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Some Salt Effects on *t*-Butyl Chloride and *t*-Butyl Bromide Solvolyses in Aqueous Acetone Solutions[1]

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RECEIVED AUGUST 27, 1954

The effects of 0.1 *M* salts, mainly lithium chloride, lithium bromide and lithium perchlorate, on the solvolysis reactions of *t*-butyl bromide and *t*-butyl chloride in aqueous acetone solutions at 24.80° have been studied. The results are expressed by empirical equations. Several alternative interpretations of the effects are discussed.

Much of the published data concerning salt effects on organic halide solvolyses has been obtained in aqueous acetone.[2] We have chosen the same solvent system so that our results might be placed in the pattern of earlier results.

Experimental Part and Calculations

The methods of preparing acetone and the *t*-butyl halides have been described.[3] The lithium salts (N.F. or C.P. grades) were recrystallized from water. Other salts were commercially produced C.P. or Analytical grades and were not further purified. Aqueous acetone solutions of the salts were prepared by weight from water, acetone and standardized, concentrated aqueous salt solutions. For all solutions of the same N_w the same batch of acetone was used so that the ratios of the weight of water to the weight of acetone might differ by less than one part in 1000. The *t*-butyl chloride and the *t*-butyl bromide experiments were performed with the same stock solvents. Because different batches of acetone contained differing amounts of water, the value of N_w for a given set of solvents was calculated from the rate equation for the solvolysis of *t*-butyl bromide of Cropper, Spieth and Olson.[3]

In a previous paper[3] we have described the preparation of reaction mixtures and the method of following the reaction by titration of acid at various times. The same stock solution of alkyl halide was used for a set of runs at constant N_w. The runs in a set were not prepared one after another; instead, sample bulbs for a set were prepared in an alternating manner among the several runs so that should any change in the stock solution, such as evaporation, reaction or moisture absorption, occur during the preparation of the set it would not appear as the effect of a salt. No evidence for change in the stock solution was found. The temperature of the experiments was 24.80 ± 0.02°. Except for some of the slowest *t*-butyl chloride runs conducted in the absence of salts, which were followed for little more than a half-life, runs were followed through two or three half-lives. Initial *t*-butyl halide concentrations, *a*, were in the range 0.03 to 0.055 *M*. Thus, deviations from first-order kinetics arising from an acceleration by the hydrogen halide produced were not noticeable except at the lowest water concentrations. Since the reactions proceeded slowly in solvents of low water concentration, there was time to make a number of analyses early enough in each run so that extrapolation of the first-order rate constant to hydrogen halide free conditions (*i.e.*, zero time) involved making little (*i.e.*, ~1%) or no correction to the earliest measured *k* values.

For the reaction of *t*-butyl bromide in the presence of lithium chloride, substitution of chloride for bromide occurred in addition to the hydrobromic acid forming reactions. In our experiments the lithium chloride concentration always was more than twice the initial *t*-butyl bromide concentration and the chloride substitution relative to hydrolysis and elimination was small so that chloride ion concentration could be considered a constant throughout the course of reaction. Furthermore, the specific rate of solvolysis of *t*-butyl bromide was 65 to 85 times greater than the specific rate of solvolysis of *t*-butyl chloride so the *t*-butyl chloride formed could be considered unreactive during the solvolysis of *t*-butyl bromide. Thus, the unreacted *t*-butyl bromide can be expressed by $[a - (1 + x)(H^+)]$, where *x* is the rate of chloride substitution relative to the rate of acid formation or the ratio of the concentration of *t*-butyl chloride to the concentration of acid. Then, the total first-order specific rate constant, k_T, for reaction of *t*-butyl bromide is given by $k_T = 1/t \times \ln a/[a - (1 + x)(H^+)]$. From time–acid concentration data the value for *x* was obtained by trial and error adjustment of *x* to the value which gave no trend in k_T. Since *x* is always of the order of 0.1, a 10% error in *x* produces a 1% error in k_T. Therefore, although k_T is found with good precision by this method, *x* is not so precisely determined. A check on the kinetically evaluated *x*, within the limits of experimental error, was always obtained from the titration for acid after about 7 half-lives of the *t*-butyl bromide solvolysis when $x \simeq [a - (H^+)]/(H^+)$.

Because the sensitivity of the rates to water concentration required that precision in preparation of solutions be directed toward obtaining a constant water to acetone ratio, salt solutions were not made up to precisely 0.100 molar. At $N_w = 0.504$, Δk, *i.e.* $(k - k^0)$, the increase in rate over the no salt rate was found to be proportional to lithium perchlorate concentration up to 0.4 mole per liter. Therefore, values of Δk for 0.100 *M* salts were calculated from the experimentally measured values on the assumption that Δk is proportional to the salt concentration. These adjustments usually fell within ±3% but in several instances they amounted to nearly 10%.

Results

The effect of one-tenth molar lithium bromide, lithium chloride and lithium perchlorate, on the specific rate of solvolysis of *t*-butyl chloride in aqueous acetone can be expressed empirically, throughout the experimental range of solvent composition, *i.e.*, $N_w = 0.308$ to $N_w = 0.701$, by

$$\log \Delta k = \alpha + \beta N_w \qquad (1)$$

where Δk is the difference $(k - k^0)$, between the specific rate in the presence of one-tenth molar salt and the specific rate in the absence of salt. The slope β and the (hypothetical) intercept, α, are characteristic of the salt. The data obtained from lithium bromide and lithium chloride solutions are sufficiently precise to show that a plot of $\log k$ *vs.* N_w is slightly concave upward so that there is a trend in the deviations from a linear fit. No trend in deviations is found when a straight line is drawn through a plot of $\log \Delta k$ *vs.* N_w. Thus, although *k* (or k/k^0) are not excluded as the fundamental quantities, the simplest empirical formulation is in terms of Δk.

Because the *t*-butyl bromide solvolysis is faster than the *t*-butyl chloride solvolysis, the overlapping region of solvent composition in which Δk could be found by our experimental method for *t*-butyl bromide was smaller, *i.e.*, $N_w = 0.308$ to $N_w =$

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(1) This work was supported by the Office of Naval Research, United States Navy.

(2) For example, see L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940), and references given there; B. L. Archer, R. F. Hudson and J. E. Wardill, *ibid.*, 888 (1953); O. T. Benfy, E. D. Hughes and C. K. Ingold, *ibid.*, 2488 (1952); C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

(3) W. H. Cropper, F. Spieth and A. R. Olson, *ibid.*, **76**, 6248 (1954).

0.504. Furthermore, since the rates for both alkyl halides were determined with about the same precision and since Δk for *t*-butyl bromide is smaller percentagewise (though actually larger) than Δk for *t*-butyl chloride at a given N_w, values of Δk for *t*-butyl bromide are, at each N_w, less precisely established than those for *t*-butyl chloride. Thus, the empirical form, equation 1, which has also been chosen to represent the *t*-butyl bromide results, did not emerge from the *t*-butyl bromide data but was imposed on them.

Figure 1 shows plots of log Δk against N_w for *t*-butyl chloride. Figure 2 shows similar plots for *t*-butyl bromide. In Table I are recorded the values of α, β and the precision with which the equations fit the data. The precision of fit is about the average experimental error in Δk if values of k and k^0 are found to between one-half and one per cent. This corresponds to the internal consistency of k and k^0 rather than the accuracy of the absolute values.

TABLE I

THE EFFECTS OF 0.100 *M* SALTS AT 24.80°

Constants for the equation, log $\Delta k = \alpha + \beta N_w$[a]

	t-Butyl chloride[b] ($N_w = 0.308$ to $N_w = 0.701$)			*t*-Butyl bromide[c] ($N_w = 0.308$ to $N_w = 0.504$)		
0.100 *M* salt	α	β	Av. $\frac{(\Delta k_{obs.} - \Delta k_{cal.})}{\Delta k_{obs.}}$, %	α	β	Av. $\frac{(\Delta k_{obs.} - \Delta k_{cal.})}{\Delta k_{obs.}}$ %
LiCl	−4.551	3.350	± 2.4	−2.693[d]	2.903[d]	±4.2
LiBr	−4.772	4.117	± 3.8	−2.826	3.240	±7.4
$LiClO_4$	−5.156	4.510	±14.7[e]	−2.986	3.517	±4.1

[a] $\Delta k = 0.100(k - k°)/(M \text{ salt})$. The units are reciprocal hours. [b] For *t*-butyl chloride in the absence of salts, the first-order specific rate constant from $N_w = 0.308$ to $N_w = 0.704$ is given with a precision of ±2.5% by the expression, log $k°$ (hr.$^{-1}$) = 6.752 N_w − 5.634. [c] For *t*-butyl bromide in the absence of salts, the first-order specific rate constant from $N_w = 0.170$ to $N_w = 0.606$ is given by the expression, log $k°$ (hr.$^{-1}$) = 5.524 N_w − 3.172. See reference 3. [d] The value of k used for *t*-butyl bromide in the presence of lithium chloride is $k_T/(1 + x)$, where k_T is the total first-order specific rate of reaction of *t*-butyl bromide and x is the ratio of chloride substitution to acid formation. [e] The principal contribution to this poor precision is made by the experimental point at $N_w = 0.504$ (see Fig. 1). That this point is actually too high is substantiated by experiments at 0.2 and 0.4 *M* $LiClO_4$ which yield values of Δk adjusted to 0.100 *M* in agreement with the calculated value.

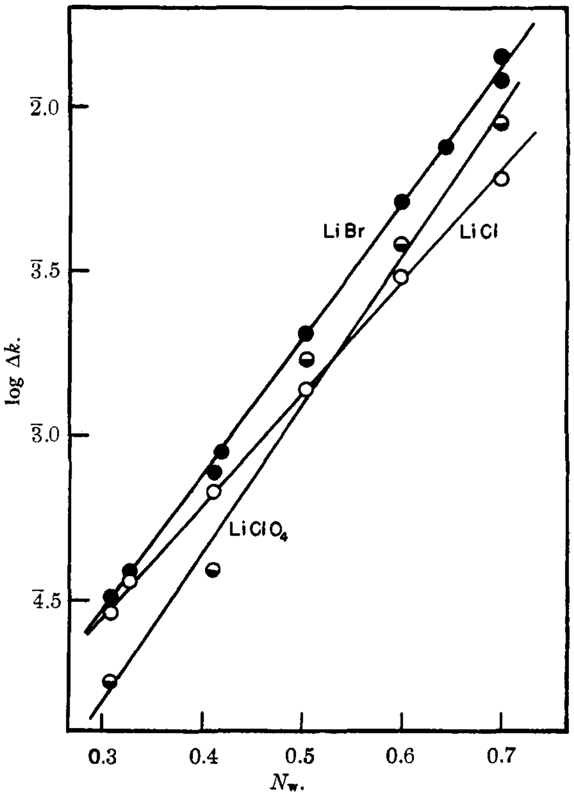

Fig. 1.—log Δk *vs.* N_w for *t*-butyl chloride at 24.8°.

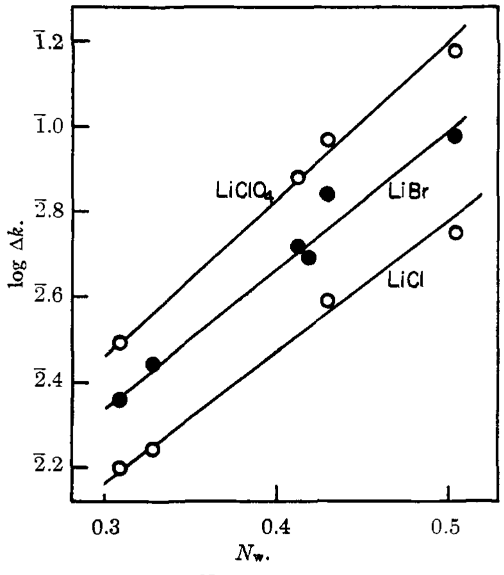

Fig. 2.—log Δk *vs.* N_w for *t*-butyl bromide at 24.8°. The ordinate is labeled for the LiCl curve. This scale is to be shifted 0.20 unit upward for the LiBr curve and 0.40 unit upward for the $LiClO_4$ curve.

Among the experiments summarized in the six plots of Figs. 1 and 2, those on the solvolysis of *t*-butyl bromide in the presence of lithium chloride were unique in that they did not show first-order kinetics in terms of $[a - (H^+)]$, the quantity directly determined. Assumption of an additional reaction, *i.e.*, substitution of chloride for bromide, made possible the calculation of a total first-order specific rate of reaction of *t*-butyl bromide, k_T, and the ratio of chloride substitution to acid formation, x. The results of these experiments are summarized in Table II. It is apparent that there are two increments in the specific rate constant: (1) Δk_T, the total increase in specific rate of reaction of *t*-butyl bromide and (2) Δk, the increase in the specific rate of acid formation. If chloride substitution occurs in a rate-determining step, the salt effect on the rate identified by k^0 is correctly given by Δk. On the other hand, if the products, isobutene, *t*-butyl alcohol and *t*-butyl chloride, are formed in rapid reactions of an intermediate whose formation is rate determining, the salt effect on the rate of formation of the intermediate is correctly given by Δk_T and further, if the intermediate in the solvolysis of *t*-butyl chloride should be the same species, the apparent specific rate of solvolysis of that compound in the presence of lithium chloride is low because of the regeneration of *t*-butyl chloride by reaction of the intermediate with chloride ion.

TABLE II

SOLVOLYSIS OF *t*-BUTYL BROMIDE IN AQUEOUS ACETONE CONTAINING LITHIUM CHLORIDE AT 24.80°

N_w	k^0 (hr.$^{-1}$)^a	LiCl, M	k_T (hr.$^{-1}$)^b	x^c	Δk_T (hr.$^{-1}$)^d	Δk (hr.$^{-1}$)^e	f_{Cl^-}^{f}
0.308	0.0331	0.1028	0.0576	0.165	0.0240	0.0158	0.14_0
.328	.0431	.0975	.0694	.15	.0269	.0176	$.13_3$
.430	.160	.1070	.228	.13	.0639	.0393	$.11_0$
.504	.412	.1062	.513	.09	.095	.056	$.07_9$

^{a} $k°$ is the specific rate of solvolysis in the absence of salt. ^{b} k_T is the total first-order specific rate of reaction of *t*-butyl bromide in the presence of lithium chloride. ^{c} x is the ratio of chloride substitution to acid formation. ^{d} $\Delta k_T = 0.100 (k_T - k°)/(M \text{ LiCl})$. ^{e} $\Delta k = 0.100 (k - k°)/(M \text{ LiCl})$, where $k = k_T/(1 + x)$. ^{f} f_{Cl^-} is the fraction of *t*-butyl bromide which is substituted by chloride corrected to 0.100 M LiCl, *i.e.*, $0.100 x k_T/(M \text{ LiCl})(1 + x)(k° + \Delta k_T)$.

On the basis of these alternative mechanisms, the effects of lithium chloride on *t*-butyl chloride and *t*-butyl bromide solvolyses are made comparable either by adding to Δk for *t*-butyl chloride the rate of regeneration of *t*-butyl chloride or by subtracting from Δk_T for *t*-butyl bromide the rate of formation of *t*-butyl chloride.[4] We have chosen the latter method. In Fig. 2 is plotted log Δk *vs.* N_w for *t*-butyl bromide in the presence of lithium chloride.

If bromide substitutes for chloride during the solvolysis of *t*-butyl chloride in the presence of lithium bromide or if bromide reacts with an intermediate to regenerate *t*-butyl bromide during the solvolysis of *t*-butyl bromide in the presence of lithium bromide, an analogous correction ought to be applied to the lithium bromide effect. However, *t*-butyl bromide solvolyzes so much more rapidly than *t*-butyl chloride that, if it is formed, its concentration cannot build up sufficiently to be detected in our experiments on the solvolysis of *t*-butyl chloride. Therefore, we have used the experimental values of Δk in the presence of lithium bromide for the plots in Figs. 1 and 2.

The empirical relationship brings to light certain generalizations about these systems. Although the magnitude of the salt effect, Δk, always increases with increasing water concentration, the percentage salt effect, *i.e.*, 100 $\Delta k/k^0$, always decreases with increasing water concentration because k^0 is more strongly dependent on N_w than is Δk. (See notes *b* and *c* below Table I.) This qualitative effect of salts has been shown by Bateman, *et al.*,[2] and Brown and Hudson[2] for several other solvolytic reactions in aqueous acetone.

The percentage salt effect falls off with N_w more rapidly for *t*-butyl chloride than for *t*-butyl bromide. Throughout the region of solvent composition which we have investigated the percentage salt effects at a given N_w are less for *t*-butyl bromide than for *t*-butyl chloride.[5] Nevertheless, the trend suggests that under other environmental conditions the order might be reversed.

The fractional rate of increase in Δk with N_w, *i.e.*, d ln $\Delta k/dN_w = 2.303\beta$, is greater with a given salt for *t*-butyl chloride than for *t*-butyl bromide. The ratio of β^{BuBr} to β^{BuCl} is 0.79 with lithium bromide, 0.79 with lithium perchlorate, and 0.87 with lithium chloride. The uncertainties in the β^{BuBr} values make it possible that these three ratios are the same. Indeed, they fall around the ratio of the *b*-values ($\log k^0 = a + bN_w$) for the two alkyl halides which is 0.82.

The order according to magnitude of effect in which the salts fall does not remain constant with N_w. The intercepts, α, for both alkyl halides indicate that as N_w approaches zero the largest effect is produced with lithium chloride and the smallest effect is produced with lithium perchlorate. The sums, $\alpha + \beta$, for both alkyl halides indicate that as N_w approaches unity the order of salts is inverted. Inversion of order actually occurs in the experimental region for *t*-butyl chloride with the lithium perchlorate–lithium chloride pair at $N_w \simeq 0.52$ and for *t*-butyl bromide with the lithium bromide–lithium chloride pair at $N_w \simeq 0.40$ and with the lithium perchlorate–lithium chloride pair at $N_w = 0.46$. (The intersections of these latter effects are not illustrated by Fig. 2 because the ordinate scale has been shifted for each curve to eliminate confusion of points.) For both alkyl halides, as N_w increases inversion occurs, first with the lithium bromide–lithium chloride pair, next with the lithium chloride–lithium perchlorate pair, and finally with the lithium bromide–lithium perchlorate pair.

Olson and Konecny[6] have found the thermodynamic dissociation constant for lithium bromide in aqueous acetone to increase from about 0.01 to 0.1 in the region from $N_w = 0.3$ to $N_w = 0.5$. We can expect lithium chloride to be weaker. We know that in pure acetone lithium perchlorate is about ten times stronger than lithium bromide. The differences in effects of salts at low N_w cannot arise primarily from differences in ionic concentration for then lithium perchlorate would have the largest effect whereas it actually has the smallest. Possibly it is significant that the ratio of β^{BuCl}_{LiCl} to β^{BuCl}_{LiBr} is 0.81, whereas the ratio of *b* for *t*-butyl bromide to *b* for *t*-butyl chloride is 0.82.[7] If such an inverse correlation of β-values with *b*-values is valid, we can predict the *b*-value for *t*-butyl perchlorate, *i.e.*, $\beta^{BuCl}_{LiCl} b_{BuCl}/\beta^{BuCl}_{LiClO_4} = \beta^{BuBr}_{LiBr} b_{BuBr}/\beta^{BuBr}_{LiClO_4} = 5.0$.

Evidence that the salt effect is primarily a negative ion effect exists in the work of Lucas and Hammett[8] who investigated the influence of some elec-

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[4] Other mechanistic pictures such as the formation of quite different intermediates from the two alkyl halides or the association of chloride ion or lithium chloride with *t*-butyl chloride to form an unreactive species also require corrections to be applied to the observed values of Δk, but the magnitude of these corrections is not necessarily related to the amount of substitution of chloride for bromide in *t*-butyl bromide.

[5] Our equations predict the crossing of the percentage salt effects for the two alkyl halides with lithium chloride at $N_w = 0.772$ where the Δk values are too small to be measured with the accuracy necessary for testing. The calculated crossings of percentage salt effects with lithium bromide and lithium perchlorate fall at $N_w = 1.68$ and 1.28, respectively.

[6] A. R. Olson and J. Konecny, THIS JOURNAL, **75**, 5801 (1953).

[7] It is redundant to state that the ratio of β^{BuBr}_{LiCl} to β^{BuBr}_{LiBr} is near to this same value since the relationship between the β-values for *t*-butyl chloride and *t*-butyl bromide has already been mentioned, *i.e.*, $\beta^{BuBr}_{LiCl}/\beta^{BuCl}_{LiCl} \simeq \beta^{BuBr}_{LiBr}/\beta^{BuCl}_{LiBr} \simeq \beta^{BuBr}_{LiClO_4}/\beta^{BuCl}_{LiClO_4} \simeq 0.82$. Actually, for *t*-butyl bromide this ratio, $\beta^{BuBr}_{LiCl}/\beta^{BuBr}_{LiBr}$ is high, *i.e.*, 0.90, which we would expect if β^{BuBr}_{LiCl} is slightly high and β^{BuBr}_{LiBr} slightly low, a circumstance indicated by the previously mentioned relationship of β-values.

[8] G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1928 (1942).

trolytes on the solvolysis of *t*-butyl nitrate at 25.0° in 75 weight % dioxane in water. They found that sodium perchlorate and perchloric acid have about the same effect and lithium nitrate and potassium nitrate have about the same effect, which is appreciably less than the perchlorate effect. (The effect of sodium chloride is smaller than that of the nitrates. Sodium hydroxide causes a slight depression of the rate.)

Obviously, the differences between the effects of the several lithium salts reported in this paper arise from the negative ions. The results of some experiments with sodium bromide and tetramethylammonium bromide are consistent with a negative ion hypothesis, but, because tetramethylammonium bromide is so insoluble at the lowest water concentrations, experiments with this salt are not especially significant. For *t*-butyl chloride with sodium bromide we found at N_w equal to 0.328, 0.419 and 0.504 values of Δk equal to 0.000366, 0.00078 and 0.00204, respectively, to be compared with calculated Δk values from lithium bromide experiments equal to 0.000379, 0.00090 and 0.00201, respectively. On the other hand, at low water concentrations the acids produced during the solvolysis in the absence of added salts have smaller effects on the rates than the corresponding salts. It would be difficult to test the hypothesis that the salt effect depends only on the negative ion since secondary interference of the positive ion through ionic association is expected at low water concentration where Δk values can be found most accurately.

Experiments with iodides were complicated by iodine formation and were not pursued because a satisfactory method of excluding or expelling oxygen while maintaining a constant N_w was not developed. However, two experiments on the effect of sodium iodide on the *t*-butyl bromide solvolysis indicate that $\beta_{\text{NaI}}^{\text{BuBr}}$ is greater than $\beta_{\text{LiBr}}^{\text{BuBr}}$ which suggests that b for *t*-butyl iodide is less than b for *t*-butyl bromide.

Bateman, Hughes and Ingold[9] have measured the effects of lithium bromide and lithium chloride on the solvolysis of *t*-butyl bromide in 90% aqueous acetone, *i.e.*, $N_w = 0.312$, at 50.0°. The heat of activation found by these authors for the reaction in the absence of salt, 20.54 kcal., corresponds to the average heat of activation found by Cropper, Spieth and Olson[3] indicating that their results ought to be comparable with the results found in this laboratory. Referring their 50.0° specific rate constant to 24.8° we find their solvent to correspond to $N_w = 0.332$, a reasonable discrepancy in water concentration since different batches of acetone contain different quantities of water. From their rate data at 50.0° we find $\Delta k/k^0$ to be 0.47 with lithium bromide and 0.43 with lithium chloride to be compared with our calculated values of $\Delta k/k^0$ at 24.80°, which are 0.39 and 0.41, respectively. This result does not necessarily imply that the order of the salts has been reversed with a change in temperature because N_w is very near to the inversion point for this pair of salts where small experimental errors can reverse their order. Clearly, the temperature coefficients of $\Delta k/k^0$ are small, and their precise measurement would not be justified at this time because of our lack of information about other temperature dependent quantities such as the strength of the electrolytes. Lucas and Hammett[8] found in aqueous dioxane for *t*-butyl nitrate a slightly negative temperature coefficient of the sodium perchlorate salt effect.

The rate data of Bateman, Hughes and Ingold indicate that the fraction of *t*-butyl chloride formed at 50.0° in the *t*-butyl bromide solvolysis is about 0.07 whereas we find this fraction at 25.0° to be about 0.13 (Table II) in the same solvent. This large decrease percentagewise in *t*-butyl chloride formation corresponds to a heat of activation for chloride substitution which is about 5 kcal. less than the weighted average of the heats of activation of the acid forming reactions.

The simple method used for calculating from rate data the fraction of *t*-butyl chloride formed is less reliable when applied to the work of Bateman, Hughes and Ingold at 50.0°, for two reasons: (1) in the 50.0° work a larger initial concentration of *t*-butyl bromide was used than in the 24.8° work; and (2) at 50.0° the specific rate of solvolysis of *t*-butyl chloride is somewhat nearer to that of *t*-butyl bromide than at 24.8°. The method certainly fits the 50.0° data less satisfactorily than the 24.8° data. We conclude that the heat of activation for chloride substitution is probably less than the weighted average of the heats of activation of the acid forming reactions but that the value of this difference remains uncertain.

Discussion

The observation that lithium chloride has a smaller effect than lithium bromide on the solvolysis of *t*-butyl chloride cannot at our present state of knowledge be used as evidence that (1) the reaction is slowed in the presence of lithium chloride because of regeneration of *t*-butyl chloride by reaction of chloride ion with an intermediate or (2) the reaction is accelerated in the presence of lithium bromide because of substitution of bromide followed by rapid solvolysis of *t*-butyl bromide. The assumption in this type of reasoning is that the two salts have a common effect on which is superimposed an additional effect of one salt or the other. That this assumption is unjustified is illustrated by our results on *t*-butyl chloride at $N_w = 0.308$ (approximately 90 volume per cent. acetone) where the rate is increased by 58, 102 and 106% with lithium perchlorate, lithium chloride and lithium bromide, respectively. Variations in the effectiveness of salts have been found for similar reactions, for example, in the work of Lucas and Hammett[8] and in the work of Coburn, Grunwald and Marshall.[10] The treatment of salt effects on the solvolysis of *t*-butyl bromide in aqueous acetone proposed by Bateman, *et al.*,[2,9] is inconsistent with our findings in that the magnitude of the effect depends on the salt and, in the region of low water concentration where the salts become somewhat weak, the weakest salt has the greatest effect. The prediction of Bateman, *et al.*,[2] that *t*-butyl chloride would exhibit percentage salt effects of

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(9) L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 960 (1940).

(10) W. C. Coburn, Jr., E. Grunwald and H. P. Marshall, THIS JOURNAL, **75**, 5735 (1953).

about the same magnitude as or slightly smaller than those of *t*-butyl bromide is contrary to experiment. Briefly, the electrostatic interpretation of positive salt effects on the solvolysis of alkyl halides suggested by these authors is that ionic atmospheres about the dipoles stabilize the transition state dipole relative to the ground state dipole. Their quantitative treatment is based on a transition state model which is "... two point charges ... separated by a fixed distance ..., and surrounded by a dilute atmosphere of point-ions of charges ..." in a continuous dielectric medium. The qualitative picture cannot be abandoned merely because this model fails.

Another interpretation of these salt effects is that the salts, principally the negative ions, introduce new reaction paths without altering appreciably the paths which occur in the absence of salts. This is the obvious implication of an empirical expression of the effects in terms of Δk. In a previous paper[3] we have shown that for each alkyl halide the logarithm of the specific rate of solvolysis in the absence of salts is linear with N_w over a considerable region of N_w. We have also shown that this linearity, though precisely established, actually arises in the neighborhood of an inflection point in a complex curve. Thus, the solvolytic reactions depend on solvent composition in a complicated manner. We would not necessarily expect other reactions of these alkyl halides to show similar dependences on solvent composition. However, if the very large increase in rate of the solvolytic reactions with water concentration is caused mainly by the interaction of water with the halogen of the carbon–halogen bond, other reactions in which the carbon–halogen bond is broken could show comparable dependences on solvent composition. Thus, the linearity of log Δk with N_w through the experimental region of N_w is consistent with the postulate that Δk is the rate of some additional reaction or reactions of the alkyl halide.

The array of constants given in Table I abounds with possibilities for correlations some of which we have mentioned in the previous section. Some of these correlations may be significant. For example, it is consistent with a mechanistic interpretation that β^{BuBr} is always less than β^{BuCl} since b_{BuBr} is less than b_{BuCl}. We certainly do not, *a priori*, expect these constants to be related as ratios although, in fact, they appear to be.

If the negative ions behave as bases in the reactions in which they participate, chloride ion would be more effective than bromide ion. We could assume that at low water concentrations, chloride ion is sufficiently better than bromide ion as an effective participant in the reaction to compensate for the association of lithium chloride which is greater than the association of lithium bromide. As the water concentration increases, equilibria between the anion bases and the acid, water, favors the reduction of effectiveness of chloride ion, *i.e.*, the stronger base, relative to that of bromide ion. Similarly, interaction of water with the halogens of *t*-butyl halides is greater for *t*-butyl chloride than for *t*-butyl bromide. Again, we do not, *a priori*, expect these two kinds of solvent interactions as contained in β- and b-values to be related quantitatively by an inverse proportion, although the data show such a relationship.

In order to make reasonable the proposal that Δk represents the rate of one or more reactions it is necessary to outline a reasonable mechanism. A correlation with the basicity of the anions immediately suggests catalysis of the elimination reaction. We have not analyzed for products in aqueous acetone, but analyses performed by Lucas and Hammett[8] for the products of solvolysis of *t*-butyl nitrate in aqueous dioxane showed that the increase in fraction of olefin formed in the presence of sodium perchlorate was insignificant compared to the effect of that salt on the rate of solvolysis. At least for this system it would be necessary to postulate the introduction of a new path for *t*-butyl alcohol formation also.

The mechanism of substitution of an anion followed by rapid solvolysis of the substitution product seems to be excluded as a general explanation because it cannot account for the effect of lithium chloride on *t*-butyl chloride solvolysis or the effects of lithium chloride and lithium bromide on *t*-butyl bromide solvolysis. However, Doering and Zeiss[11] have proposed that the solvolytic reaction itself involves the formation of an energetic reaction intermediate *via* the ordinary inversion path, *i.e.*, backside approach of the solvent molecule, and that the intermediate can react rapidly by several paths to form the solvolysis products. Such a model implies that anions could also react with the alkyl halide to form energetic intermediates. Thus, catalysis of *t*-butyl chloride solvolysis by chloride ion, for example, might be expected.

A third and quite different picture is that water molecules oriented about the negative ions behave as a new reaction species. This type of mechanistic interpretation tends to merge with thermodynamic interpretations of salt effects and is similar to the proposal of Lucas and Hammett[8] that the effect of salts on hydrolysis rates arises because of their effect on the activity of water. Both of these explanations are inadequate in that they do not account for a reversal of order of salts according to magnitude of effect for two different solvolytic reactions. Hydration theories as well as electrostatic theories of salt effects on solvolysis rates appear to fail in the same way that these theories fail when applied to the equilibrium problem of salting out effects on non-electrolytes.[12] The parallelism of these two kinds of effects is striking. It is clear that salt effects such as those described in this paper cannot be used as a criterion of reaction mechanism as suggested by Bateman, *et al.*[2] Present theory, which cannot predict all of the qualitative results, cannot be used to distinguish a particular kind of transition state dipole. Although the rate phenomena depend on the effect of salts on the transition states relative to the ground states we might expect to identify a relationship between the effects of salts on activities and solvolytic rates by direct experiment.

(11) W. von E. Doering and H. H. Zeiss. THIS JOURNAL. **75**, 4733 (1953).

(12) For a recent discussion of this problem see F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

One such experimental approach would be a determination of the effects of salts on the partial pressures of the *t*-butyl halides at various solvent compositions and temperatures. This method was used at zero salt concentration in aqueous methanol by Olson, Ruebsamen and Clifford.[13]

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(13) A. R. Olson, W. C. Ruebsamen and W. E. Clifford, THIS JOURNAL, **76**, 5255 (1954).

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The Effect of Solvent on the Visible Absorption Spectrum of Biacetyl

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RECEIVED OCTOBER 5, 1954

The visible absorption spectrum of biacetyl has been measured in 25 solvents. The intensity of the long wave length peak is diminished when biacetyl is dissolved in solvents that contain oxygen, nitrogen and fluorine atoms. There is no correlation between this diminution and the following macroscopic solvent parameters: dipole moment, molar refraction, refractive index, dielectric constant, or hydrogen-bonding tendency. This effect is ascribed to intermolecular dispersion forces. The visible band is the result of two electronic transitions. The intensity of one of these transitions is strongly dependent on solvent.

The effect of solvent on absorption spectra has been the subject of many investigations.[2] Although most of these have been concerned with shifts in band position, a number have treated variations in band shape[3] and intensity.[4] The possibility that solvent effects may be used to characterize electronic transitions[5,3a,3b] has prompted this study, which is preliminary to an extensive investigation of the luminescence and photochemistry of biacetyl solutions.

In the visible absorption spectrum of a hexane solution of biacetyl there are four distinct maxima[6] which disappear when the solvent is changed to an alcohol.[7] The biacetyl vapor spectrum has been interpreted as a sharp singlet-triplet (T ← S) band superimposed on a broad singlet-singlet (S′ ← S) band.[8] In this study, the absorption spectra of biacetyl in a variety of solutions have been determined with the purpose of explaining the loss of structure in alcohol solutions and attempting a determination of the number of electronic transitions involved.

Experimental

Purification of Materials.—Biacetyl, a Lucidol product, was dried for several weeks over anhydrous calcium sulfate, vacuum distilled, and the middle fraction stored under vacuum, in the dark at $-78°$. The refractive index, n^{19}_{D} 1.3940 (lit. $n^{18.5}_{\mathrm{D}}$ 1.3933), and the absorption spectrum were unchanged upon redistillation of the biacetyl. Biacetyl samples were withdrawn by freezing out shortly before use. The solutions were prepared and the spectra determined as quickly as possible thereafter. With the exception of aqueous and alcoholic solutions the extinction coefficients were unchanged with time.

All solvents were dried and distilled in an all-glass still. Small amounts of water had no effect on the absorption spectrum.

Spectrophotometric Measurements.—The absorption spectra were determined with a Beckman Model B spectrophotometer. The wave length scale was calibrated against a Corning 5120 filter (didymium glass). A correction of 4 mμ was added to all scale readings. The absorbance was determined every 10 mμ in the region 320–400 mμ, every 2 mμ from 400–415 mμ and every mμ from 415–450 mμ. Atmospheric oxygen was without effect on the spectra and no attempt was made to exclude it. A temperature variation of 10° had a negligible effect on the spectra and extinction coefficients of all solutions except biacetyl in water. When the biacetyl concentration exceeded 0.085 *M*, a 1-mm. cell was used, otherwise a 10-mm. cell was used. The spectrum of liquid biacetyl was determined by preparing a thin film of the pure liquid between two glass plates.

Molar extinction coefficients were calculated from the equation $\log I_0/I = \epsilon lc$, with l in cm. and c in moles/l.

Results

The biacetyl solutions may be divided into three classes, 1, 2 and 3, according to their general appearance. A representative spectrum from each of these classes is reproduced in Fig. 1, and the solvents are grouped according to class in Table I. In Fig. 2 the biacetyl vapor spectrum (redrawn[8]) is compared with the heptane and benzene solution spectra. Only in the heptane solution are the three distinct maxima discernible, the shapes of the remaining Class 1 solution spectra resemble that of biacetyl in benzene, although there are small differences in the maximum extinction coefficients, $\epsilon_{\max}$. The positions of the maxima, $\nu_{\max}$, and the $\epsilon_{\max}$ of the Class 1 solutions are tabulated in Table I. It will be noted that the long wave length peak (maximum II) is enhanced more than the short wave length peak (maximum I) when biacetyl is dissolved in Class 1 solvents (Fig. 2).

In the spectra of Class 2 solutions, maximum II is no longer present and only a broad shoulder remains, while in Class 3 solutions even this shoulder disappears. The relevant data for these two classes are listed in Table I. The variation in appearance of the Class 2 spectra can be seen in Fig. 1 (ether) and Fig. 3. The spectra of biacetyl in chloroform, fluorobenzene and anisole are nearly identical in shape.

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(1) Supported by a Frederick Cottrell grant from The Research Corporation.

(2) For references see L. N. Ferguson, *Chem. Revs.*, **43**, 394 (1948).

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(6) L. Light, *Z. physik. Chem.*, **122**, 419 (1926).

(7) R. Holman, W. Lundberg and G. Burr, THIS JOURNAL, **67**, 1669 (1945).

(8) G. N. Lewis and M. Kasha, *ibid.*, **67**, 994 (1945).