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Effect of pressure on the rate of solvolysis of *t*-butyl chloride in ethanol–water mixtures[1]

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The effect of pressure on the rate of spontaneous solvolysis of *t*-butyl chloride in ethanol–water mixtures in the range 0 to 40% v/v ethanol at 0 °C has been measured up to a maximum pressure of 3 kbar. The results have been examined from several points of view and the conclusions are briefly described in the summary.

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1. Introduction

Several reactions are now known (1–3) for which the constant-volume parameters of activation vary in a simpler manner with solvent composition than the constant-pressure parameters. One of the strongest variations of the constant-pressure parameters with solvent composition occurs for the solvolysis of *t*-butyl chloride in ethanol–water mixtures (4), and a study of the constant-volume parameters for this system is clearly required.

Furthermore, the constant-pressure entropy of activation in water is 12 cal deg^{-1} mole^{-1} at 25 °C. The mechanism is undoubtedly S_N1

$$t\text{-BuCl} \rightarrow t\text{-Bu}^+ + \text{Cl}^-$$

and the transition state has presumably an appreciably higher dipole moment than the initial state. This implies an appreciable loss of entropy when the transition state is formed due to dipole–solvent interaction. The observed positive entropy of activation presumably implies that the *t*-Bu and Cl are well separated in the transition state so that the gain in entropy due to their looser attachment to one another more than compensates the loss of entropy due to increased interaction with the solvent. A relatively large separation of the *t*-Bu and Cl might affect the activation volume.

Consequently, the solvolysis of *t*-butyl chloride in ethanol–water at 0 °C has been followed to a maximum pressure of 3 kbar.

2. Experimental

Reagents

t-Butyl chloride was prepared (5) from Eastman Kodak White Label *t*-butanol. The final fraction boiling at 50.0 to 50.5 °C was > 99.5% pure by gas chromatographic analysis, and was used. Pure dry ethanol was prepared from commercial absolute ethanol (5) and used for preparing ethanol–water mixtures by volume. Distilled water was degassed by boiling and was stored out of contact with air.

Kinetics

The rate of hydrolysis at various pressures was measured using the conductance technique described previously (6). The thermostat bath was a vigorously stirred mixture of ice and water, whose temperature was constant to ±0.02 °C. In order to prevent water from coming into contact with the leads, the top of the pressure vessel was fitted with a sliding brass cylinder sealed with an O-ring at the bottom to keep the water out. The cylinder normally protruded above the water level, and the empty space inside it was filled with cotton wool for thermal insulation.

The vessel with mercury, the conductance cell and its associated parts, hydraulic oil, and the solvent (~100 ml in a volumetric flask) were kept in a refrigerator at −5 °C. 20 μl of *t*-butyl chloride was quickly added to the solvent and the solution stirred. The cell was rinsed, filled with the solution, and assembled with the cooled vessel, mercury, oil, etc. The vessel was lowered to the thermostat bath and pressurized slowly. The assembly was carried out as quickly as possible, and with experience the time taken from adding the *t*-butyl chloride to pressurizing the vessel was 7 min. In highly aqueous ethanol–water at high pressure, the reaction becomes too fast for the use of this technique and the runs, therefore, had to be restricted to lower pressures.

The time for thermal equilibrium was checked by pressurizing aqueous 0.002 *M* hydrogen chloride to 1000 bars in the kinetics apparatus. The conductance reached a constant value in 12 to 15 min after pressurizing. In all the runs the first reading was taken a minimum of 20 min after pressurizing.

3. Results

For the accuracy desired in this work, there was no need to correct the conductances for the change in equivalent conductance with concentration. The rate constants were obtained by the

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[1] NRCC No. 11081.

TABLE 1

Rate constants for the solvolysis of *t*-butyl chloride in water–ethanol at 0 °C and various pressures

	$10^6\ k/\mathrm{s}^{-1}$ at % v/v ethanol in water			
p/bar	0	10	25	40
50	712	481	$266._0$	60.8
100				63.6
249		501	$295._4$	72.1
348				78.3
496	745	545	$328._7$	87.6
595				92.2
741		576	$359._5$	99.3
987	771	605	$385._6$	110.5
1480	808	665	434	131.8
1973				144.7
2472				155.4
2955				163.8

Guggenheim method of analysis using least-squares on an IBM-360 computer as in the earlier work (6). The rate constants are given in Table 1 and are reproducible to about 0.5%, except in 0 and 10% v/v ethanol where the reproducibility, since the reaction is fast, is about 1%. These errors were estimated from the standard deviations, the agreement between a few duplicated runs, the deviations of the rate constants at various pressures from fitted lines as described in section (4.5), and the deviations from a smooth line in Fig. 2.

Graphical plots of ln k vs p are given in Fig. 1. The rate constants extrapolated to zero pressure are compared with those of Winstein and Fainberg (4) in Table 2. The agreement is good.

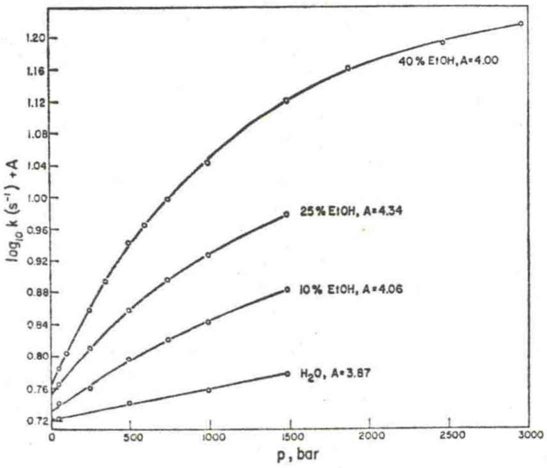

FIG. 1. Rate constants for the solvolysis of *t*-butyl chloride in water–ethanol at 0 °C. The numbers on the curves are the % v/v ethanol.

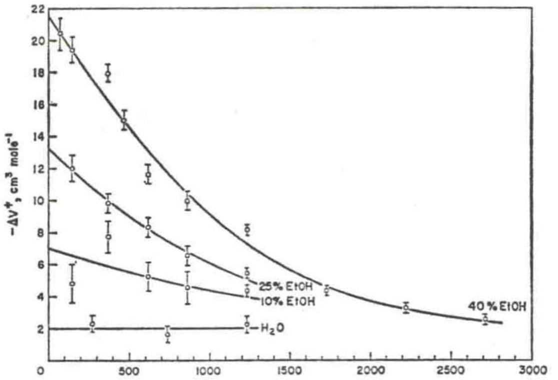

FIG. 2. Mean volumes of activation for the solvolysis of *t*-butyl chloride in water–ethanol at 0 °C. The numbers on the curves are the % v/v ethanol.

Mean volumes of activation $\Delta V^{\ddagger}{}_{\mathrm{mean}}$ calculated between adjacent pressures p_1 and p_2 from the relation

$$[1] \qquad \Delta V^{\ddagger}{}_{\mathrm{mean}} = \frac{-RT}{(p_1 - p_2)} \ln \frac{k_1}{k_2}$$

are plotted against the mean pressure $(p_1 + p_2)/2$ for the various solvents in Fig. 2. The zero-pressure intercepts are the volumes of activation at zero pressure.

The difference in $\Delta V^{\ddagger}$ between solvents can be expressed as

$$[2] \qquad -\Delta\Delta V^{\ddagger} = RT \frac{\partial \ln k_1/k_2}{\partial p}$$

where k_1 and k_2 are now the rate constants in solvents 1 and 2 at the same pressure. Plots of ln k_1/k_2 against p are shown in Fig. 3 and the slopes at zero pressure give the difference $\Delta\Delta V^{\ddagger}$ of activation volume for the various solvent pairs as follows

$$\Delta\Delta V^{\ddagger}\ (0\text{–}10) = 5.0 \pm {\sim}0.4$$
$$\Delta\Delta V^{\ddagger}\ (0\text{–}25) = 10.7 \pm {\sim}0.5$$
$$\Delta\Delta V^{\ddagger}\ (0\text{–}40) = 19.9 \pm {\sim}0.5$$
$$\Delta\Delta V^{\ddagger}\ (10\text{–}25) = 6.7 \pm {\sim}0.6$$
$$\Delta\Delta V^{\ddagger}\ (10\text{–}40) = 15.0 \pm {\sim}0.8$$
$$\Delta\Delta V^{\ddagger}\ (25\text{–}40) = 8.2 \pm {\sim}0.6$$

Since ln k vs. p for water (see Fig. 1) is essentially linear, the volume of activation in water is −2.0

TABLE 2

Comparison of rate constants at 1 bar for the solvolysis of *t*-butyl chloride in water–ethanol at 0 °C

% v/v ethanol in water	$10^6\ k/\mathrm{s}^{-1}$	
	This work	Reference 4
0	712	727
10	469	475
25	258	259
40	57.9	57.6

± 0.5 $\mathrm{cm}^3\ \mathrm{mole}^{-1}$ which is consistent with the value extrapolated from the plot in Fig. 2. From this value and the first three relations above, the volume of activation in the mixed solvents can be obtained. The last three relations are included as a check. The activation volumes obtained are consistent with those obtained from Fig. 2, and with the limiting slopes in Fig. 1. They are summarized in Table 3, which also gives the thermal expansivities α and compressibilities κ for the solvents obtained from the literature (7, 8). The only other measurements of the effect of pressure on the rate of solvolysis of *t*-butyl chloride are rough values of Buchanan and Hamann (9) in 80% aqueous ethanol at 25 °C which yield a volume of activation of about $-21\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$, and those of Hyne, Golinkin, and Laidlaw (10) in 80% v/v aqueous ethanol at 30 °C, which by least-squares gives a value of $-22.2 \pm 0.9\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$ (10) and by a graphical reanalysis $-20 \pm \sim 1.5\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$. Olavi and Virtanen (11) have measured the activation volume for the solvolysis of *t*-butyl bromide in several organic or largely organic solvents and obtained values in the range -20.6 to $-41.7\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$. Because the solvents were quite different, these values cannot be compared with ours.

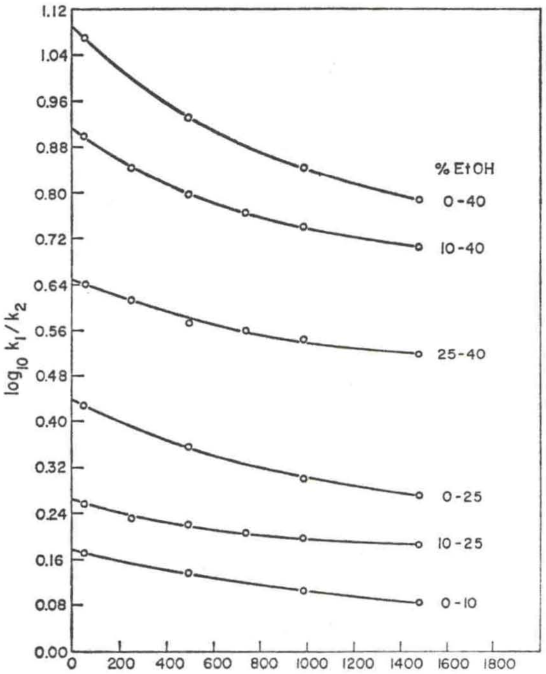

FIG. 3. Ratio of rate constants in different solvents for the solvolysis of *t*-butyl chloride. The numbers attached to the curves are the % v/v ethanol of the solvent.

The activation enthalpy and entropy at constant pressure according to Winstein and Fainberg (4) are given in Table 4. Since their enthalpies and entropies refer to 12.5 °C, they were adjusted to 0 °C using heat capacities of activation graphically interpolated from those recently measured by Martin and Robertson (12). The data in the last column of Table 3 were used to obtain the constant-volume energy and entropy of activation by means of the expressions

$$\Delta U_V^{\ddagger} = \Delta H_P^{\ddagger} - T\alpha\Delta V^{\ddagger}/\kappa$$

$$\Delta S_V^{\ddagger} = \Delta S_P^{\ddagger} - \alpha\Delta V^{\ddagger}/\kappa,$$

and they are given in the last two columns of Table 4. The change of activation parameters with solvent composition are plotted in Fig. 4.

4. Discussion

1. Volume of Activation in Water

It is well established (13) that the solvolysis of *t*-butyl chloride occurs in two steps, the first being the slow ionization of the halide and the second a fast combination of the *t*-butyl carbonium ion with the solvent. Presumably, the transition state is

$$(\mathrm{CH_3})_3\mathrm{C}^{\delta+}\text{ - - - - - }\mathrm{Cl}^{\delta-}$$

in which the C—Cl bond is stretched and partial charges have appeared on the separating fragments. Two factors contribute essentially to the volume change of this reaction (14, 15); (*i*) the change of volume of the substrate and (*ii*), the change of volume due to changes in the interaction of the solvent with the substrate.

A rough estimate by Evans (16) suggested that the C—Cl bond is stretched by about 0.7 Å to form the transition state, and this multiplied by

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TABLE 3

Thermal expansivity and compressibility of water–ethanol mixtures, and volumes of activation for the solvolysis of *t*-butyl chloride in these mixtures at 0 °C

% v/v ethanol in water	$10^6\,\alpha$ deg^{-1}*	$10^6\,\kappa$ bar^{-1}*	$\Delta V^{\ddagger}$ cm^3 mole^{-1}	$T\alpha\Delta V^{\ddagger}/\kappa$ cal mole^{-1}
0	−68.1	50.3	$-2.0\pm\sim0.5$	$18\pm\sim5$
10	25.3	44.1	$-7.0\pm\sim1.0$	$-26\pm\sim5$
25	241	38.1	$-13.2\pm\sim0.6$	$-545\pm\sim50$
40	625	44.3	$-21.5\pm\sim1.0$	$-1979\pm\sim100$

*Values of α and κ for water are from ref. 7, and for other solvents, from ref. 8.

TABLE 4

The activation parameters for the hydrolysis of *t*-butyl chloride in water–ethanol mixtures at 0 °C

% v/v ethanol in water	$\Delta G_p^{\ddagger}$ cal mole^{-1}	$\Delta H_p^{\ddagger}$ cal mole^{-1} ± 150	$T\Delta S_p^{\ddagger}$ cal mole^{-1} ± 150	$\Delta U_V^{\ddagger}$ cal mole^{-1} ± ~200	$T\Delta S_V^{\ddagger}$ cal mole^{-1} ± ~200
0	19 864	24 258	4·394	24 240	4 376
10	20 095	24 555	4 460	24 581	4 486
25	20 424	22 700	2 276	23 245	2 821
40	21 240	20 858	−382	22 837	1 597

the cross section of the molecule yields a volume expansion of about 12 cm^3 mole^{-1}. This estimate compares favorably with the observed values listed in Table 5 for several unimolecular decompositions in which large changes in the interaction with the solvent probably do not occur. Hamann (17) has reviewed a number of free-radical decompositions which have similar volumes of activation.

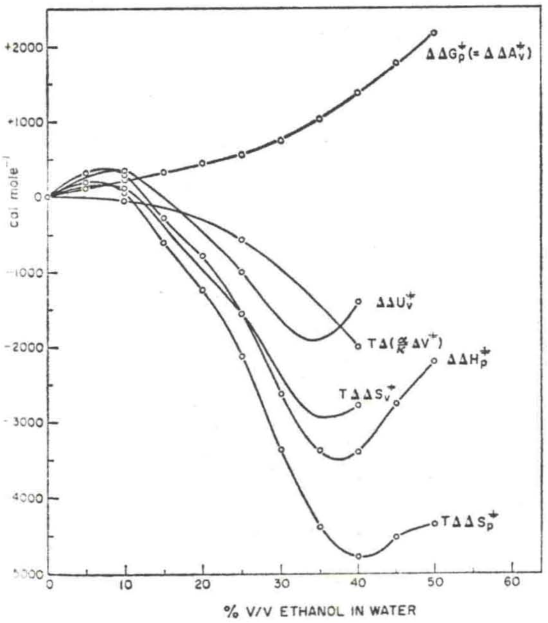

FIG. 4. Changes in the activation parameters for the solvolysis of *t*-butyl chloride with composition in ethanol–water at 0 °C.

The transfer of charge from Cl to *t*-Bu will tend to make the Cl part expand due to the decreased nucleus–electron attraction and the *t*-Bu part contract due to the increased nucleus–electron attraction (18). The two effects will tend to compensate one another, and for lack of knowledge they are neglected.

The increased electrostatic interaction with the solvent when the transition state is formed causes a volume decrease. This might be expected to be similar to the volume decrease accompanying the formation of zwitter-ions of α-amino acids

$$[3] \qquad NH_2CHRCO_2H \rightleftharpoons \overset{+}{N}H_3CHRCO_2^-$$

but probably somewhat smaller because the charges will not be so well separated in the transition state. According to density measurements of Cohn and others (19, 20*a*), the volumes of formation of zwitter-ions from the unionized amino acids are in the range −13 to −18 cm^3 mole^{-1}.

If the charges are almost fully developed in the transition state for the solvolysis of *t*-butyl chloride, the expansion due to the stretching of the

TABLE 5

Volumes of activation for several unimolecular decompositions in which large changes in the interaction with the solvent are not expected

Reaction	Temperature °C	Solvent	$\Delta V^{\ddagger}$/cm^3 mole^{-1}	Reference
$CHCl_3 + OH^- \rightarrow H_2O + [CCl_2\text{---}Cl]^{\ddagger -}$	25	H_2O	16	34
$CCl_3CO_2^- \rightarrow [CCl_3\text{---}CO_2]^{\ddagger -}$	85	H_2O	13	35
	163	H_2O	10	36*
$t\text{-Bu}\overset{+}{S}Me_2 \rightarrow [t\text{-Bu---}SMe_2]^{\ddagger +}$	61.4	EtOH	10	
$t\text{-Bu}\overset{+}{S}Me_2 \rightarrow [t\text{-Bu---}SMe_2]^{\ddagger +}$	71	H_2O	9	36,37
$t\text{-Am}\overset{+}{S}Me_2 \rightarrow [t\text{-Am---}SMe_2]^{\ddagger +}$	53.8	80% v/v EtOH in H_2O	14	37
$ArN_2^+ \rightarrow [Ar\text{---}N_2]^{\ddagger +}$	Various 21–71	H_2O	10	37
$EtHg^+ \rightarrow [Et\text{---}Hg]^{\ddagger +}$	114	H_2O	6	36
$\text{iso-PrHg}^+ \rightarrow [\text{iso-Pr---Hg}]^{\ddagger +}$	46.4	H_2O	9	36

*Several others decarboxylations are also reported.

bond and the contraction due to the electrostatic interaction are therefore expected to be of a similar magnitude, and the experimental activation volume of -2 cm^3 mole^{-1} can be qualitatively understood. The large separation of charge was derived by Scatchard (21) from the large effect of solvent composition on the rate.

2. *Origin of the Volume of Formation of Zwitter-ions*

The cause of the contraction in reaction [3] is worth a brief discussion. Gucker, Klotz, and Allen (22) and Gucker, Lamb, Marsh, and Haag (23) have discussed the solvation of zwitter-ions based on a model in which the zwitter-ion is represented as an incompressible dipolar sphere (24) of radius a and the solvent as a continuous dielectric of permittivity ε. A model (15) in which the zwitter-ion is compressible, or alternatively is in a compressible cavity in the solvent, is more realistic and is adopted here. The contribution to the volume of reaction [3] due to the interaction of the zwitter-ion with the solvent is (15), on the basis of this model when electric saturation of the dielectric is ignored,

$$[4] \quad \Delta V_{es} = \frac{3}{2} N \frac{\mu^2}{a^3} \times \left\{ \frac{1}{2} \frac{\partial \varepsilon^{-1}}{\partial p} + \left(1 - \frac{3}{2\varepsilon}\right) \frac{\partial \ln a}{\partial p} \right\}$$

where μ is the dipole moment of the zwitter-ion.

For glycine the volume of zwitter-ion formation is (19)

$$\Delta V = -13 \quad \text{cm}^3\ \text{mole}^{-1}$$

and the dipole moment (20*b*) is

$$[5] \quad \mu = \sim 15 \quad \text{D}$$

The molar volume of crystalline glycine is 46.6 cm^3 mole^{-1} (25), and so, taking glycine to be spherical, $a^3 = 77$ Å^3. Then

$$[6] \quad \tfrac{3}{2} N \frac{\mu^2}{a^3} = 2.6 \times 10^6 \quad \text{cm}^3\ \text{bar mole}^{-1}$$

and so from eqs. [4]–[6]

$$[7] \quad \left\{ \frac{1}{2} \frac{\partial \varepsilon^{-1}}{\partial p} + \left(1 - \frac{2}{3\varepsilon}\right) \frac{\partial \ln a}{\partial p} \right\} = -5.0 \times 10^{-6} \quad \text{bar}^{-1}$$

For water

$$[8] \quad \frac{1}{2} \frac{\partial \varepsilon^{-1}}{\partial p} = -0.30 \times 10^{-6} \quad \text{bar}^{-1}$$

If the model is a reasonable representation of glycine in water, it follows from eqs. [7] and [8] that little of the volume of zwitter-ion formation is an electrostriction of the solvent as described by eq. [8]. Almost all of it, which is described by the second term on the right-hand side of eq. [4] or on the left-hand side of eq. [7], is a compression of the zwitter-ion due to the ion–solvent interaction, and the correct volume change is predicted by eq. [4] if

$$\partial \ln a / \partial p = -4.6 \times 10^{-6} \quad \text{bar}^{-1}$$

which is at least not unreasonable.

The model will of course fail in so far as other interactions contribute to the volume of ionization, and if saturation of the dielectric occurs.

It seems likely, however, that the conclusion that electrostriction of the solvent is relatively small and the compression of the ion contributes the major part of the volume of ionization will not be changed by a more elaborate analysis. The density of crystalline (zwitter-ionic) glycine of 1.61 g cm^{-3} (25) is appreciably higher than that expected for a molecular crystal of glycine. This confirms that there is a considerable contraction of the molecule when the zwitter-ion is formed in a condensed phase. The compression of the ion is also an important part of the volume of solvation of ordinary ions (18).

3. Effect of Solvent on the Activation Volume

The activation volume in 40% v/v ethanol–water is ten times its value in water (see Table 3). The extra contraction is of course due to the change in the interaction with the solvent when the transition state is produced. It is possible that this interaction causes the breaking C---Cl bond to be less elongated in the transition state in the mixed solvents; but this seems unlikely to contribute more than a small fraction of the observed effect.

In water, the contraction due to the interaction with the solvent seems to be about -14 cm^3 mole^{-1} according to section (4.1). If we assume that the intrinsic volume of the transition state is independent of the solvent composition, then the contraction due to interaction with the solvent appears to become about -19, -25, and -34 cm^3 mole^{-1} in 10, 25, and 40% v/v ethanol–water.

The detailed cause of the large variation in the contribution of the interaction with the solvent to the volume of activation is not directly known, although it is not unprecedented experimentally. There is, for example, an appreciable increase in the value of $-\Delta V^{\neq}$ for the spontaneous solvolysis of benzyl chloride in ethanol–water mixtures (10) as the concentration of ethanol increases. Furthermore, there is a definite increase in $-\Delta V^{\neq}$ even for the acid-catalyzed hydrolysis (2) of methyl acetate and ethylene oxide in acetone–water mixtures as the concentration of acetone increases, and a similar change in $-\Delta V^{\neq}$ for the acid-catalyzed iodination of acetone and of acetophenone (1) in ethanol–water mixtures, although these reactions are not usually thought of as occurring with large changes in the interaction with the solvent. These effects, as was pointed out earlier (1), cannot be described by eq. [4] if the dielectric constant ε of the mixture is given by Oster's (26) equation in the form suitable for high dielectric constants

$$[9] \qquad \varepsilon = \textstyle\sum_i \varepsilon_i \phi_i$$

where ε_i and ϕ_i are the dielectric constants of the pure components and their volume fractions in the mixture. According to this equation, $\partial\varepsilon^{-1}/\partial p$ changes little in the range 0 to 40% v/v ethanol–water (1). It is possible, of course, that eq. [9] does not give the correct pressure variation of the dielectric constant, and a verification is desirable. It seems likely, however, as was concluded earlier for some other reactions (1, 2), that the effect of solvent on the volume of activation cannot be accounted for by dielectric theory, unless saturation occurs.

Arnett and co-workers (27) have shown that a large part of the solvent effect on the activation enthalpy and entropy for this reaction (and for others also) is in fact an effect on the enthalpy and entropy of solution of the initial state. Following this lead, Golinkin, Lee, and Hyne (28) have shown that the solvent variation of the activation volume for the solvolysis of benzyl chloride in water–ethanol is largely caused by a variation with solvent of the partial volume of the initial state benzyl chloride. It is quite possible that the solvolysis of *t*-butyl chloride behaves in a similar way, and so causes at least a part of the observed effect. However, the partial volume of *t*-butyl chloride would have to change by about $-20\,\text{cm}^3\,\text{mole}^{-1}$ in the composition range studied if all the change in the activation volume were caused in this way, and this is about 20% of the molar volume of the pure liquid.

The effect of solvent on the activation volume under pressure is quite different. At 1230 bar the activation volumes are (Fig. 2) -2.0, -3.9, -5.0, and -7.2 cm^3 mole^{-1} in 0, 10, 25, and 40% v/v ethanol–water, and if the curves in Fig. 2 for 0, 10, and 25% v/v can be extrapolated to 3 kbar, the activation volume appears to become almost independent of solvent. No other reaction appears to have been reported for which the effect of solvent on the activation volume is so sensitive to the pressure. The effect of solvent on the rate constants is also sensitive to the pressure, but much less so than the activation volume. For example, the ratio of rate constants in 0 and 40% v/v ethanol–water is 117 at 50 bar and 61.3 at

1480 bar. The only comparable measurements of the effect of solvent and pressure on the activation volume are those on the solvolysis of benzyl chloride at 50 °C in ethanol–water mixtures by Hyne, Golinkin, and Laidlaw (10) and in glycerol–water by Gay and Whalley (29), and there is a partial analogy with the acid-catalyzed enolization of acetone and acetophenone in ethanol–water mixtures (1), and with the acid-catalyzed hydrolysis of methyl acetate and ethylene oxide in acetone–water mixtures (2). Spectacular effects of the kind described here occurred in none of these measurements.

It is possible to speculate that part of the explanation is that the partial volume of *t*-butyl chloride is less dependent on solvent composition at 3 kbar than it is at zero pressure. It appears very difficult to check this speculation experimentally.

4. Activation Parameters at Constant Volume

By transforming to constant-volume conditions, the large minima in the activation enthalpy and entropy at constant pressure cannot be entirely transformed away, but are approximately halved. For two other reactions, the acid-catalyzed hydrolysis of methyl acetate in acetone–water (2) and the neutral solvolysis of benzyl chloride in ethanol–water (3), the minima in the constant-pressure parameters disappears when transformed to constant volume. Clearly, only about a half of the minimum in the constant-pressure parameters for the solvolysis of *t*-butyl chloride can be ascribed to the use of constant-pressure conditions. The minimum in the constant-volume parameters presumably reflects fundamental processes that occur in the solution.

5. Representation of the Rate Constant as a Function of Pressure

Sometimes (30–32) rate constants are fitted to a function of pressure by least squares, either for interpolation or for calculating the activation volume. The function most commonly used is a power series, no doubt because it is linear in the parameters and so is relatively easy to fit. A power series is probably useful for small departures of ln *k* from linearity in the pressure, but might not be useful for large departures such as shown by the present results in 40% v/v ethanol.

According to Fig. 2, the activation volume in 40% v/v ethanol–water seems to be approaching asymptotically a value near zero, and to represent it by a power series in the pressure requires at least three terms

$$\Delta V^{\ddagger} = a + bp + cp^2$$

If the rate constant is represented by a power series, at least a cubic is required, and since power series of second and higher order might have extrema for real values of the pressure, all power series must fail at high enough pressures unless the extrema occur at imaginary pressures. This suggests that the equation

$$[10] \qquad \log_{10} k = \frac{a + bp}{1 + cp}$$

might be a better representation than a power series with the same number of parameters. This equation implies that at zero pressure

$$\ln k\,(p = 0) = a$$

$$\Delta V^{\ddagger}\,(p = 0) = -RT(b\text{-}ac)$$

and in the limit of high pressure

$$\lim\nolimits_{p \to \infty} \ln k = b/c$$

$$\lim\nolimits_{p \to \infty} \Delta V^{\ddagger} = 0$$

and k has no extrema. When fitted by least squares, this equation yielded

$$a = 1.7560 \pm 0.002$$

$$b = (1.8534 \pm 0.05) \times 10^{-3} \quad \text{bar}^{-1}$$

$$c = (764.4 \pm 20) \times 10^{-6} \quad \text{bar}^{-1}$$

and the standard deviation of the points about the curve was 0.0022.

For comparison, a quadratic

$$[11] \qquad \log_{10} k = a + bp + cp^2$$

yielded

$$a = 1.7834$$

$$b = 319 \times 10^{-6} \quad \text{bar}^{-1}$$

$$c = 60.6 \times 10^{-9} \quad \text{bar}^{-2}$$

with a standard deviation of 0.012 and a highly non-random S-shaped curve of deviations against the pressure. A cubic equation was fitted with the following parameters

$$a = 1.7649 \pm 0.003$$

$$b = (413 \pm 9) \times 10^{-6} \quad \text{bar}^{-1}$$

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$$c = -(146 \pm 8) \times 10^{-9} \quad \text{bar}^{-2}$$

$$d = (19.7 \pm 2) \times 10^{-12} \quad \text{bar}^{-3}$$

with a standard deviation of 0.0028.

The quadratic eq. [11] is clearly not useful. The cubic equation with four parameters fits about as well as eq. [10] with three parameters, and might have slightly more nearly random deviations. Equations [10] and [11] and the cubic equation yield activation volumes of -26.7, -16.7, and -21.6 cm^3 mole^{-1}, respectively. The last value is the only one that is even close to the value of $-21.5 \pm \sim 1$ cm^3 mole^{-1} determined from Fig. 2. The large difference in the values obtained from eq. [10] and the cubic, although both equations are moderately good fits to the original data, cautions against too great reliance on fitted equations. An attempt (33) to use another empirical equation does not give reliable volumes of activation at zero pressure (17).

It is concluded, therefore, that while the power series is not as good as eq. [10] in fitting log k against pressure for the reaction considered provided the same number of parameters is used, it gives a better activation volume if a larger number of parameters is used. It seems likely that the method used in Fig. 2 is the most reliable way of obtaining the activation volume.

Summary

1. The activation volumes for the spontaneous solvolysis of *t*-butyl chloride in 0, 10, 25, and 40% v/v ethanol in water at 0 °C are -2.0, -7.0, -13.2, and -21.5 cm^3 mole^{-1}. In pure water, the small value is a result of the expansion in the transition state due to the lengthening of the C—Cl bond and the opposing contraction due to the changing interaction with the solvent when the transition state is produced. Analogy with the activation volumes for the unimolecular decomposition of ions, and with the volume of formation of zwitter-ions of glycine and other amino acids supports this view.

2. Most of the volume of formation of glycine zwitter-ion, which is -14 cm^3 mole^{-1}, appears to be due to the compression of the zwitter-ion by the dipole–solvent interaction. Electrostriction of the solvent contributes only a small part.

3. The effect of solvent on the activation volume is of course largely caused by the changing interaction with solvent when the transition state is produced. It cannot be accounted for by the solvation of the transition state on the basis of the usual dipole-in-dielectric theory. It is possibly due in part to the effect of solvent on the partial volume of *t*-butyl chloride, by analogy with Golinkin, Lee, and Hyne's analysis of similar effects of solvent on the activation volume for the solvolysis of benzyl chloride. Unfortunately, experimental verification of this speculation will not be easy.

4. At 3 kbar, the activation volume appears to be little dependent on the pressure. The cause of this is not known, although it is possible to speculate that the partial volume of the initial state *t*-butyl chloride depends little on the solvent at this pressure.

5. The minimum in the constant-pressure activation enthalpy and entropy as a function of solvent composition is approximately halved if the constant-volume activation energy and entropy are considered. The minima here do not appear to be entirely an artifact of using constant-pressure conditions, as they do for several other reactions.

6. The rate constant as a function of pressure cannot be represented by a power series of less than third order. If an empirical equation is required, a rational function of the form $\ln k = (a + bp)/(1 + cp)$ appears to be more suitable than a power series with the same number of parameters. However, the rational function gives a poor value of the activation volume at zero pressure. It is concluded that graphical methods are the best for extracting activation volumes from the rate constants.

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