant of solvolysis. In this case, the μ terms are negligible in dilute solution.

We plot the values of log k_1 against D-1/2D + 1 and obtained the two curves shown in Diagram III for dioxane-water and acetone-water solvents. The two isolated points on this diagram correspond to 80% aq. ethanol and nitromethane-water-dioxane mixture.

From those curves we can deduce the two following important informations.

1° The rate of hydrolysis in acetone-water mixtures is in excellent agreement with the formula above for an S_{NI} mechanism (ionic dissociation). The log of the rate is perfectly proportional to D - 1/2D + 1 and the proportionality factor is quite high.

2° The plot of the log of the rate in dioxane-water may be divided into three parts: a) for D lower than about 10, interferences of a non-electrostatic nature do not permit to draw any significant conclusion: b) from D = 10 up to D equal to about 18 the increase of the logarithm of the rate is almost proportional to D - 1/2D + 1 but the proportionality factor is much lower than for the acetone-water mixtures; c) above D = 18, the proportionality factor increases quite fast until it reaches the same value than that for the acetone-water solvents after what it seems to remain constant.

Our interpretation of this curve is the following: for low values of the dielectric constant, the ester is hydrolyzed through a combination of both unimolecular dissociation and

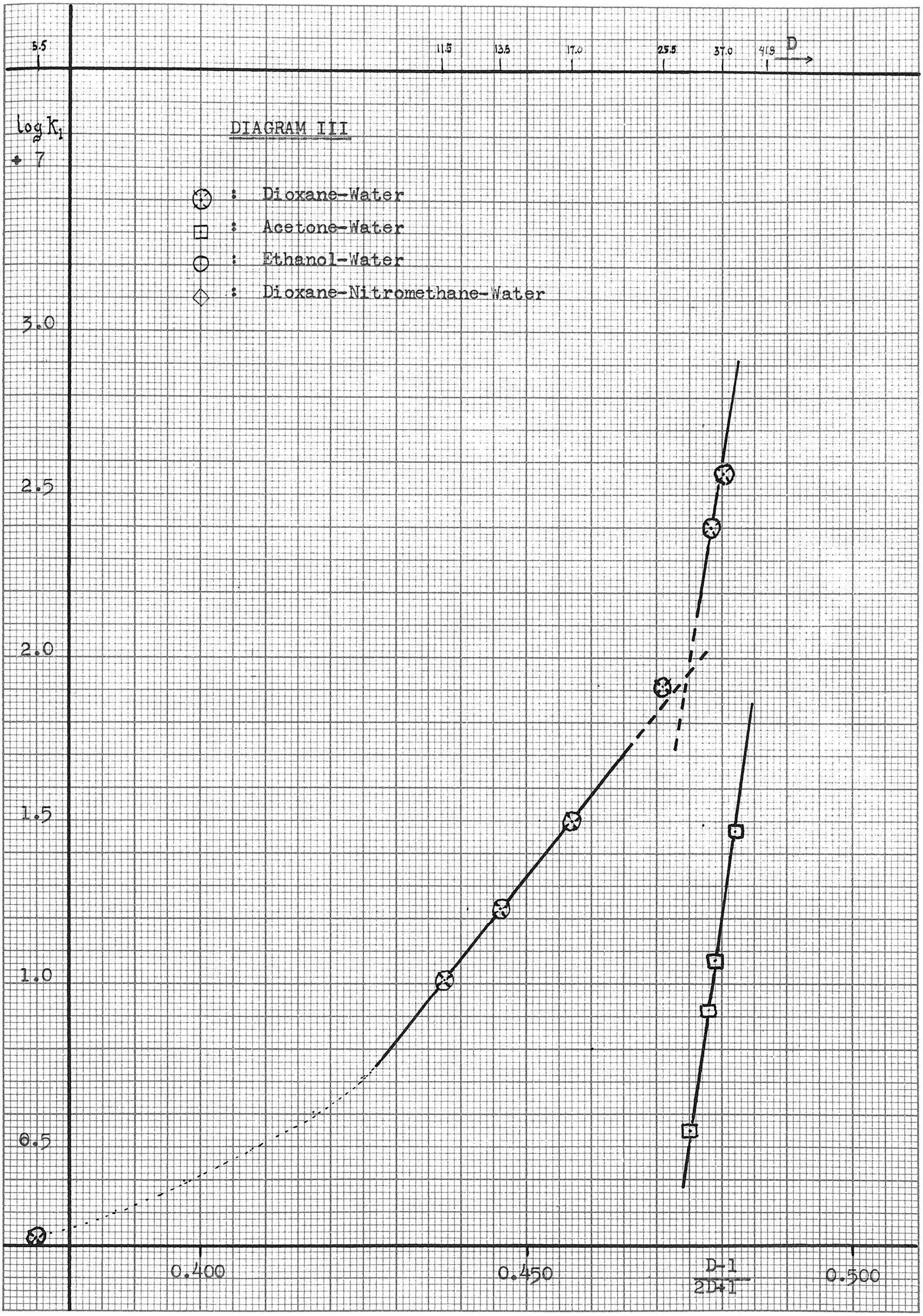

DIAGRAM III

5.5
11.5
13.5
17.0
25.5
37.0
41.9
D →
log K₁ + 7
⊗ : Dioxane-Water
⊞ : Acetone-Water
⊖ : Ethanol-Water
◇ : Dioxane-Nitromethane-Water
3.0
2.5
2.0
1.5
1.0
0.5
0.400
0.450
D-1 / 2D+1
0.500

bimolecular displacement; the amount of the last one increases constantly with D; for values of D above 25, the solvolytic mechanism is almost entirely an S_N1.

The formulas given in the previous pages are in favor of this explanation since, according to Auer's calculations, (ref. 16) the term

$$\frac{m^2_{RX}}{b^3_{RX}} - \frac{m^2_{t}}{b^3_{t}} > 0$$

indicates a strongly polar transition state while the similar term for a displacement mechanism:

$$\frac{m^2_{RX}}{b^3_{RX}} + \frac{m^2_{HO}}{b^3_{HO}} - \frac{m^2_{T}}{b^3_{t}} \ngtr 0$$

is not very different from zero. This is because the transition state is much less polar in character and also because of the introduction of the term $m^2_{H_2O}/b^3_{H_2O}$ into the equation.

It is important to remember that when the bimolecular mechanism is involved, the part of the total first order rate constant corresponding to this mechanism ($\underline{k}_1^{bi}$) is also a function of the concentration of water

$$\underline{k}_1 = \underline{k}_1^{bi} + \underline{k}_1^{uni}$$

$$\underline{k}_1^{bi} = \underline{k}_2\ (H_2O)$$

Therefore the formula given for the S_N2 displacement becomes

$$\ln \underline{k}_1^{bi} = \frac{\Delta\mu^\circ}{kT} - \frac{C}{kT} \frac{D - 1}{2D + 1} - \ln (H_2O)$$

since it was actually $\underline{k}_2$ which was a function of D - 1/2D + 1. (C here is written for the term in <u>m</u>'s and <u>b</u>'s.)

One can see that to find the actual variation of $\underline{k}_2$ in function of the dielectric constant of the medium, it is necessary to subtract the corresponding value of ln (H_2O) from the curve representing the variation of ln $\underline{k}_1^{bi}$. When both bi- and unimolecular mechanism are combined as in the present case, one should subtract from the values of ln $\underline{k}_1$ the corresponding value of ln (H_2O) proportionally to the contribution of the bimolecular mechanism in the solvolysis, a contribution that unfortunately we do not know.

In any case the curve would be still more horizontal as soon as the bimolecular mechanism is used in the solvolysis. This would lead to a quite small value for the term C as it is proposed in the theory.

The solvent effect is extremely interesting in that it gives a good qualitative picture of the change of mechanism occuring when the dielectric constant of the medium is increased, but it fails however to furnish any quantitative data in regard to the proportions in which each mechanism is involved in the solvolytic process.

We do not know how the rate of a pure bimolecular solvolysis of sec-butyl toluenesulfonate varies with the dielectric strength. The only way to find it out would be to use media of very low dielectric constant but we have seen that in such solvents important non-electrostatic effect arise.

The fact that the rate in acetone-water solvents is lower than the rate in dioxane-water mixtures of equal dielectric constant is probably due to some specific solvent effect. Similar variations are observed for tert-butyl bromide, the rate of which in acetone-water is slightly slower than in ethanol-water mixture of same dielectric constant.

3° The Ionic Strength Effect

After having determined the value of the specific rate constant in 60% aq. dioxane, we add some sodium perchlorate to the mixture in order to see whether or not an ionic strength effect will appear.

This effect has been thoroughly investigated by Hughes, Ingold and their co-workers (ref. 9,11) on different esters and especially on tert-butyl bromide.

Those authors, from statistical considerations on one hand and by calculating a value for the activity coefficient of the transition state (by a method similar to that used by Kirkwood; (ref. 17) on the other hand, finally obtained the following formula for the rate of hydrolysis of alkyl esters by unimolecular dissociation:

$$\frac{d\underline{x}}{d\underline{t}} = \underline{k}_1^{(o)} (\underline{a} - \underline{x}) \text{ antilog.}_{10} (0.912\ 10^{16} \delta\mu / D^2T^2)$$

where $\delta = z^2 d$; $k_1^{(o)}$: specific first order rate constant at zero ionic strength $\underline{a} - \underline{x}$ = ester concentration; $0.912\ 10^{16} = \frac{4\pi}{1000} \frac{Ne^4}{ka} \frac{1}{2.303}$ (d is the distance between two point charges $\underline{ze}$ surrounded by an ionic atmosphere of charge $\pm\underline{e}$; N, μ, k and D have their usual signification.)

Unfortunately if this formula gives a good quantitative picture of the progressive increase of the rate during the hydrolysis (mentioned in the first part of this discussion,) it does not fit too well when some salt is added to the solution.

Instead of the preceeding formula, we like much better the more general one obtained by combination of the same value of the activity coefficient for the transition state with the Bronstoed equation (ref. 14,16):

$$\ln \underline{k} = \ln \underline{k}_o - \frac{4\pi Ne^2}{1000k2} \frac{1}{(DT)2} \left[\sum_R \frac{m_R}{a_R} - \frac{m_\ddagger}{a_t} \right] \mu$$

the m's are the dipole moments of the polar species; the indices r and t mean reactants and transition state.) the $\underline{a}$'s are the radii of spheres of effective interaction of polar species and real ions in solution).

From this equation one sees immediately that an increase of μ must lead to an increcrease of <u>k</u> if the term

$(\sum_R \frac{m_R}{d_R} - \frac{m_t}{d_t})$ is negative, in other words if the transition state is more polar in character than the sum of the reactants.

Of course this formula is only true if all molecules are dipoles and all effects other than electrostatic ones may be neglected.

Unfortunately, nobody knows the exact value of the term $(\sum_R \frac{m_R}{a_R} - \frac{m_t}{a_t})$ or of the parameter σ of Hughes and Ingold which is in effect proportional to this term (ref. 16).

However if the quantitative picture is not available, the qualitative one is quite significant. If the rate of hydrolysis of an ester is increased by addition of a salt which does not interact with it, we have a strong argument in favor of an S_nI mechanism. A bimolecular mechanism is also speeded up by an increase of ionic strength but to a much smaller extent.

On the other hand, the absence of such an effect is by no means against an ionic dissociation nor is it especially in favor of an S_N2 type of mechanism when working in a medium of high solvating power, like 60% aq. dioxane.

In that medium for sec-butyl toluenesulfonate we have practically no effect (Table IV). The only thing that we may deduce from the absence of an ionic strength effect is that the transition state is either highly polar in character the effect being negligible because of the large amount of water present, or it is only slightly polar in character (S_NI or S_N2) in which case no effect is to be expected.

In an other experiment, we studied the influence of ionic strength upon the rate in a 75% aq. dioxane medium. Here the increase was not at all negligible (Table IX); the ratio of $(\underline{k}_1)_o$observed over $(\underline{k}_1)_o$ for the hydrolysis in the absence of salt was 1.10 for a sodium perchlorate concentration three times as high as the ester concentration.

Although we had strong evidence in that medium for the presence of a large amount of S_N2 character, a considerable part of the hydrolysis was probably still proceeding by a unimolecular dissociation mechanism.

Therefore we believe that the increase of the rate observed is due to the presence of a highly polar transition state in the unimolecular dissociation. The increase to only 1.10 compared with 1.40 for <u>tert</u>-butyl bromide in 90% aq. acetone (Ester concentration = LiCl concentration ≐ 0.1 molal) (ref. 11) is ascribed to the only partial contribution of this mechanism to the hydrolysis and to the still considerable amount of water present.

If we admit the presence of a highly polar transition state in 75% aq. dioxane, there is no apparent reason why this would not be the case in 60% aq. dioxane (higher solvating power.); the effect here being completely masked by a large amount of water.

As a further evidence, the rate in 75%aq. acetone is influenced still more by an addition of sodium perchlorate. This can be predicted if by observation of the curve showing the solvent effect: which indicate a pure S_NI mechanism in that case.

For acetone-water mixtures, the steepness of slope indicates a highly polar transition state or in other words an ionization mechanism.

4° The Mass law Effect

This effect has already been mentioned in the first part of this discussion; it is produced by the addition to the solution of a salt having an ion identical with one of the products of the ionic dissociation.

If we have a look again at the general equation of such a unimolecular mechanism,

$$R\text{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + X^- \xrightarrow[H_2O]{k_{s}^{(3)}} R\text{-}OH + H^+ + X^-$$

we notice immediately that it is actually a combination of three reactions the rates of which may be written:

$$v_1 = \underline{k}_1\ (RX) \qquad v_{-1} = \underline{k}_{-1}\ (R^+)(X^-) \qquad v_s = \underline{k}_s\ (R^+)$$

with the general condition: $\underline{k}_1 < \underline{k}_s$

At equilibrium, $v_1 = v_{-1} + v_s$ and what we actually measure when we titrate the acidity produced is the velocity of the second step.

$$\frac{dx}{dt} = v_s = \frac{v_1}{v_{-1} + v_s} \times v_s$$

by replacing the v's by their values given above, in this equation, one finally comes out with the expression:

$$\frac{dx}{dt} = \frac{k_1\ (a - x)}{\alpha \underline{x} + 1}$$

Here $\alpha = \underline{k}_1/\underline{k}_s$ is a measure of the intensity of the mass law effect.

Therefore when the coefficient is small, one can easily see from previous expression that the rate equation retains its normal form:

$$dx/dt = \underline{k}_1\ (\underline{a} - \underline{x})$$

Hughes, Ingold and co-workers (ref. 9) give different curves showing the variation of the ratio of $\underline{k}_1/\underline{k}_1^0$ during the course of a reaction for different values of .

It is seen that for values of this coefficient lower than 5, the maximum deviation from pure first order kinetics is less than 10 %.

However when a salt having an ion identical with one of the products of the dissociation is added, the rate expression obtained is the following:

$$\frac{dx}{dt} = \frac{k_1 \quad (a-x)}{\alpha(x+c)+1}$$

Here, c is the salt concentration.

In our experiments we have measured the initial rate constants. In this case, the initial rate constant is given by:

$$(dx/dt)_{t=0} = \frac{k_1^o}{\alpha c + 1} \cdot a = k_1^{o\prime} a$$

Here, k_1^o is the initial specific rate constant in the absence of salt and $k_1^{o\prime}$ is the initial rate constant in the presence of a concentration <u>c</u> of the "common ion" salt.

Table V shows the results that we obtained for this effect, in 60% aq. dioxane. The ratio of k_1^o over $k_1^{o\prime}$ is of the order of 1.04 for a salt concentration of 0.01371. Since $k_1^o/k_1^{o\prime} = 1.04, = \alpha . 0.014 + 1$, this leads to the value of $\alpha = 2.85$.

According to the results of Hughes and Ingold mentioned above, this value is much too small to permit the observation of any decrease of the specific rate constant during the hydrolysis in the absence of "common ion" salt.

Like the absence of an ionic strength effect, the absence of a mass law effect is by no means opposed to a unimolecular mechanism of hydrolysis. The small effect observed is even a proof that such a mechanism is certainly partially present. It seems extremely possible that the large p-toluenesulfonate ion, once hydrated, shows only a weak tendency of recombining through the transition state with the sec-butyl ion.

In other words, the value of $\underline{k}_{-1}/k_s$ must be quite small. If no bimolecular mechanism is involved at all, it must have a value of the order of 2.85 as it has been calculated above.

Since no effect was apparent in 60% aq. dioxane there is still less chance that it would appear in media of lower dielectric constant in which the unimolecular mechanism responsible for this effect would be even less likely. An experiment in 80%aq. dioxane has confirmed this point of view.

5^{o} Hydroxyl ion Effect

The increase of rate as well as the departure from first order kinetics when a certain amount of hydroxyl ion is added to the solution gives some information about the mechanism involved.

If the solvolysis mechanism is actually a unimolecular dissociation the presence of OH^- ions does not influence the kinetics, it simply increases the rate due to an ionic strength effect.

If on the other hand a bimolecular displacement is operating, the rate will be affected by the presence of the hydroxyl ions.

However if the tosylate group is displaced by OH^- ions to a certain extent, it will not necessarily be displaced to the same extent by the water molecules, for these last are much less electronegative and therefore show a considerable less affinity to displace the tosylate or halogen group.

Furthermore even in the presence of hydroxyl ions the ester molecules are still perfectly able to react with water by both mechanisms.

Consequently, we only obtained a qualitative idea of the mechanism by studying this effect.

1) If hydroxyl ions have no action on the rate, in other words if the ester is not able to react by an S_N2

mechanism with this strongly negative specie, there is a strong probability that it will not react by such a mechanism with the much less electronegative water molecules.

2) If some effect is observed, it shows that the ester is able to react by an S_N2 mechanism but does not necessarily imply that it reacts with water molecules by that mechanism.

3) If a strong effect is observed, the ester is very probably hydrolyzed to a large extent or even entirely through a bimolecular mechanism in the presence or absence of hydroxyl ions.

The calculated value of k_2 gives the magnitude of the OH^- ion effect. It is important however to refer also to the concentration of those ions in the solution since an ionic strength and a solvent effects are actually superposed on the OH^- effect and increase the value of $\underline{k}_2$.

The ionic strength effect is extremely small in a 60% aq. dioxane medium but the solvent effect is considerable. The ratio of $\underline{k}_2/\underline{k}_1$ is 2.25 for an initial hydroxyl ion concentration, $(OH^-)_o = 0.02$ and 4.65 for $(OH^-)_o = 0.043M$ (mean value).

In 75% aq. dioxane the same ratio has the values: 40.0 for $(OH^-)_o = 0.045M$ (the ionic strength effect, important here being deduced) and 32.5 for $(OH^-)_o = 0.011M$.

In 75% aq. acetone it is only 16.5 for $(OH^-)_0$ = 0.013M.

Those results are in excellent agreement with the solvent effect in the sense that they show a strong hydroxyl ion influence in 75%aq. dioxane whereas a bimolecular mechanism was predicted to be partly present; a much lower influence in 75% aq. acetone and a still lower in 60%aq. dioxane, two media where the unimolecular mechanism was proposed to be predominant.

The presence of a higher effect in 75%aq. acetone than in 60% aq. dioxane seems logical on the basis of the respective amounts of water present.

V CONCLUSIONS

The hydrolysis of *sec*-butyl *p*-toluenesulfonate in 60% aq. dioxane works largely through a unimolecular dissociation of the ester molecules. A small amount of bimolecular displacement is quite possible. The nature of the ester, the solvent effect and the OH^- ions effect are in favor of this while the ionic strength and the "common ion" effects are not opposed.

The hydrolysis of the same *sec*-butyl ester in 75%aq. dioxane possess a large amount of bimolecular character as shown by the solvent effect and the hydroxyl ions effect but it still contains quite an important amount of unimolecular character as the ionic strength effect demonstrates.

Finally the hydrolysis in acetone-water media has a unimolecular mechanism as the ionic strength effect in the 75% solvent indicates. In this medium however a small contribution of the bimolecular mechanism is not excluded since the hydroxyl ion effect is not negligible.

The absence of any important mass law effect in every case simply indicates that the tosylations show almost no tendency to reform the original ester or more exactly that the back reaction is rather slow compared with the second step forward reaction.

We believe that we have here in dioxane-water media experimental evidence for a transition from the unimolecular mechanism of solvolysis at the higher percentages of water to the bimolecular displacement of an ester by the solvent molecules at the lower percentages of water.

This transition is extended over a quite considerable range of dielectric strength and it is unfortunately not yet completed on the bimolecular side for low dielectric constant media.

It is therefore impossible to know the variation of the rate of a pure bimolecular solvolytic displacement of <u>sec</u>-butyl toluenesulfonate.

If the variation of this with dielectric constant were known, it probably would be possible to determine by analyzing the "solvent effect" curve, the proportions of each mechanisms present for any medium of intermediate dielectric constant.

Hughes and Ingold (ref. 8) mentioned that methyl, ethyl and <u>iso</u>propyl bromides show approximately the same increase of rate when a large amount of water is added to ethyl alcohol.

However for high solvating media the variation of the rate of <u>iso</u>propyl bromide becomes larger and approaches the corresponding variation for <u>tert</u>-butyl bromide.

They conclude that a change of mechanism occurs for <u>iso</u>propyl bromide. Change of mechanism which is not sharp but spread over a certain range of values of the solvating power of the medium.

The results that we have obtained completely agree with this.

We think that any alkyl halide or similar ester like the toluenesulfonates are probably theoretically able to react by both mechanisms.

They all must possess a curve similar to the one shown here by sec-butyl toluenesulfonate and mentioned by Hughes and Ingold for the alkyl halides. Unfortunately the transition region, which may spread over a quite large range of dielectric strength, is for most compounds out of the reach of the experiment.

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