

has previously been measured by Buchanan and Hamann¹⁰ and by Hyne *et al.*¹⁸ in 80% by volume (0.43 mole fraction) aqueous ethanol and a value of $\Delta V^* = -22$ ml/mole can be derived from both sets of results. The large value of $-\Delta V^*$ found in 0.74 mole fraction acetone and its pronounced decrease with increase in pressure suggest that acetone takes part in the solvation of the transition state in this solvent.

The methanolysis of *t*-butyl chloride in methanol has been measured at atmospheric pressure by Winstein *et al.*²⁰ and our results agree with theirs. David and Hamann²² measured the rate at 36° at pressures up to 15,000 atm, but their

TABLE 2
VOLUMES OF ACTIVATIONS OF REACTIONS LISTED IN TABLE 1

| Reaction | Temp. | ΔV^* (ml/mole) | | | | | |
|----------|-------|------------------------|---------|----------|----------|----------|----------|
| | | 1 atm | 500 atm | 1000 atm | 1500 atm | 2000 atm | 3000 atm |
| (1)† | 39.8° | -5.8 | -5.2 | | -4.0 | | -3.7 |
| | 49.7 | -7.2 | -6.1 | | -4.3 | | -3.7 |
| | 54.7 | -7.8 | -6.8 | | -5.3 | | -4.0 |
| (2) | 65.0 | -12 | | -7 | | -4 | -2 |
| (3) | 30.0 | -14.5 | | -10.0 | | -7.5 | -6.5 |
| (4) | 30.0 | -11.5 | | -7.5 | | -5.5 | -4.5 |
| (5) | 25.1 | -10.5 | | -8.0 | | -5.5 | -4.0 |
| (6) | 25.1 | -20 | | -15 | | -11 | |
| (7) | 25.0 | -16.5 | -14.8 | -11.8 | | | |
| (8) | 50.0 | -24 | | -15 | | -8 | |
| (9) | 25.0 | -20 | | -14 | | -9 | -6 |
| | 40.0 | -20 | | -14 | | -10 | -7 |
| (10) | 60.0 | -32 | | | -18 | | -6 |
| (11) | 25.0 | -31 | | -20 | | -13 | -10 |
| | 50.0 | -33 | | -21 | | | |
| (12) | 32.1 | | | | | | |

† See numbered headings in Table 1 for description of reactions.

lowest pressure measurement was at 5000 atm and does not allow calculation of ΔV^* at low pressures. Their results are not inconsistent with our low pressure results and show that even at the highest pressures ΔV^* is still negative for this S_N1 reaction. David, Hamann, and Lake²³ also measured the rate of the methanolysis of ethyl chloride in methanol at pressures up to 30,000 atm at 65°, and our measurements at 850 atm fit in with their lowest pressure value at 3000 atm and permit the calculation of a low pressure value of ΔV^* .

The alkaline cyclization of 4-bromobutylcatechol monoether (BBCE) in methanol proceeds by a different mechanism to the other reactions¹ discussed in this paper.

The rate-determining nucleophilic attack by the negatively charged oxygen on the bromine carrying carbon is preceded by the equilibrium ionization of the

²² David, H. G., and Hamann, S. D., *Trans. Faraday Soc.*, 1954, **50**, 1188.

²³ David, H. G., Hamann, S. D., and Lake, S. J., *Aust. J. Chem.*, 1955, **8**, 285.

phenolic hydrogen. Both the initial and the transition state therefore carry a charge, and the reaction has its bimolecular analogue in the reaction of *n*-butyl bromide with phenoxide ion which was investigated by Brower²⁴ in ethanol. Brower's results give a value of $\Delta V^* = 11$ ml/mole for the linear reaction, while we find $\Delta V^* = 0$ ml/mole for the monomolecular cyclization after allowing for the change of ionization equilibrium with pressure.[†] Such a difference in ΔV^* has been found for the acid-catalysed lactonization of hydroxybutyric acid ($\Delta V^* = -2.7$ ml/mole in water) compared with the acid-catalysed reaction of simple alcohols with acetic acid ($\Delta V^* = -9$ ml/mole).³ For these reactions this difference has been attributed to the exclusion of solvent from the centre of the cyclic transition state,³ and this may also be the case for the cyclization of BBCE. However, this effect would be expected to be smaller rather than greater for the eight-membered ring formed by BBCE than for the five-membered lactone.

DISCUSSION

Gonikberg and El'yanov⁶ have suggested a method of estimating an upper limit to the number of solvent molecules involved in the solvation of a highly polar transition state from the change of ΔV^* with pressure. It is assumed that the solvating molecules are incompressible compared to the bulk solvent, and that the intrinsic volume change²⁵ ΔV_1^* is constant in the pressure range considered. The pressure equivalent to the electrostriction around an ion has been estimated²⁶ to be of the order of 10,000 atm. Although electronic charges may not be fully developed, the electrostriction around the transition state will be similar²⁷ and the above assumption should hold for pressures up to about 3000 atm. One can then express the solvation part of the volume of activation,²⁵ ΔV_2^* as

$$\Delta V_2^* = -n(V_{s,P} - V_{s,10000}) \quad (1)$$

where $V_{s,P}$ is the molar volume of the solvent at pressure P ,

$V_{s,10000}$ is the molar volume of the solvent at $(P+10^4)$ atm, and

n is the number of solvent molecules transferred to the solvation shell as the transition state is formed.

According to this equation, a plot of ΔV^* at various pressures against the molar volume of the solvent at the same pressures should be a straight line with slope $-n$. Our results in water and methanol give such straight lines within the error of ± 1 ml/mole of the value of ΔV^* . Gonikberg and El'yanov have shown the same for a number of Menschutkin reactions in a range of solvents.^{6,28} In pure solvents the volume difference on the right-hand side of equation (1) can be calculated from

[†] Assuming the concentration of base to be constant, it can be shown that the true rate constant k is related to the observed first-order rate constant k' by $k = k'(1 + 1/K[\text{base}])$. The value of K at different pressures was found by measuring k' at different concentrations of base.

²⁴ Brower, K. R., *J. Am. chem. Soc.*, 1963, **85**, 1401.

²⁵ Hamann, S. D., "Chemical Kinetics" in "High Pressure Physics and Chemistry". (Ed. Bradley.) Vol. II. (Academic Press: London 1963.)

²⁶ Hepler, L. G., *J. phys. Chem.*, 1965, **69**, 965.

²⁷ Whalley, E., *J. chem. Phys.*, 1963, **38**, 1500.

²⁸ Gonikberg, M. G., and El'yanov, B. S., *Dokl. Akad. Nauk SSSR*, 1960, **130**, 545.