

which vapor pressures of the chloride are used, but mole fractions of water and alcohol. The probability is discussed that the equation of Olson and Halford is, like this, a special approximation and does not represent a fundamental rate law.

Contrary to the conclusions of Olson and Halford, their results do not prove that the hydrolysis and alcoholysis of *t*-butyl chloride in mixed solvents is a bimolecular reaction, for the rates can also be accurately calculated on the assumption

of a termolecular transition state by either of the two approximate kinetic equations.

It is shown that the product composition exhibits a dependence on solvent composition which is consistent with the view that the rate-determining step is an ionization, the solvent serving to solvate the anion, and that the solvent components then compete for the cation in rough proportion to their mole fractions.

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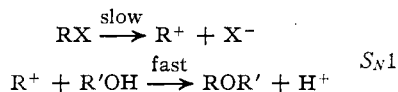
RECEIVED FEBRUARY 21, 1939

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The Solvolysis of *t*-Butyl Chloride. Solvolytic Reactions and the Walden Inversion

BY SAUL WINSTEIN

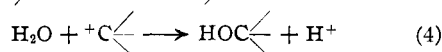
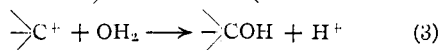
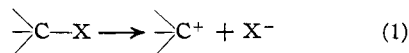
A serious problem at the present time is the exact interpretation of first-order solvolytic reactions of organic halides. Ingold and collaborators¹ suppose that these reactions proceed by an ionic mechanism, S_N1



in which the halide RX ionizes, the cation R^+ reacting rapidly with solvent molecules. Hammett and co-workers² believe these solvolytic reactions to be polymolecular, while Olson and Halford³ and Taylor⁴ have presented evidence that they are bimolecular. It is the purpose of the author to present in the following paragraphs evidence and discussion in favor of the polymolecular interpretation of solvolytic reactions of halides and opposed to the ionic mechanism, and to discuss the polymolecular mechanism from the standpoint of the steric results obtained using optically active halides.

Objections to the Ionic Mechanism.—It may be satisfactory for some purposes to speak of solvolytic reactions as involving an ionization with stress placed on the role of solvation in the ionization. But unless solvation is considered explicitly, it is impossible to discuss logically the steric results and product compositions (if mixed solvents are used) from solvolytic reactions of halides. To see this clearly let us formulate the

first-order hydrolysis of a halide as involving an ionization of this halide, first without including any mention of solvation in the reaction equations and then allowing for solvation of the organic cation. First let us consider reactions 1-4, which relate to the hydrolysis of a halide molecule by the so-called ionic mechanism



without being explicit about solvation of the organic cation. Reaction 1 represents the ionization process and reaction 2 the process of flattening-out of the cation, permitting it to react to give products with either one of two enantiomorphic configurations, as shown by reactions 3 and 4. One would predict that if the life of the cation were long enough to permit one to speak of the existence of the cation, reaction 2 would be fast enough to give rise to a racemic alcohol from an optically active halide.

Ingold and collaborators⁵ explain the usual steric result^{2a,6} of solvolytic reactions (predominant inversion with more or less racemization) by the argument that usually X^- will shield R^+ sufficiently so that reaction occurs more easily from the side away from X^- than from the side toward

(1) Gleave, Hughes and Ingold, *J. Chem. Soc.*, 236 (1935).
 (2) (a) Steigman and Hammett, *THIS JOURNAL*, **59**, 2536 (1937);
 (b) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937).
 (3) Olson and Halford, *ibid.*, **59**, 2644 (1937).
 (4) Taylor, *J. Chem. Soc.*, 1853 (1937).

(5) Cowdrey, Hughes, Ingold, Masterman and Scott, *ibid.*, 1252 (1937).

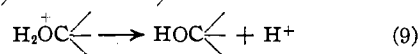
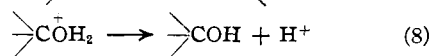
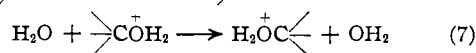
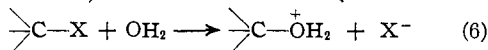
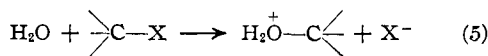
(6) (a) Hughes, Ingold, and Masterman, *ibid.*, 1196 (1937); (b) Hughes, Ingold and Scott, *ibid.*, 1201 (1937).

X^- , so that inversion predominates. In certain cases, such as the solvolysis of α -bromopropionate ion,⁷ these workers expect⁵ and find complete retention of configuration. It is believed by them that the intermediate zwitterion in this case is stabilized in a pyramidal form and a solvent molecule reacts with it at the place left vacant by bromide ion.

The above arguments do not seem to me to be at all reasonable. It would seem that if ionization were complete enough to permit the reaction to be called unimolecular, then the ion R^+ would be free enough from shielding effects so that a completely racemic product would result from the reaction of R^+ with solvent molecules.

Further, it is my opinion that the correct explanation of the retention of configuration in the first-order solvolysis of α -bromopropionate ion is not that the reaction proceeds by mechanism S_N1 with stabilization of the intermediate zwitterion, but that instead the carboxylate ion group substitutes for the bromine atom by an intramolecular variety of the usual bimolecular exchange leading to Walden inversion.⁸ The formation of the α -lactone is assumed to be the rate-determining step. The α -lactone then rapidly reacts with solvent molecules with a second inversion in the manner of epoxides⁹ or β -lactones¹⁰ under some conditions.¹¹

If we continue to describe the first-order hydrolysis of a halide as involving an ionization of the halide but now consider solvation explicitly we must admit that only through solvation does the activation energy of such a reaction become low enough to give rise to a reasonable rate for the process of hydrolysis. Thus, as Ogg and Polanyi¹² have pointed out, the hydrate of the carbonium ion and not a bare cation is to be expected from any ionization of a halide in water. Reactions 1-4 are now replaced by 5-9. Reactions 5 and 6 represent the formation of two optically different cation hydrates, depending on the mode of reaction. These cation hydrates we recognize as



oxonium compounds of alcohols. Reaction 2 is replaced by 7, which represents a racemization brought about by a water exchange. Reactions 8 and 9 represent the loss of protons by the oxonium compounds. When the reaction is represented in this way it seems desirable not to speak of an ionization mechanism but rather to regard the solvent as a reactant. One has no reason to suppose that reaction 7 is rapid, so that the steric result of the hydrolysis is determined with the formation of the oxonium compounds. Ogg and Polanyi suggested that ionization goes only by reaction 5, but the considerable racemization accompanying most solvolytic reactions^{2a,6} indicates the occurrence of both reactions 5 and 6. How water is able to enter into both reactions 5 and 6 will be seen later.

Hydrolysis and Alcoholysis of *t*-Butyl Chloride.—If, as is discussed above, we regard the solvent as a reactant, further insight into the nature of solvolytic reactions of halides can be gained by studying the solvolyses in mixed solvents. In the case of the first order hydrolysis and alcoholysis of tertiary butyl chloride in mixtures of water with either methyl or ethyl alcohol, considerable data are at hand.^{3,13} Olson and Halford³ have suggested that rates of hydrolysis and alcoholysis of *t*-butyl chloride in binary solvents should be proportional to the fugacities of halide and water or alcohol. Thus the total rate of hydrolysis plus alcoholysis is given by equation 10, where k_m is the measured first-order specific reaction rate constant for the

$$k_m = (k_w p_w + k_a p_a)(p/N)_{RCl} \quad (10)$$

formation of hydrogen chloride, p_w and p_a are vapor pressures of water and alcohol, respectively, k_w and k_a are constants characteristic of pure water and alcohol, respectively, and $(p/N)_{RCl}$ is the Henry's law constant for the halide in a given solvent. P_A , the mole per cent. of the reaction product which is *t*-butyl alcohol and not its

(7) Cowdrey, Hughes and Ingold, *J. Chem. Soc.*, 1208 (1937).

(8) (a) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (b) Meer and Polanyi, *Z. physik. Chem.*, **19B**, 164 (1932).

(9) Winstein and Lucas, *THIS JOURNAL*, **61**, 1576 (1939).

(10) Olson and Miller, *ibid.*, **60**, 2687 (1938).

(11) Recently⁹ it has been found that 3-bromo-2-butanol reacts with hydrobromic acid with complete retention of configuration. In this case an argument based on stabilization of an intermediate carbonium ion in a pyramidal form is not possible but a role for the bromine atom similar to the role of the negative oxygen in α -bromopropionate ion can be and has been formulated.

(12) Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 619 (1935).

(13) (a) Hughes, *J. Chem. Soc.*, 255 (1935); (b) Bateman, Hughes and Ingold, *ibid.*, 881 (1938).

alkyl ether, is thus predicted by equation 11

$$P_A = (100/k_m)(k_w p_w)(p/N)_{\text{RCl}} \quad (11)$$

Olson and Halford were able to fit exceedingly well the rates of hydrogen chloride formation in water-methyl alcohol and water-ethyl alcohol mixtures with equation 10, k_w being identical in both cases. This same k_w predicted quite well the rates in a water-acetone mixture and a water-dioxane mixture where only *t*-butyl alcohol and no ether results. These facts caused Olson and Halford to conclude that the reaction between *t*-butyl chloride and water or alcohol is bimolecular and not unimolecular.

Olson and Halford neglected to analyze the product of the reaction to see whether the composition agreed with equation 11. Bateman, Hughes, and Ingold^{13b} did this and found serious disagreement between observed compositions and those expected from equation 11. These authors felt that this was evidence in favor of the unimolecular (S_N1) mechanism; that is, they assume that solvent plays a significant role in the ionization of the halide but the product composition is given by the inaccessible rate constants for the reactions of R^+ with water or alcohol.

However, the failure of equation 11 to predict the composition of the product does not necessarily indicate that the unimolecular mechanism is the correct one. Alternative explanations are that the solvolysis is not bimolecular but of a higher order or that a fugacity equation such as equation 10 is not applicable. While full justification for the use of fugacity rate expressions is still lacking, nevertheless the suggestion that fugacities should be used instead of concentrations for treating rates in binary solvents where association and solvation occur seems a sensible one. The validity of the use of fugacity rate expressions is assumed in the following discussion.

I have found that equation 12

$$k_m = (k_{w2} p_w^2 + k_{wa} p_w p_a + k_{a2} p_a^2) (p/N)_{\text{RCl}} \quad (12)$$

corresponding to the reaction of tertiary butyl chloride with two solvent molecules, fits the data of Olson and Halford³ and Hughes¹³ as well as equation 10. Here $k_{w2} p_w^2$ is the term representing reaction involving two water molecules and giving rise to *t*-butyl alcohol, $k_{wa} p_w p_a$ is the term representing reaction with one water molecule and one alcohol molecule and giving rise to either *t*-butyl alcohol or *t*-butyl alkyl ether, and $k_{a2} p_a^2$ is the term representing reaction with two

alcohol molecules and giving rise to ether. The value of k_{w2} was determined from the data on the water-acetone mixture and the water-dioxane mixture as is shown in Table I, that of k_{a2} from

TABLE I

DETERMINATION OF k_w FROM DATA ON THE HYDROLYSIS OF *t*-BUTYL CHLORIDE IN ACETONE-WATER AND DIOXANE-WATER MIXTURES³

Solvent	Acetone-H ₂ O	Dioxane-H ₂ O	Mean
Mole % H ₂ O	50.3	83.2	
p_w (mm.)	17.8	19.7	
k_m	6.90×10^{-3}	644×10^{-3}	
$(p/N)_{\text{RCl}}$ (mm.)	1.65×10^3	96.5×10^3	
$k_{w2} \times 10^8$	1.319	1.719	1.519
$k_{w3} \times 10^{10}$	7.41	8.73	8.07
$k_{w4} \times 10^{11}$	4.16	4.43	4.30

the rate in pure methyl or ethyl alcohol, and that of k_{wa} from the rate in the alcohol solution containing the most water. Tables II and III give a comparison between observed values of k_m and those calculated by Olson and Halford from equation 10 and by the author from equation 12. Values in parentheses are those used in obtaining the constants (k_{wa} , etc.). It is evident that equation 12 fits the data fully as well as equation 10.

In the case of the data in methyl alcohol-water mixtures still another fugacity equation was tried.

$$k_m = (k_{w3} p_w^3 + k_{w2a} p_w^2 p_a + k_{wa2} p_w p_a^2 + k_{a3} p_a^3) (p/N)_{\text{RCl}} \quad (13)$$

It was found that equation 13 fits the data just as well as equation 10 or 12. Equation 13 represents the reaction of *t*-butyl chloride with three solvent molecules, all of water, all of alcohol, or some of each. The value of k_{w3} was determined from the data on the water-acetone mixture and the water-dioxane mixture as is shown in Table I, and the other constants were evaluated as described for equation 12. Table II lists the values of k_m calculated from equation 13; it is obvious that the equation represents k_m satisfactorily.

Whereas the product compositions were not well predicted by equations 10 and 11, treatment of the data with the aid of equations 12 and 13 leads to satisfactory agreement between predicted and obtained product compositions if one makes reasonable assumptions regarding the terms which lead to a mixture of products. Thus, in the case of equation 12, P_A in the methyl alcohol study is given satisfactorily by equation 14 and

$$P_A = (100/k_m)(k_{w2} p_w^2 + 0.11 k_{wa} p_w p_a) (p/N)_{\text{RCl}} \quad (14)$$

in the ethyl alcohol study by equation 15. On

$$P_A = (100/k_m)(k_{w2} p_w^2 + 0.01 k_{wa} p_w p_a) (p/N)_{\text{RCl}} \quad (15)$$

TABLE II
SUMMARY OF DATA AND CALCULATIONS FOR HYDROLYSIS AND ALCOHOLYSIS OF *t*-BUTYL CHLORIDE IN METHYL ALCOHOL-WATER MIXTURES

$$\text{I. } k_m = (k_{w2}p_w^2 + k_{wa}p_w p_a + k_{a2}p_a^2) (p/N)_{\text{RCI}}$$

$$k_{w2} = 1.52 \times 10^{-8} \quad k_{wa} = 3.15 \times 10^{-9} \quad k_{a2} = 1.23 \times 10^{-10}$$

$$\text{II. } k_m = (k_{w3}p_w^3 + k_{w2a}p_w^2 p_a + k_{wa2}p_w p_a^2 + k_{a3}p_a^3) (p/N)_{\text{RCI}}$$

$$k_{w3} = 8.07 \times 10^{-10} \quad k_{w2a} = 1.18 \times 10^{-10} \quad k_{wa2} = 3.73 \times 10^{-11} \quad k_{a3} = 9.72 \times 10^{-18}$$

Mole % H ₂ O	p_w mm.	p_a mm.	$(p/N)_{\text{RCI}}$ $\times 10^{-3}$	$10^8 k_m$			
				Obsd. (O. + H.)	(O. + H.) ^a	Calculated (S. W.)(I)	(S. W.)(II)
49.7	13.7	70.2	53.5	347	(347)	(347)	(347)
43.2	12.5	76.7	29.8	188	182	182	180
38.3	11.5	81.9	19.8	110	115	115	113
34.6	10.7	84.9	13.8	75.4	76.5	75.7	73.6
28.2	9.10	92.5	8.6	40.7	43.4	42.7	41.3
23.0	7.63	98.0	6.0	25.4	27.2	26.5	(25.4)
17.5	5.92	105	4.1	15.4	16.3	15.8	15.1
7.0	2.46	118	2.1	6.24	5.9	5.7	5.6
0.0	0	126.6	1.48	2.92	(2.92)	(2.92)	(2.92)

TABLE III
SUMMARY OF DATA AND CALCULATIONS FOR HYDROLYSIS AND ALCOHOLYSIS OF *t*-BUTYL CHLORIDE IN ETHYL ALCOHOL-WATER MIXTURES

$$k_m = (k_{w2}p_w^2 + k_{wa}p_w p_a + k_{a2}p_a^2) (p/N)_{\text{RCI}}$$

$$10^8 k_{w2} = 1.52 \quad 10^9 k_{wa} = 2.79 \quad 10^{10} k_{a2} = 3.65$$

Mole % H ₂ O	p_w mm.	p_a mm.	$10^{-2}(p/N)_{\text{RCI}}$	$10^8 k_m$		
				Obsd. (Hughes) ¹³	Calculated (O. + H.) ^a	(S. W.)
82.9	20.5	25.4	577	4660	4950	(4660)
76.4	19.9	28.6	182	1320	1530	1440
68.4	19.2	31.4	59.2	453	487	453
58.1	17.9	34.5	16.2	145	126	114
44.8	16.6	38.4	6.0	32.9	44.4	39.0
26.2	11.5	45.5	1.68	6.16	9.2	7.1
0.0	0.0	59.0	0.63	0.8	(0.8)	(0.8)

treating the methyl alcohol-water data with equation 13, it turns out that product compositions are given satisfactorily by equation 16.

$$P_A = (100/k_m)(k_{w2}p_w^2 + 0.61k_{wa}p_w p_a + 0.01k_{wa2}p_w p_a^2) (p/N)_{\text{RCI}} \quad (16)$$

The comparison between observed¹⁴ values of P_A and those predicted by equations 11, 14, 15 and 16 is shown in Table IV. It is clear that equations 14, 15, and 16 are satisfactory and equation 11 is not.

Thus, if one assumes the validity of rate equations based on fugacities, one obtains evidence that the solvolysis of *t*-butyl chloride in water-alcohol mixtures involves two or more solvent molecules. It is apparent that the data available do not per-

(14) In writing down the values of P_A (observed) in Table IV it is necessary to take into account the small amount of olefin produced^{13b} in the reaction. In the case of the methyl alcohol-water data Dr. P. D. Bartlett has pointed out to the author that the amount of olefin is proportional to the amount of ether in the reaction product and therefore that the olefin is to be regarded as ether which has been sidetracked. In the case of the ethyl alcohol-water data it would appear that the olefin arises from the sidetracking of both ether and alcohol. A reasonable assumption appears to be that the amount of ether which has been sidetracked amounts to about 40% of the observed ether.

TABLE IV
COMPARISON OF OBSERVED AND CALCULATED PRODUCT COMPOSITIONS FOR THE SOLVOLYSIS OF TERTIARY BUTYL CHLORIDE

$$\text{I } P_A = (100/k_m)(k_{w2}p_w^2 + 0.11k_{wa}p_w p_a) (p/N)_{\text{RCI}} \text{ for MeOH} + \text{H}_2\text{O}$$

$$P_A = (100/k_m)(k_{w2}p_w^2 + 0.01k_{wa}p_w p_a) (p/N)_{\text{RCI}} \text{ for EtOH} + \text{H}_2\text{O}$$

$$\text{II } P_A = (100/k_m)(k_{w3}p_w^3 + 0.61k_{wa2}p_w p_a^2 + 0.01k_{wa2}p_w p_a^2) (p/N)_{\text{RCI}} \text{ for MeOH} + \text{H}_2\text{O}$$

Solvent	Mol % H ₂ O	$P_A = \text{Mol \% alcohol in product}$ Calculated			
		Obsd. ¹³ (O. + H.) ^a	I	II	
MeOH + H ₂ O	49.0	55	83	49	53
	28.4	28	71	31	30
	16.4	14	57	18	14
Mean dev. from P_A (obsd.)			38	4	1
EtOH + H ₂ O	68.3	78	92	74	
	44.7	62	89	64	
	26.4	43	82	48	
Mean dev. from P_A (obsd.)			27	4	

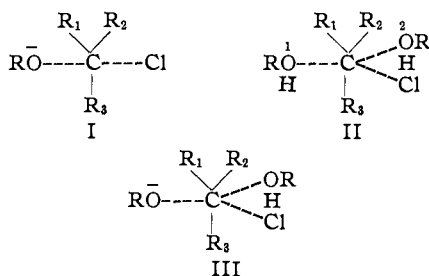
mit a more definite statement to be made; any treatment involving two or more solvent molecules is satisfactory.

The Polymolecular Mechanism.—Hammett and co-workers already have proposed,² in connection with solvolyses of benzhydryl chloride

and α -phenylethyl chloride, that solvolytic reaction is a polymolecular one and takes place within a solvation complex. These workers noted that small amounts of water catalyze the alcoholysis of benzhydryl chloride linearly without diverting very much material to benzhydrol, and, also, that small amounts of hydroxylic solvent in acetone are ineffective in hydrolyzing or alcoholizing benzhydryl chloride. Bateman, Hughes, and Ingold¹⁵ have noted recently that the benzhydryl chloride data of Farinacci and Hammett cannot be treated by equations 10 (but assuming $(p/N)_{\text{RCl}}$ is constant) and 11 to predict product compositions and have felt again that the ionic mechanism is indicated. The situation here is similar to that for *t*-butyl chloride. Actually, the data in the case of benzhydryl chloride cover only a narrow range of solvent composition and Henry's law constants for the halide are unknown, so further calculations with vapor pressure rate equations cannot be carried out.

The author agrees essentially with Hammett and co-workers² concerning the nature of solvolytic reactions of halides and feels that the difference in steric results obtained from solvolytic reactions and from bimolecular exchanges³ can be discussed as is done below.

In the case of an ordinary bimolecular substitution of RO^- for Cl^- a transition state⁵ such as I is imagined. RO^- is oriented away from the chlorine and clean-cut inversion is the result of reaction through transition state I.



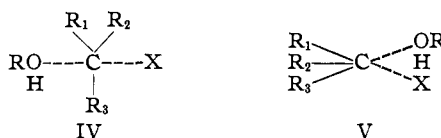
In the case of a solvolytic reaction, let us for the sake of convenience write only two solvent molecules into the transition state II, one in back of the carbon-chlorine dipole and one, due to the tendency toward hydrogen-bond formation to the halogen, on the same side as the chlorine. Products can be obtained from II in two ways, either with inversion, if solvent molecule 1 becomes bonded to the central carbon atom and solvent molecule 2 leaves as part of the solvation sphere

(15) Bateman, Hughes and Ingold, *THIS JOURNAL*, **60**, 3080 (1938).

of the chloride ion, or with retention of configuration, if solvent molecule 2 becomes bonded to the central carbon atom. From the usual steric results of solvolytic reactions of halides, we would say that solvent molecule 2 competes more or less successfully with solvent molecule 1 for electron donation to the central carbon atom, the predominating process being the one in which solvent molecule 2 leaves as part of the solvation sphere of the chloride ion with solvent molecule 1 becoming bonded to the central carbon atom.

It might be argued that transition state I is an oversimplification and that transition state III should be considered when RO^- replaces a chlorine atom. We see, however, that a solvent molecule would have little success in competition with a negative ion in the same transition state, since a negative ion is a much better electron donor than a solvent molecule. Thus, with reaction going through transition state III we would still expect clean-cut inversion, the solvent molecule always leaving as part of the solvation sphere of the chloride ion.

When a solvolytic reaction is carried out in an inert solvent containing smaller and smaller concentrations of hydroxylic compound, a bimolecular mechanism should be reached. Transition states of the type IV and V seem possible. If the



solvent can aid in removing halide ion mechanism IV with inversion is possible. Mechanism V¹⁶ with retention of configuration is possible even when the solvent cannot aid in removing halide ion. Actually, the hydrolysis of *t*-butyl bromide seems to approach a bimolecular mechanism at very low concentrations of water in acetone.⁴ More work in this direction and the investigation of the steric result of reactions of this sort under conditions where the mechanism is definitely second-order would serve to yield information about the relative extent of operation of mechanisms IV and V.

Other First-Order Reactions of Halides.—In other first-order reactions of halides more detailed attention should be given to the role of sol-

(16) Mechanism V has been suggested by Taylor, *J. Chem. Soc.*, 1962 (1937), and is similar to some suggested in other connections.⁵

