

Kinetics of the Hydrolysis of Alkyl Halides in Perchloric Acid-Water Mixtures

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The first-order rate constants of the hydrolysis of ethyl bromide, butyl chloride, butyl bromide, butyl iodide, isopropyl chloride, isopropyl bromide, isopropyl iodide, t-butyl chloride, and benzyl chloride in perchloric acid-water mixtures containing from zero to about 45 % perchloric acid, in some cases up to about 66 % perchloric acid, were measured and also the rate constants of the hydrolysis of butyl, isopropyl and t-butyl chlorides in sodium perchlorate-water mixtures containing from zero to about 50 % or 60 % sodium perchlorate. The activity coefficients of butyl, isopropyl, and benzyl chlorides in perchloric acid-water mixtures were evaluated by the distribution method.

A linear relationship was found between $\log k$ and the concentration of perchloric acid or sodium perchlorate over the entire range of mixtures studied for all substrates except t-butyl chloride, isopropyl halides, and benzyl chloride in mixtures containing high concentrations of perchloric acid. The exceptional results were interpreted in terms of acid catalysis; the logarithm of the first-order rate constant of the acid-catalysed reaction obtained by extrapolation was linearly related to the acidity function H_0 . The activation enthalpies and entropies of the hydrolysis of the alkyl halides except of ethyl bromide and t-butyl chloride in water were calculated from rate constants obtained over a wide range of temperature.

The effects of electrolytes on the rates of hydrolysis of alkyl halides have been studied by several authors,¹⁻⁴ but in only one case¹ has the salt effect been previously studied in water solutions. The effects of different electrolytes present in high concentration on the hydrolysis of t-butyl chloride in water was explained by Clarke, Williams and Taft¹ semi-quantitatively by dipole-ion interactions. Some electrolytes, however, exerted exceptional effects, and additional factors were assumed to be responsible for the observed differences. A special interaction of hydronium and ammonium ions with t-butyl chloride was invoked to explain the unexpected salting-in effect of these ions compared with other cations. From kinetic data for the hydrolysis reaction in pure water and deuterium oxide it was concluded¹ that water

probably is hydrogen-bonded to the chlorine of *t*-butyl chloride in the transition state.

The solvolyses of various fluorides have been demonstrated⁵⁻⁸ to be subject to acid catalysis. Acid catalysis of the reactions of other alkyl halides has been observed mainly in organic solvents; *e.g.* in the elimination reaction of *t*-butyl chloride in nitromethane⁹ and aniline.¹⁰ Also phenols and alcohols catalyse the reaction in nitromethane.¹¹ Swain and Spalding⁵ studied the hydrolysis of benzyl chloride in a 90 % water-acetone mixture and found that the rate decreases continuously when the concentration of sodium perchlorate is increased from zero to 6 M, whereas the rate is a minimum in the presence of perchloric acid in about 4 M concentration. The hydrolysis of methyl bromide is continuously retarded when the concentration of perchloric acid increases in the same concentration range. The authors⁵ concluded that an acid-catalysed reaction may be the reason for the increase in the rate of hydrolysis of benzyl chloride in concentrated perchloric acid solutions.

The present study was undertaken to obtain more information about the possible acid catalysis of the hydrolysis of alkyl halides in concentrated mineral acids.

EXPERIMENTAL

Materials. The alkyl halides (Fluka AG, puriss.) were purified by fractional distillation and the impurities checked by gas chromatography. Perchloric acid (E. Merck AG, 70 % guaranteed reagent) was purified by fractional distillation at a pressure of about 15 mm Hg. The concentration of the acid was determined by titration with a standard base solution. Sodium perchlorate and silver nitrate (E. Merck AG, guaranteed reagents) were used as received. The water content of sodium perchlorate was calculated from the loss of weight on drying a sample. Cyclohexane (E. Merck AG, guaranteed reagent) was purified by fractional distillation to remove small amounts of impurities revealed by gas chromatography.

Rate measurements. Solutions of the alkyl halides were prepared by introducing a small amount of alkyl halide from a micro syringe into a known volume of water and shaking the mixture vigorously for a few minutes. The solutions were initially about 0.0006 M in the butyl halides, 0.002 M in the propyl halides and benzyl chloride, and about 0.05 M in ethyl bromide. The reactions took place in vapour-free reaction vessels made from 50-ml all-glass syringes. A small volume of gas evolved from only a few of the reaction mixtures. The amount of alkyl halides in the gas phase was estimated and found in all cases to be small enough to affect the rate in solution less than the experimental errors from other sources. The temperature of the electrically controlled thermostats was kept constant to about $\pm 0.02^\circ\text{C}$.

Samples from the reaction mixtures were mixed with cold water or dioxane to arrest the reaction. An addition of dioxane increased the potential jump at the equivalence point and increased also the accuracy of the titration especially at the low substrate concentrations used in most of the experiments. Each sample was weighed and titrated potentiometrically with aqueous silver nitrate solution using a silver electrode and a mercurous sulphate reference electrode. A 0.001 M to 0.05 silver nitrate solution was used depending on the initial concentration of alkyl halide in the experiment. The final values were taken after about 10 half-lives of the reaction.

The reaction mixture in the hydrolysis of butyl iodide and isopropyl iodide in solutions containing perchloric acid became light yellow towards the end of the reaction, the iodide ion being partly oxidised to iodine. Before the samples were titrated, an excess of aqueous sodium sulphite solution was added to convert all the iodine to iodide. In acid solutions sodium sulphite did not interfere with the titration of iodide ions with silver nitrate.

In mixtures containing more than about 50 % perchloric acid the reaction mixture became slightly coloured when solutions of the slowly reacting primary alkyl halides were kept in the thermostat for several days. The hydrolysis of *t*-butyl chloride was too

Table 1. Rate constants, k , activation enthalpies, ΔH^* , and activation entropies, ΔS^* , of the hydrolysis of alkyl halides in water.

	$10^5 k, \text{sec}^{-1}$					ΔH^* kcal at 51°C	ΔS^* e.u. at 51°C
	0.50°	25.00°	40.00°	60.00°	80.00°		
<i>t</i> -BuCl	82.9						
<i>i</i> -PrCl		0.0203	0.161	1.92	15.81	24.70	- 6.22
<i>i</i> -PrBr		0.377	3.05	32.9	251	24.15	- 4.03
<i>i</i> -PrI		0.259	2.37	29.4	228	25.17	+ 0.50
PhCH ₂ Cl		1.246	7.27	55.5	289	20.00	-13.45
<i>n</i> -BuCl			0.0136	0.126	1.14	23.83*	-14.10*
<i>n</i> -BuBr		0.0299	0.232	1.99	14.74	23.05	-10.94
<i>n</i> -BuI			0.772	8.28	68.0	23.93*	- 5.30*
<i>n</i> -PrBr					13.9		
EtBr				3.25	26.4		

* At 60°C.

Table 2. Values of rate constants, k , activation enthalpies, ΔH^* , and entropies, ΔS^* , obtained by different authors for the hydrolysis of alkyl halides in water.

<i>t</i> -BuCl	ΔH^* , kcal ΔS^* , e.u. $10^5 k, \text{sec}^{-1}$	t° 12.5° 12.5° 1°	This work	Ref. 12 23.60 9.7 84.2	Ref. 1 24.75 95.0	Ref. 13 23.22 12.2 85.0	Ref. 14 23.54 81.2
<i>i</i> -PrCl	ΔH^* , kcal ΔS^* , e.u. $10^5 k, \text{sec}^{-1}$	50° 50° 60°	This work 24.70 -6.22 1.92	Ref. 15 24.70 -5.1			
<i>i</i> -PrBr	ΔH^* , kcal ΔS^* , e.u. $10^5 k, \text{sec}^{-1}$	50° 50° 60°	This work 24.15 -4.03 32.9	Refs. 15-17 24.36 -1.43 34.9			
<i>i</i> -PrI	ΔH^* , kcal ΔS^* , e.u. $10^5 k, \text{sec}^{-1}$	50° 50° 60°	This work 25.17 0.50 29.4	Refs. 15, 18 25.23 1.86 31.15			
PhCH ₂ Cl	ΔH^* , kcal ΔS^* , e.u. $10^5 k, \text{sec}^{-1}$	50° 50° 60°	This work 20.00 -13.45 55.5	Ref. 19 20.36 -12.34 58.2	Ref. 20 20.35 56.7		

fast to be measured by the method used over the entire range of perchloric acid-water mixtures. Samples of the reaction mixture were usually taken between 10 % to 80 % change and the calculated first-order rate constants showed no drift within this range. The results are shown in Tables 1–4.

Distribution measurements. The distributions of alkyl halides between cyclohexane and mixtures of water and perchloric acid at 0°C were measured in a 10-litre Dewar flask filled with crushed ice and water. 1 ml of a solution of alkyl halide in cyclohexane was shaken with 50 ml of the aqueous solution for about 10 min and allowed to stand for about 30 min before the two liquid layers were separated. No detectable hydrolysis of the alkyl halides was observed during this time. The hydrolysis of *t*-butyl chloride was too fast to allow accurate distribution experiments. 10 ml samples of the aqueous solution were sealed in ampoules and kept at 80°C for a period sufficient for total hydrolysis of the alkyl halide. The amount of alkyl halide in the sample was calculated from the consumption of silver nitrate solution. The results are shown in Table 7.

Table 3. Values of $\Delta \log k = \log k$ (in $\text{HClO}_4\text{-H}_2\text{O}$ mixture) – $\log k$ (in water) for the hydrolysis of alkyl halides in mixtures of perchloric acid and water.

HClO_4 wt. %	t-BuCl 0°	i-PrCl 80°	i-PrBr 60°	i-PrI 60°	PhCH_2Cl 60°	n-BuCl 80°	n-BuBr 80°	n-BuI 80°	EtBr 60°
0	0	0	0	0	0	0	0	0	0
11.4	+0.112	-0.044	-0.111	-0.095	-0.100	-0.151	-0.196	-0.181	-0.188
21.2	+0.283	-0.154	-0.222	-0.246	-0.189	-0.366	-0.410	-0.374	-0.333
30.0	+0.434	-0.188	-0.299	-0.347	-0.200	-0.562	-0.573	-0.618	-0.575
37.8	+0.623	-0.170	-0.448	-0.412	-0.140	-0.780	-0.817	-0.818	-0.748
44.8	+0.018	-0.106	-0.402	-0.499	+0.008	-0.975	-1.057	-1.132	-1.020
51.0	+1.440	+0.085	-0.306	-0.608	+0.261		-1.246	-1.330	
56.5		+0.414	-0.020	-0.586	+0.640		-1.375	-1.540	
61.7		+0.908	+0.306	-0.480					
66.2		+1.617	+0.772	-0.269					

Table 4. Values of $\Delta \log k = \log k$ (in $\text{NaClO}_4\text{-H}_2\text{O}$ mixture) – $\log k$ (in water) for the hydrolysis of alkyl halides in mixtures of sodium perchlorate and water.

NaClO_4 wt. %	n-BuCl 80°C	i-PrCl 80°C	t-BuCl 0°C
0	0	0	0
8.7		-0.007	0.141
15.7	0.094	-0.008	0.225
28.6	0.123	0	
34.4			0.658
39.7	0.369	0.073	0.787
48.2	0.333	0.092	0.940
52.0			1.044
56.7	0.502	0.140	1.306

DISCUSSION

The results are shown in Tables 1–4 and in Fig. 1. Also earlier results^{1,12–20} are given in Table 2. The agreement between the present and earlier values

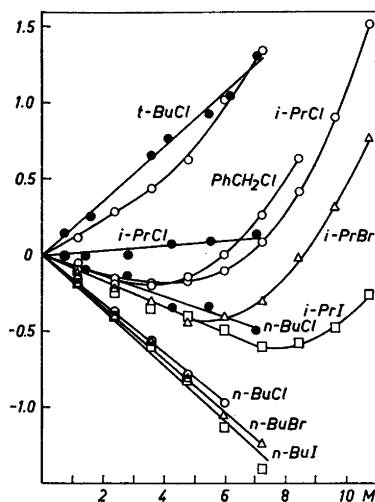


Fig. 1. Values of $\log k/k_0$ for the hydrolysis of alkyl halides in sodium perchlorate-water mixtures (filled circles), or in perchloric acid-water mixtures (unfilled points). k_0 is the first-order rate constant in water and k the first-order rate constant in the electrolyte-water mixture. \circ [HClO_4] or \bullet [NaClO_4].

is in most cases satisfactory. The experimental error in the titration method used in the present study is obviously larger than the error in the conductometric method used by other authors.^{12,14-20} Clarke, Williams and Taft¹ observed that the effect of added electrolytes on the rate of hydrolysis of *t*-butyl chloride in water at low electrolyte concentrations is given by the Setschenow equation²¹

$$\log k/k_0 = (B_a - B_x) c = B c \quad (1)$$

where k_0 and k are the rate constants in pure water and in a solution containing added electrolyte, respectively, c is the concentration of the electrolyte and the constants B_a and B_x refer to the initial and transition states, respectively. Values of B obtained by Clarke, Williams and Taft¹ for perchloric acid (+0.14) and sodium perchlorate (+0.28) in water at 15°C differ somewhat from the values, +0.104 and +0.177, respectively, at 0°C, obtained in the present

Table 5. Values of the constant B in the equation $\Delta \log k = B c$ for reactions of alkyl halides in perchloric acid-water and sodium perchlorate-water mixtures at the temperature given in Tables 3 and 4 (the linear parts of the curves in Fig. 1).

	<i>t</i> -BuCl	<i>i</i> -PrCl	<i>i</i> -PrBr	<i>i</i> -PrI	BzCl	<i>n</i> -BuCl	<i>n</i> -BuBr	<i>n</i> -BuI
HClO_4	+0.104	-0.067	-0.090	-0.086	-0.080	-0.160	-0.172	-0.180
NaClO_4	+0.177	+0.016				-0.068		
Difference	0.073	0.083				0.092		

study (Table 5). The differences may be due to the different temperature used in the present experiments.

The results in Fig. 1 show that the Setschenow equation is valid for the hydrolysis of butyl halides in perchloric acid-water and sodium perchlorate-water mixtures over the whole electrolyte concentration range up to about 6 M. In contrast curvilinear plots are obtained for the hydrolyses of isopropyl halides and *t*-butyl chloride in perchloric acid-water mixtures whereas straight lines were obtained for the reactions in sodium perchlorate-water mixtures. In addition to the usual salt effect perchloric acid seems to have a special influence on the hydrolyses of isopropyl halides and *t*-butyl chloride when it is present in high concentration whereas no such effect was observed in dilute acid mixtures or in the hydrolysis of primary butyl halides or ethyl

Table 6. Rate constants k_a of the acid-catalysed hydrolysis of alkyl halides in perchloric acid-water mixtures.

HClO ₄ wt. %	-H ₀ (Ref. 27)	log 10 ⁵ k _a				
		<i>t</i> -BuCl 0°C	PhCH ₂ Cl 60°C	<i>i</i> -PrCl 80°C	<i>i</i> -PrBr 60°C	<i>i</i> -PrI 60°C
21.2	1.06	1.064		0.117		
30.0	1.59	1.462		0.496		
37.8	2.19	1.852	1.224	0.790	0.550	
44.8	2.87	2.627	1.583	1.149	0.954	
51.0	3.61	3.175	1.937	1.566	1.405	0.326
56.5	4.52		2.342	2.095	1.792	0.728
61.7	5.64			2.814	2.281	1.094
66.2	6.76					

bromide. This additional effect could be due to a simultaneous acid-catalysed reaction. This view is supported by the observation that the deviation from linearity of the data for the hydrolysis of isopropyl halides starts at acid concentrations different for each halide and increases in the order RCl < RBr < RI. This order is that expected from the decreasing proton affinity of the respective ions in water.

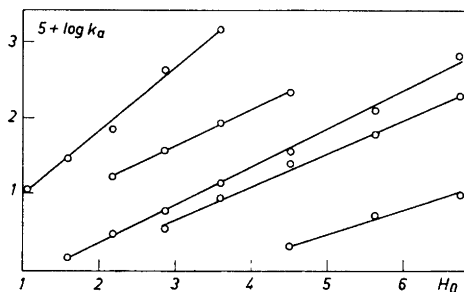


Fig. 2. Logarithm of the first-order rate constant of the acid catalysed hydrolysis reactions of alkyl halides in perchloric acid-water mixtures. H_0 is the acidity function.

In order to separate the possible acid-catalysed reactions from the spontaneous hydrolysis reactions of the alkyl halides, it was assumed that the spontaneous hydrolysis obeys the Setschenow equation over the entire concentration range. The linear parts of the curves at low acid concentrations were extrapolated to evaluate the spontaneous rate constants. The differences in the extrapolated and experimental rate constants k_a are given in Table 6. A plot of $\log k_a$ against the acidity function H_0 of the reaction mixture is shown in Fig. 2. The slope is close to unity only for the hydrolysis of t-butyl chloride (0.83) whereas the slopes 0.49, 0.44, 0.41, and 0.43 were obtained for isopropyl chloride, isopropyl bromide, isopropyl iodide and benzyl chloride, respectively.

The value of the slope indicates almost complete protonation of t-butyl chloride in the transition state of the acid-catalysed hydrolysis reaction, whereas the low values of the slopes for the acid-catalysed hydrolysis of isopropyl halides and benzyl chloride indicate incomplete protonation. Possible mechanisms are a fast pre-equilibrium hydrogen bonding of the alkyl halide and hydronium ion or a rate-determining slow protonation of the alkyl halide.⁵ Important front side assistance by substances such as water or alcohols which are able to form hydrogen bonds with alkyl halides has been suggested previously to promote the solvolysis of alkyl halides.^{1,11,28} The negative charge on the halogen atom in the transition states of the hydrolysis reactions of alkyl halides increases in the order primary < secondary < tertiary alkyl halide. An increase in the strength of the interaction of the halide with hydronium ion would be expected to increase in the same order, in agreement with the obtained results. An acid-catalysed reaction seems to be a reasonable explanation for the effects observed in reaction mixtures containing high concentration of perchloric acid in the case of all other alkyl halides except the primary halides.

The acid-catalysed reactions in perchloric acid-water mixtures of high acid content contribute to only a negligible extent to the hydrolysis reactions at low acid concentrations. The magnitude of the salt effect of an electrolyte depends both on the electrolyte and on the alkyl halide. Both positive and negative values of the slope B of the Setschenow equation (1) are obtained. In the case of the normal and secondary alkyl halides studied the salt effect is approximately of the same magnitude for chlorides, bromides, and iodides. As shown in Table 5, the difference between the values of B obtained for perchloric acid and sodium perchlorate is approximately constant for all the alkyl halides studied. According to Clarke, Williams and Taft¹ the salt effect of sodium perchlorate in the hydrolysis of t-butyl chloride can be explained by simple electrostatic theory whereas the unexpected effects of acids are due to additional specific effects of the hydrogen ion. The present results indicate that this specific effect of the hydrogen ion is similar for all the alkyl halides studied despite the different mechanisms of the hydrolysis reactions.

Salts influence reaction rates by changing the activity coefficients of the initial and transition states.

Thus:

$$\frac{k}{k_0} = \frac{f_A a_w}{f_x} \quad (2)$$

Table 7. Distribution of alkyl halides between cyclohexane and mixtures of water and perchloric acid at 0°C.

RCI	HClO wt. %	c_{RCI} mole/l in water	c'_{RCI} mole/l in cyclohexane	$K = \frac{c'}{c}$	$\frac{K}{K_0}$
n-BuCl	0	0.00092	0.904	980	1.00
	11.08	0.00113	0.894	790	1.24
	20.65	0.00101	0.900	890	1.10
	29.51	0.00096	0.902	940	1.04
	37.19	0.00075	0.913	1220	0.80
	44.07	0.00085	0.908	1070	0.92
i-PrCl	0	0.00241	0.416	173	1.00
	0	0.00460	0.875	190	
	0	0.00650	1.76	270	
	11.02	0.0027	0.402	149	1.16
	20.74	0.0024	0.417	174	1.00
	37.22	0.0023	0.422	184	0.94
	44.07	0.0017	0.452	266	0.65
	50.27	0.0020	0.437	218	0.80
	55.93	0.0016	0.457	286	0.60
	61.20	0.0014	0.467	334	0.52
	65.82	0.0013	0.472	364	0.48
PhCH ₂ Cl	0	0.0043	0.435	1000	1.00
	0	0.0093	0.803	980	
	0	0.00142	1.68	1180	
	11.12	0.00061	0.426	700	1.43
	20.92	0.00074	0.419	570	1.76
	29.60	0.00081	0.416	510	1.96
	37.40	0.00069	0.421	610	1.64
	44.07	0.00080	0.416	520	1.92
	50.50	0.00077	0.418	550	1.82
	55.91	0.00066	0.420	630	1.59

where k_0 and k are the first-order rate constants in pure water and in an electrolyte solution, respectively. In reactions occurring by the S_N1 mechanism only the activity coefficients of the alkyl halide, f_A , and the transition state, f_x , are affected, but for reactions occurring by the S_N2 mechanism also the activity of water, a_w , has to be included. If it can be assumed that a dilute solution of an alkyl halide in cyclohexane is ideal then the ratio K_0/K given in Table 7 is equal to the activity coefficient of the alkyl halide in the aqueous solution. The changes in the activity coefficients of alkyl halides in perchloric acid-water mixtures are similar for butyl chloride and isopropyl chloride. No accurate values were obtained for t-butyl chloride because of its fast hydrolysis reaction, but preliminary experiments indicated that the activity coefficient of this halide seems to change in a similar way as the activity coefficients of the other two alkyl halides. The large differences in the salt effects observed for primary, secondary and tertiary halides are therefore not due to changes in the activity coefficients of the alkyl halides.

The transition states in the hydrolysis of alkyl halides are polar in all cases, the charge separation decreasing in the order tertiary > secondary >

primary alkyl halide. Ion-dipole interactions therefore vary somewhat in electrolyte solutions but should not cause a change in the sign of the salt effect. Some additional effects seem to be involved which cause the large differences observed in the salt effects. The role of water in nucleophilic substitution reactions is not clearly understood. It has been suggested²² that water acts in two ways in a push-pull mechanism. One of the water molecules acts as a nucleophile and the other as an electrophile and these interactions may vary in relative importance. The importance of nucleophilic action in the hydrolysis reactions increases in the order tertiary < secondary < primary alkyl halide. In aqueous solutions containing different concentrations of electrolyte, ion-water interactions alter the nucleophilic and electrophilic properties of water. The retardation of the hydrolysis of primary and secondary alkyl halides in solutions containing an electrolyte may be due to a decrease of the nucleophilicity of water. In the hydrolysis of *t*-butyl chloride water is not present as a nucleophile in the transition state and the observed effect of an added electrolyte is due to electrostatic dipole-ion interactions.

The observed salt effects may be used to decide the reaction mechanisms of hydrolysis reactions. The values of the slopes *B* obtained for isopropyl halides and benzyl chloride are between the values obtained for primary alkyl halides reacting by a bimolecular S_N2 mechanism and *t*-butyl chloride which reacts by the unimolecular S_N1 mechanism. The hydrolysis of isopropyl halides and benzyl chloride then evidently occurs by a borderline mechanism involving only a weak nucleophilic contribution of water in the transition state. Similar conclusions have been drawn previously by other authors.^{19,22-26} The similarity of the salt effects in the hydrolysis of isopropyl chloride and benzyl chloride suggests a similar mechanism for these compounds.

Instead of one mechanism of the borderline type, these substances could also react by concurrent S_N1 and S_N2 mechanisms. The linear salt effects observed are not in accordance with the assumption of two simultaneous reactions. A curved plot is expected in sodium perchlorate-water mixtures instead of the linear one obtained for isopropyl chloride (Fig. 1) because the increase in salt concentration should result in a decrease of the rate of a bimolecular reaction and an increase in the rate of a unimolecular reaction, similarly as observed for reactions occurring by only one mechanism. It can be concluded that the reaction occurs by a single borderline mechanism lying somewhere between the limiting unimolecular and bimolecular mechanisms.

The activation enthalpies of the hydrolysis of the three isopropyl halides do not vary in the order RCl, RBr, and RI. A similar irregularity is observed also for the butyl halides (Table 1). The activation enthalpies of isopropyl halides are about 1 kcal higher than the activation enthalpies of butyl halides. A value of 20.42 kcal was calculated for the hydrolysis of *t*-butyl chloride at 51°C from values given in the literature.¹² This value is about 4.3 kcal smaller than obtained for isopropyl chloride. The activation enthalpy for benzyl chloride, 20.00 kcal/mole, is close to the value for *t*-butyl chloride. In a hydrolysis reaction by the S_N2 mechanism the transition state is more crowded than the initial state and the activation enthalpy of the reaction involves contributions from an increase in non-bonded interactions around the reacting carbon atom. An opposite effect is observed in reactions occurring by a S_N1 mechanism

where the transition state is less crowded than the initial state and the activation enthalpy is decreased by partial release of the non-bonding interactions. The high value of the activation enthalpy observed in the hydrolysis of isopropyl halides seem to indicate a crowded transition state caused by weak nucleophilic interaction of a water molecule.

The activation entropies increase in the order $RCl < RBr < RI$ for both isopropyl and butyl halides. The difference in activation entropy between an alkyl chloride and an alkyl iodide is similar for both primary and secondary halides, 8.8 and 7.7 e.u., respectively. A value of +9.0 e.u. was calculated for the activation entropy of *t*-butyl chloride hydrolysis at 51°C from values given in the literature.¹² The activation entropy increases in the order $n\text{-BuCl} < i\text{-PrCl} < t\text{-BuCl}$. Such a change is expected when the mechanism changes from S_N2 to S_N1 owing to a decrease in the nucleophilic interaction between the alkyl halide and water and also owing to change in the non-bonded interactions mentioned earlier.

The activation entropy in the hydrolysis of benzyl chloride, -13.45 cal/deg., is close to the value obtained for *n*-butyl chloride -14.10 cal/deg. The activation energy for benzyl chloride, however, was close to the value found for *t*-butyl chloride. The values of the activation entropies and energies do not allow any simple deductions about the mechanism of hydrolysis of benzyl chloride. Other results,^{19,23-25} such as salt effects indicate a borderline mechanism. The activation entropy has often been used as a tool to decide between several possible reaction mechanisms. The results presented above show that such a simple treatment may lead to erroneous conclusions.

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