butyl bromide to decyl bromide between 0 and 100° as determined by Bayer, are given.

Note: Equation (1) has been found to apply to some types of solutions as accurately as to pure liquids. Further investigations are being made along this line.

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The Mechanism of Solvolytic Reactions of Organic Halides and the Use of Activity Coefficients in the Equation for a Reaction Velocity

BY PAUL D. BARTLETT

Of the theories about the dependence of reaction velocity in solution upon the solvent, the two which have received the most attention in this century are those of van't Hoff[1] and of Brönsted,[2] later refined by other workers and commonly known, respectively, as the "activity-rate theory" and the "transition-state theory." It is consistent with both theories to regard the activated complex as a molecular species in equilibrium with the reactants. The activity-rate theory then demands that the rate of reaction shall be proportional to the fugacity of the activated complex, while the transition-state theory makes the rate proportional to the concentration of this complex.

For reactants forming nearly ideal solutions below their limits of solubility, the activity-rate theory predicts specific reaction rates inversely proportional to their solubilities in a series of solvents. This prediction was shown by von Halban[3] in 1913 to fall hopelessly short of the facts in the formation of p-nitrobenzyltrimethylammonium chloride. Here the introduction of corrections for solubility increased the range of observed velocity constants in eighteen solvents from 9300-fold to over 400,000-fold, when according to the theory it should have rendered the corrected rate independent of solvent.

It has thus long been evident that the activity-rate theory does not possess general validity. Since this is so, the success recently attained by Olson and Halford[4] in reviving this theory and applying it to the calculation of reaction rates in a graded series of methanol–water and ethanol–water mixtures is surprising. The rate of production of hydrogen chloride by t-butyl chloride in these series of solvents varies 100-fold for the

former and 750-fold for the latter series, and these rates have been calculated in terms of the vapor pressures of the reactants within less than the uncertainty of the data employed in the calculation.

Such agreement cannot be entirely accidental, and from the standpoint of the theory of reaction velocity it is important to try to decide between two possibilities. Either (1) the activity-rate theory is fundamentally true for a solvolytic reaction in mixed solvents, while lacking general validity, or (2) it is not fundamentally true, but represents a useful approximation because of special relationships among the quantities appearing in the equations. It is the purpose of this paper to approach this question by inquiring whether the activity-rate theory fits the data of Olson and Halford uniquely, and to draw such conclusions as may be possible about the factors determining the rate of reaction and the mechanism of this particular reaction.

The liberation of hydrogen chloride from t-butyl chloride in these experiments proceeds with the formation of three organic products—t-butyl alcohol, methyl t-butyl ether, and isobutylene. The reaction is an unfortunate one for testing a kinetic formulation on account of the difficulty in making a convincing demonstration of what is going on. The reaction has been variously designated by Farinacci and Hammett[5] as polymolecular, by Olson and Halford[4] as bimolecular, and by Ingold, Hughes,[6] and their co-workers as unimolecular, depending upon the extent to which attention has been focussed upon the role of the solvent in the rate-determining step. In a recent note[7] the British workers have indicated that the difference between their "unimolecular" and Hammett's "polymolecular" is a matter of language

(1) Van't Hoff. *Vorlesungen.* 1. 219 (1901).

(2) Brönsted. *Chem. Rev.* 5. 269 (1938); also *Z. physik. Chem.* 115. 327 (1925).

(3) Von Halban. *ibid.* 84. 129 (1913).

(4) Olson and Halford. THIS JOURNAL. 59. 2644 (1937).

(5) Farinacci and Hammett. *ibid.* 59. 2542 (1937).

(6) Bateman. Hughes and Ingold. *J. Chem. Soc.* 881 (1938).

(7) Bateman. Hughes and Ingold. THIS JOURNAL. 60. 3080 (1938).

rather than point of view. There remains a difference between the original opinion of Olson and Halford and that of the other workers with regard to the point of attack of the solvent molecule on the chloride. Since the kinetics would be the same regardless of the form of the transition state, we shall postpone discussion of this point.

Olson and Halford[4] (p. 2647) say of their fugacity-rate equation: "This equation is in disagreement with the one obtained from transition state theory by Wynne-Jones and Eyring [*J. Chem. Phys.*, **3**, 492(1935)]] unless we assume that the fugacity coefficient of each of the three complexes which we studied remains constant throughout the whole range of experimental conditions. This appears to us highly improbable." Examination of the equations shows that there is actually a less rigid condition than this for the simultaneous perfect applicability of the two equations, owing to the fact that an observed rate is being resolved into two rates governed by different activated complexes. If an approximate equation is used, a fit may under certain conditions be obtained without correctly assigning these contributing rates to their proper transition states. Denoting by k the observed rate constant in terms of mole fractions for the appearance of hydrogen chloride in a solution of *t*-butyl chloride in a mixture of water and alcohol, by f_W, f_A, f_X and f_Y the activity coefficients (expressed as Henry's law constants) of water, alcohol and the transition states involving them, respectively, by f_B the activity coefficient of *t*-butyl chloride, and by M_W and M_A the mole fractions of water and alcohol, and assuming the reaction to occur between one molecule of solvent and one of chloride, the transition-state theory gives the equation

$$k = k_W M_W \frac{f_W f_B}{f_X} + k_A M_A \frac{f_A f_B}{f_Y} \qquad (1)$$

while the activity-rate equation as used by Olson and Halford does not contain the activity coefficients of the transition states

$$k = k'_W M_W f_W f_B + k'_A M_A f_A f_B \qquad (2)$$

The condition that both these equations shall fit the same set of data exactly is found by eliminating k/f_B from Equations (1) and (2)

$$\left(k_W \frac{f_W}{f_X} - k'_W f_W\right) M_W = \left((k'_A f_A - k_A \frac{f_A}{f_Y}\right) M_A$$

This equation may of course be true by both sides being equal to zero, through a constancy of f_X and f_Y, as recognized by Olson and Halford. It may

also be true as a result of other modes of dependence of f_X and f_Y upon solvent composition, in which case the quantities k'_W and k'_A will be composite constants. In addition to the functional relationships among the f's which can be seen to satisfy this equation, there are sure to be some others (possibly including the true one) which yield a close enough approximation to the condition of this equation to make both equations (1) and (2) fit the data.

A qualitative consideration of the probable form of the activated complex suggests a simple formulation which, if Equation (1) is correct, might be expected to yield as good an approximation as that of Equation (2). The solubility behavior of an aliphatic chloride is very similar to that of a hydrocarbon, the halogen atom making no characteristic contribution to its solubility in hydroxylic solvents. Any mechanism by which a water or alcohol molecule might attach itself to a *t*-butyl chloride molecule could only have the effect of making it much more alcoholic or aqueous in character. This suggests the provisional assumption that the activity coefficients of the transition states might be sufficiently like those of their hydroxylic components so that the two would approximately cancel, and we might write

$$k = k''_W M_W f_B + k''_A M_A f_B \qquad (3)$$

Like Equation (2), this can be derived from (1) by introducing a somewhat more flexible condition than the one which originally suggested the approximation. Equation (3) follows from (1) if

$$\left(k_W \frac{f_W}{f_X} - k''_W\right) M_W = \left(k_A - k_A \frac{f_A}{f_Y}\right) M_A$$

Equation (3) has been applied to the data of Olson and Halford for the reaction in water–methanol mixtures and the fit compared to that of Equation (2). To make this comparison, we determine the constants k_W and k_A which will give the lowest mean square percentage deviation of the calculated from the experimental rates by both these types of formulation. We assume that the percentage accuracy of the rate constants of Olson and Halford is about the same for the large and small values. To make the mean square percentage deviation a minimum in each case, Equations (2) and (3) are divided through by k and normal equations constructed from the resulting experimental equations. Table I shows the results of this comparison. The fit of Olson and Halford, not using this method, is also included.

TABLE I

Formulation	$(k'_W, k''_W) \times 10^6$	$(k'_A, k''_A) \times 10^6$	% mean deviation	% mean square deviation
O. and H.	0.393	0.0156	3.80	4.61
Least { Eq. (2)	0.379	0.01573	4.09	4.48
sq. { Eq. (3)	11.54	2.07	2.86	3.78

Figure 1 shows this situation graphically. Equations (2) and (3) can be written in the form

$$\frac{a}{b}k'_W + k_A = \frac{k}{b} \quad (4)$$

and

$$\frac{a'}{b'}k_W + k''_A = \frac{k}{b'} \quad (5)$$

wherein $a = M_W f_W f_B$, etc. Equations (4) and (5) demand, respectively, that k/b plotted against a/b, and k/b' against a'/b', should yield straight lines, and from the graphs it is apparent that this is true in both cases.
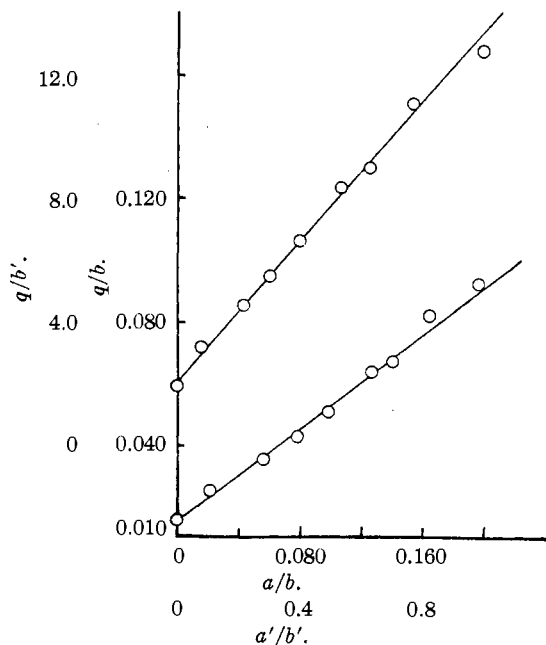

Fig. 1.—Plots of Equation (4) (lower curve) and Equation (5) (upper curve) for the reaction of t-butyl chloride with methanol–water mixtures (data of Olson and Halford).

The recalculation by Olson and Halford of Hughes' kinetic data on the solvolysis of t-butyl chloride in mixtures of water and ethyl alcohol is impressive for the wide range of velocity which it covers, but the agreement between calculated and observed rates is quite inferior to that in the methanol–water mixtures. The signs of the deviations also suggest a distinct curvature to the points, and the plots of Equations (4) and (5) in

Figs. 2 and 3 for the water–ethanol system bear this out. The point at $a/b = 0$, obtained by Olson and Halford by extrapolation of the data of Hughes, is included in this plot but not in the least squares solutions, since it is not an experimental point. One of the points in the plots is so badly out of line that I have carried through the
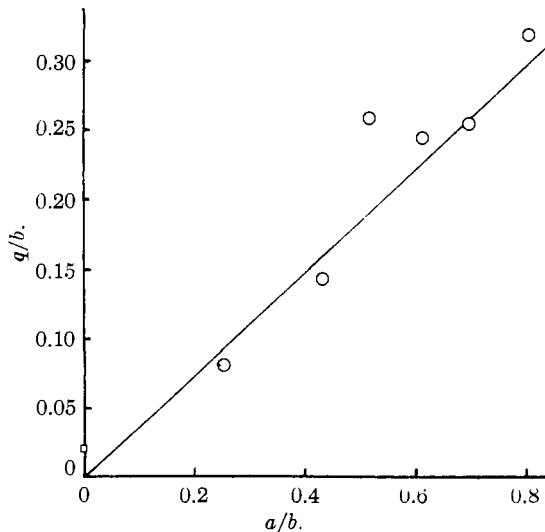

Fig. 2.—Plot of Equation (4) for the reaction of t-butyl chloride with ethanol–water mixtures (data of Hughes).
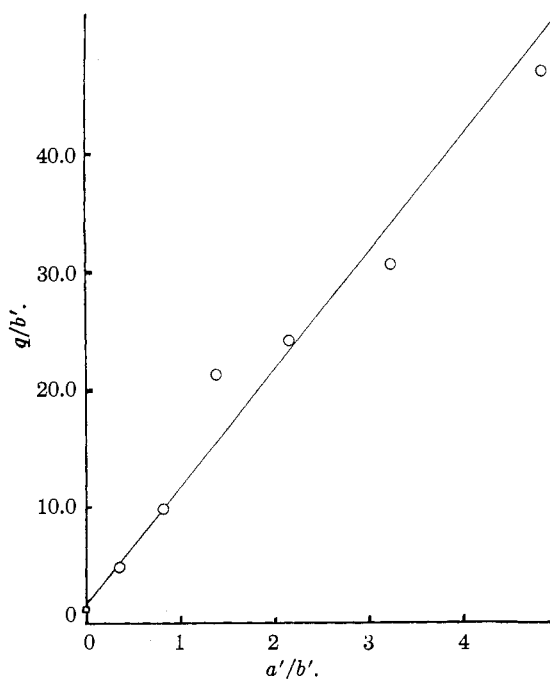

Fig. 3.—Plot of Equation (5) for the reaction of t-butyl chloride with ethanol–water mixtures (data of Hughes).

fits both with and without it. The conclusions in both cases are substantially the same.

In this system the Henry's law constants of water vary 79%, and those of alcohol 151%, over the range of solvent composition employed, compared with 27 and 10% in the methanol case. It is therefore to be expected that the two imperfect approximations to the correct formula which we are considering will both fit the facts less well than in the case of water–methanol mixtures. In fact, if we ignore the extrapolated point for pure ethanol, introduced by Olson and Halford, and consider only the experimental points, the best straight line through the points of Equation (4) (the activity equation) intersects the axis of ordinates at a negative value, making $k'_A = -0.0296 \times 10^{-6}$ if we include the suspicious point with the large deviation, and -0.0259×10^{-6} if we reject this point. A negative rate constant is permissible if k' is a composite quantity, but not if it has the fundamental significance attributed to it by Olson and Halford. In such a case, the closest fit that can be made of Equation (4) which has any physical meaning is to assume $k_A = 0$, and that all reaction is due to the water present. Table II shows a comparison of this best allowable fit with the best fit of Equation (5) to the data, both with and without the doubtful point.

TABLE II

No. of points	Formulation	$(k'_W, k'_W) \times 10^6$	$(k'_A, k'_A) \times 10^6$	% mean deviation	% mean sq. dev.
7	O. and H.	0.393	0.021	18.1	24.4
6	Eq. (2)	0.3688	0	11.4	13.91
6	Eq. (3)	10.05	1.63	9.05	10.15
5	Eq. (2)	0.35547	0	8.40	9.00
5	Eq. (3)	9.317	2.029	4.81	5.66

Here again the formulation employing mole fractions of water and alcohol fits the data fully as well as that employing vapor pressures.

Olson and Halford did not test any mechanism involving the participation of more than a single molecule of solvent in the rate-determining step. Since their data are now found to be fitted by different rate equations, it is of interest to see whether they may also be fitted by an equation which postulates three concurrent rate-determining steps in which the chloride collides with two water molecules, a water and an alcohol molecule, or two alcohol molecules. Such an equation would be written

$$k = k'_{WW} p_W^2 f_B + k'_{WA} p_W p_A f_B + k'_{AA} p_A^2 f_B \quad (6)$$

or

$$k = k''_{WW} M_W^2 f_B + k''_{WA} M_W M_A f_B + k''_{AA} M_A^2 f_B \quad (7)$$

depending upon whether vapor pressures or mole fractions of the solvent components were used in the equations. Equation (6) fits the data of Olson and Halford with a root mean square deviation of 3.85% when the following constants are used

$$k'_{WW} = 0.0155 \times 10^{-6}$$
$$k'_{WA} = 0.00299 \times 10^{-6}$$
$$k'_{AA} = 0.000127 \times 10^{-6}$$

Equation (7) fits the same data with a root mean square deviation of 3.12% using the constants

$$k''_W = 9.28 \times 10^{-6}$$
$$k''_A = 14.98 \times 10^{-6}$$
$$k''_{AA} = 2.02 \times 10^{-6}$$

Thus, not only do these data not serve to establish an activity-rate law, but they also afford no proof of the order of the reaction with respect to solvent molecules.

Although the equations using mole fractions seem in general a better approximation than those using vapor pressures, it should be pointed out that all these formulations fit the data better than the accuracy of the data themselves would lead us to expect.[8] Under these circumstances it would appear that errors in the values of f_B (the quantity known with least certainty) must have considerable regularity, if indeed they are as large as supposed. In any event, no weight is to be given to small differences in the fits of different equations.

Table III compares the calculated rates of hydrolysis of t-butyl chloride in water–dioxane and water–acetone mixtures by equations (2), (3), (6), and (7).
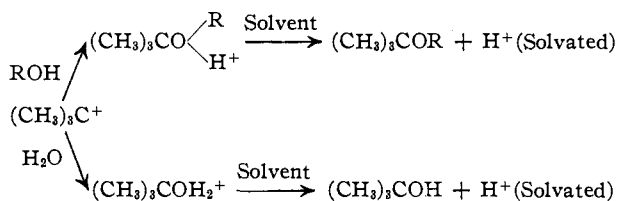
TABLE III

Method of calcn.	Dioxane k	Dioxane % dev.	Acetone k	Acetone % dev.
Observed	644		6.90	
Olson and Halford	745	15.6	11.6	68.1
Equation (2)	720	11.8	11.1	60.8
Equation (3)	927	43.9	9.58	38.8
Equation (6)	581	9.78	8.11	1.73
Equation (7)	404	37.2	2.53	63.3

In a recent paper Bateman, Hughes and Ingold[7] approve the activity formulation of Olson and Halford, but show that the lack of agreement between the predicted and found ratio of alcohol and ether in the products invalidates any idea that

(8) Professor Olson has emphasized in a private communication that the Henry's law constants of t-butyl chloride may be in error by as much as 25% or even more.

the solvolysis could be a one-step bimolecular replacement process. This argument stands also if Equation (3) is adopted. The second step of the ionization mechanism of Bateman, Hughes and Ingold

$$ROH \diagup \overset{\diagup R \quad Solvent}{(CH_3)_3CO\diagdown \underset{H^+}{\qquad} \longrightarrow (CH_3)_3COR + H^+(Solvated)}$$
$$(CH_3)_3C^+$$
$$H_2O \diagdown$$
$$(CH_3)_3COH_2^+ \xrightarrow{Solvent} (CH_3)_3COH + H^+(Solvated)$$

is subject to an activity formulation according to both of the above methods. The data of these authors and of Olson and Halford can be used to test these formulations. The relative amounts of alcohol and ether in the product, so long as the solvent composition remains constant, are supposed to be the result of simple competition between the water and the alcohol in reaction with the *t*-butyl cation. There may be some question of the reversibility of the association step, but it can scarcely be as mobile as the acid–base interchanges among the oxygen-containing compounds, and hence, if, as found by Bateman, Hughes and Ingold, the products resulting from a run are not in equilibrium, the relative forward rates of the association steps between the *t*-butyl ion and the solvent molecules should completely determine the ratio of alcohol and ether in the product. According to the activity-rate theory, the ratio of alcohol to ether in the product should remain proportional to the ratio of vapor pressures of water and alcohol in the solvent. The transition-state theory divides this latter ratio by that of activity coefficients of transition states resembling in appearance the proton alcoholate and etherate in the equation.

In Table IV Column I records the ratio of vapor pressures of water to alcohol in the solvents of Bateman, Hughes and Ingold; II is the ratio of alcohol to ether in the product; and III is the

ratio of moles of water to moles of alcohol in the solvent. It is seen that II/I is far from constant as it ought to be according to the activity-rate theory. II/III is more nearly constant, although this would scarcely be demanded by the transition state theory. It may be that no energy of activation is required in the combination of the butyl cation with a water or alcohol molecule, the ion pair representing a plateau of energy from which a change means a direct descent. In this case the near constancy of the ratio II/III would be expected.

As has been pointed out repeatedly by Ingold, Hughes, and their collaborators, the two-step nature of the solvolytic process is indicated not alone by the seeming independence of rates and product compositions, but also by the inability of the strongly basic ions, hydroxyl and alkoxyl, to influence the rate of reaction of the secondary and tertiary halides. Any mechanism which allowed a direct attack of a solvent molecule upon the central carbon atom of the halide to take part in the rate-controlling step would be attributing something like a basic function to this solvent molecule and would be at a loss to explain the failure of the far more basic ions to participate in this same manner.

Miss Ethel M. Holmes has given valuable help in these calculations by carrying through the least squares application of Equations (6) and (7) and checking all the other results.

Summary

Evidence of long standing is recalled which shows that the rate of a chemical reaction is not generally proportional to the fugacity of the reactants and to that of the transition state, as apparently found by Olson and Halford for the hydrolysis and alcoholysis of *t*-butyl chloride in mixtures of water and alcohol. A recalculation of their kinetic results and those of Hughes shows that these results are no more consistent with the activity-rate theory than with the Brönsted–Polanyi–Eyring theory of the transition state, supplemented with a not unreasonable assumption about the activity coefficients of the transition states. A special case of the assumed relationship is that the transition state involving water has a water-like activity coefficient and that involving alcohol has an alcohol-like activity coefficient.

This leads to an approximate rate equation in

TABLE IV

I	II	III	II/I	II/III
	Ethanol–Water Mixtures			
0.611	4.61	2.15	7.5	2.14
.432	2.07	0.808	4.8	2.56
.255	0.90	.359	3.5	2.50
	Methanol–Water Mixtures			
.192	1.53	0.961	8.0	1.59
.099	0.474	.397	4.8	1.19
.0525	.206	.196	3.9	1.05

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.
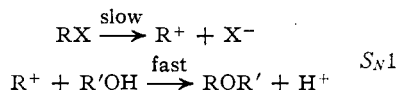

The Solvolysis of t-Butyl Chloride. Solvolytic Reactions and the Walden Inversion
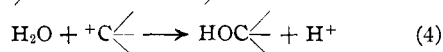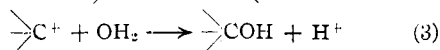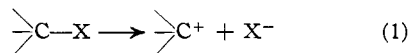
BY SAUL WINSTEIN

A serious problem at the present time is the exact interpretation of first-order solvolytic reactions of organic halides. Ingold and collaborators[1] suppose that these reactions proceed by an ionic mechanism, S_N1

$$RX \xrightarrow{\text{slow}} R^+ + X^-$$
$$R^+ + R'OH \xrightarrow{\text{fast}} ROR' + H^+ \qquad S_N1$$

in which the halide RX ionizes, the cation R^+ reacting rapidly with solvent molecules. Hammett and co-workers[2] believe these solvolytic reactions to be polymolecular, while Olson and Halford[3] and Taylor[4] 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

$$\text{\Large$>$}C-X \longrightarrow \text{\Large$>$}C^+ + X^- \qquad (1)$$

$$\text{\Large$>$}C^+ \longrightarrow {}^+C\text{\Large$<$} \qquad (2)$$

$$\text{\Large$>$}C^+ + OH_2 \longrightarrow \text{\Large$>$}COH + H^+ \qquad (3)$$

$$H_2O + {}^+C\text{\Large$<$} \longrightarrow HOC\text{\Large$<$} + H^+ \qquad (4)$$

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 collaborators[5] 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).