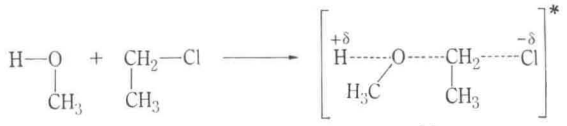
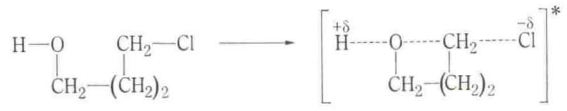
compressibility data and with $P=1$, is found to be 3·6 ml/mole in water, 10 ml/mole in methanol, and 18 ml/mole in acetone at 25°.

It should be possible to find any special solvation effects connected with the formation of a cyclic transition state by comparing the cyclization reaction with analogous bimolecular reactions for which the intrinsic volume change[25] ΔV_I^* can be assumed to be the same. Thus in the transition states (I) and (II) the same bonds are broken and formed and hence ΔV_I^* will be the same for both.



(I)



(II)

There are at least three alternative ways of interpreting the observed difference in ΔV^*.

Although the transition states (I) and (II) are very similar, access of solvent to (I) may be easier than to the more rigid structure (II), and (I) may in fact be more strongly solvated.

The exclusion of solvent from the centre of the cyclic transition state could also account for the difference in volume and has been discussed in some detail by Le Noble[4] and Whalley.[1,3]

A further explanation is suggested by an argument analogous to one used by Kohnstam[19] in discussing the difference in entropy of activation of bimolecular and monomolecular solvolysis reactions. A difference between (I) and (II) is that a solvent molecule has been incorporated in (I) but not in (II). This molecule will have lost the "free volume", which is associated with any molecule in the liquid state, when it became attached to the transition complex. This loss of volume will be in addition to that due to the partial formation of a bond included in ΔV_I^*, and must be about the same as that due to the orientation and "freezing" of a solvating molecule; both are associated with similar loss of translational and vibrational degrees of freedom. In the case of the OH group of 4-chlorobutanol these degrees of freedom are already severely restricted in the initial state and their elimination in the transition state will cause only a small contraction in volume. The total volume change for the formation of (I) should thus be more negative than that for the formation of (II), and the difference should be about the same as the contraction which occurs when one solvent molecule enters the solvent shell.

In Table 2, reaction (1) can be compared with (2), (3), and (4), and reaction (9) with (10) and (11). The difference between ΔV^* for the cyclization of 4-chlorobutanol and ΔV^* for equivalent bimolecular solvolysis reactions is then found to be 4–6

ml/mole in water and 11–12 ml/mole in methanol. By equation (*1*) these differences correspond to the volume lost on transfer to the solvation shell of 1 molecule of methanol or 1·5 molecules of water.

Our present results do not enable us to decide between the alternative interpretations. It would seem that detailed partial molar volume measurements on model compounds would be required to do this.

If one compares the cyclization reaction in water and in methanol by means of equation (*1*) one finds, from the change of ΔV^* with pressure, that in both solvents $n = 2$–$2 \cdot 5$. In spite of the large differences in ΔV^* in the two solvents, the same number of solvent molecules seem to be involved.

The small variation in ΔV^* for the hydrolysis reactions with solvent composition in aqueous ethanol and aqueous acetone is in marked contrast with the large change of ΔS^* which occurs. Thus for the hydrolysis of ethyl bromide in water[15] $\Delta S^* = -5$ e.u., while in aqueous ethanol[29] $\Delta S^* = -25$ e.u. This large difference reflects the entropy gain in water due to disruption of solvent–solvent interactions by the polar transition state; in aqueous ethanol these interactions are already disrupted and the full entropy loss due to solvation is observed. Volume effects associated with these solvent–solvent interactions are thus not nearly as pronounced as the entropy effects. This is also shown by the partial molar volume of water, which changes little when ethanol or acetone are added to it up to a molar fraction of about 0·8. The compression measurements of Stutchbury[30] show that this still holds at 1000 atm.

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[29] Robertson, R. E., *Can. J. Chem.*, 1964, **42**, 1707.
[30] Stutchbury, J. E., *Aust. J. Chem.*, 1956, **9**, 536.