

TABLE 1. Factors contributing to $(\partial\Delta V^*/\partial P)_T^a$

1. Charge	$\frac{Nz^2e^2}{2a_0} \left[\frac{\partial^2 \epsilon_0^{-1}}{\partial P^2} - 2 \left(\frac{\partial \ln a_0}{\partial P} \right) \left(\frac{\partial \epsilon_0^{-1}}{\partial P} \right) + \left(1 - \frac{1}{\epsilon_0} \right) \left(\frac{\partial^2 \ln a_0}{\partial P^2} \right) - \left(1 - \frac{1}{\epsilon_0} \right) \left(\frac{\partial \ln a_0}{\partial P} \right)^2 \right]$
2. Dipole	$\frac{3N\mu^2}{2a_0^3} \left[\frac{\partial^2 \epsilon_0^{-1}}{\partial P^2} - 3 \left(\frac{\partial \ln a_0}{\partial P} \right) \left(\frac{\partial \epsilon_0^{-1}}{\partial P} \right) + \left(1 - \frac{3}{2\epsilon_0} \right) \left(\frac{\partial^2 \ln a_0}{\partial P^2} \right) - \left(1 - \frac{3}{2\epsilon_0} \right) \left(\frac{\partial \ln a_0}{\partial P} \right)^2 \times 3 \right]$
3. Quadrupole	$\frac{5Nq^2}{2a_0^5} \left[\frac{\partial^2 \epsilon_0^{-1}}{\partial P^2} - \frac{10}{3} \left(\frac{\partial \ln a_0}{\partial P} \right) \left(\frac{\partial \epsilon_0^{-1}}{\partial P} \right) + \left(1 - \frac{5}{3\epsilon_0} \right) \left(\frac{\partial^2 \ln a_0}{\partial P^2} \right) - 5 \left(1 - \frac{5}{3\epsilon_0} \right) \left(\frac{\partial \ln a_0}{\partial P} \right)^2 \right]$

$$^a(\partial^2 \ln \epsilon_0/\partial P^2)_T = 67.28 \times 10^{-10}, \text{ ref. 22.}$$

$$(\partial^2 \ln \epsilon_0/\partial P)_T = 46.7 \times 10^{-6}, \text{ ref. 22.}$$

$$\epsilon_0 = 80.2, \text{ ref. 22.}$$

$$(\partial \ln a_0/\partial P)_T = -5 \times 10^{-6} \text{ bar}^{-1}, \text{ ref. 14.}$$

$$(\partial \ln a_0/\partial P^2)_T = 1.2 \times 10^{-9} \text{ bar}^{-2}, \text{ computed from compressibility data in ref. 23.}$$

$$e = 4.8 \times 10^{-10} \text{ e.s.u.}$$

$$\mu = 10 \text{ D (two point charges } +\frac{1}{2}e \text{ and } -\frac{1}{2}e \text{ about } 4 \text{ \AA} \text{ apart).}$$

$$q = 0.2 \times 10^{-24} \text{ e.s.u. (two point charges each } \frac{1}{2}e \text{ that are } 4 \text{ \AA} \text{ apart).}$$

$$z = 1.$$

$$a_0 = 3 \text{ \AA.}$$

$$N = 6.02 \times 10^{23} \text{ mol}^{-1}.$$

TABLE 2. Contributions to $(\partial\Delta V^*/\partial P)_T$ from charge, dipole, and quadrupole

	Term (ml/kbar mol)				$(\partial\Delta V^*/\partial P)_T$ (ml/mol kbar)
	1	2	3	4	
1. Charge	0.3	0.02	3.1	0.06	3.3
2. Dipole	0.1	0.02	5.1	0.19	5.0
3. Quadrupole	0.1	0.0	3.1	0.3	2.8

TABLE 3. Values of $(\partial\Delta V^*/\partial P)_T$ for some organic hydrolysis reactions

Substrate	Temperature (°C)	$(\partial\Delta V^*/\partial P)_T$ (ml/kbar mol)	Reference
Methyl bromide	70.0	5.5	6
Isopropyl bromide	50.0	6.0	6
Benzyl chloride	50.0	2.6	21
Allyl chloride	50.25	1.6	5
β -Methyl allyl chloride	50.25	1	5
<i>trans</i> - γ -Methyl allyl chloride	12.02	4.7	5

tained by this process is separated into contributions from charge, dipole, and quadrupole in Table 1 and evaluated on a term by term basis in Table 2. The calculated value of 5.0 ml/kbar mol for $(\partial\Delta V^*/\partial P)_T$ for a dipolar transition state agrees reasonably well with those for a number of hydrolytic reactions of organic halides, Table 3, whose transition states are thought to be dipolar.

The important contributions to the activation volume for the hydrolysis of organic halides probably arise from (1) an increase in the C—Cl bond length, (2) a contraction due to the possible formation of a new C—O bond to the incoming water, and (3) a contraction of the solvent and the transition state caused by an increased electrostatic interaction with the solvent due to the elec-

tric moments of the transition state. Contributions (1) and (2) may be equated to $\Delta V^*(r)$ and (3) to $\Delta V^*(s)$. In general there is no firm evidence about the relative contributions of these three factors to the overall activation volume (ΔV^*) and hence $(\partial\Delta V^*/\partial P)_T$. Baliga and Whalley (2) estimate that ΔV^* for the hydrolysis of tertiary butyl chloride in water is made up of contributions of +12 and -14 ml/mol from $\Delta V^*(r)$ and $\Delta V^*(s)$, respectively. If this is so we may estimate the value of $(\partial\Delta V^*/\partial P)_T$ on the following basis²

$$[2] \quad (\partial\Delta V^*/\partial P)_T = -\Delta V^*.K$$

and

$$[3] \quad \Delta V^* = \Delta V^*(r) + \Delta V^*(s)$$

therefore

$$[4] \quad (\partial\Delta V^*/\partial P)_T = -\Delta V^*(r).K + \Delta V^*(s).K$$

substituting the above values for $\Delta V^*(r)$ and $\Delta V^*(s)$ estimated by Baliga and Whalley (2), together with the assumed value of K ,² we then have

$$[5] \quad (\partial\Delta V^*/\partial P)_T = (-1.2 \times 10^{-3} \\ + 1.3 \times 10^{-3}) \text{ ml/mol atm} \\ = 0.1 \times 10^{-3} \text{ ml/atm mol}$$

This value is in the range found for this reaction in water (2). On this basis it seems that the pressure dependence of the activation volume must be viewed in terms of the compensation of the two terms in eq. 4. Also it seems likely that the pressure dependence of $\Delta V^*(r)$ may be making a significant contribution to the pressure dependence of the overall activation volume. That is to say that $(\partial\Delta V^*(r)/\partial P)_T \neq 0$, thus its contribution to $(\partial\Delta V^*/\partial P)_T$ may not be ruled out a priori. A theoretical analysis of the factors influencing $(\partial\Delta V^*(r)/\partial P)_T$ is not very straightforward and will not be attempted here. Thus further use will be made of ion-dielectric theory in trying to understand the origin and nature of $(\partial\Delta V^*/\partial P)_T$ as reflected in the behavior of $(\partial\Delta V^*(s)/\partial P)_T$.

There is a marked lack of sensitivity of the activation volume to temperature changes (5, 6, 24–27). Values of $(\partial\Delta V^*/\partial T)_P$ usually lie in the range 0.2 ml/mol deg for a variety of reactions. The implication of this is that $(\partial\Delta V^*/\partial P)_T$ should not be very temperature dependent, if $(\partial\Delta V^*/\partial P)_T$ is simply equal to $-\Delta V^*.K$. On the basis of ion-dielectric theory this behavior must be explained in terms of the changing interaction between the molecule(s) and the solvent with changing temperature. This would result in a change in $\Delta V^*(s)$ and $\Delta V^*(r)$, perhaps less C–Cl elongation as well as C–O formation. Thermodynamically $(\partial\Delta V^*/\partial T)_P = -(\partial\Delta S^*/\partial P)_T$. The complex behavior of $(\partial\Delta S^*/\partial P)_T$ cannot be explained in terms of ion-dielectric theory (6) as has been found for the hydrolysis of methyl and isopropyl bromide in water. Thus we can conclude also that the temperature dependence of the activation volume is difficult to explain quantitatively on this basis. Qualitatively this apparent lack of sensitivity of ΔV^* to temperature may be attributed to the fact that the initial and transition state volumes vary

similarly with respect to temperature. The implication here being that water molecules are being held as tightly in the initial state as in the transition state, which is highly polar. The importance of initial state solvation and its relation to solvent structure has been quite adequately demonstrated by Arnett *et al.* in their work on the partial molal heats of solution in aqueous organic solvents (18).

If terms involving $(\partial^2 \ln a_0/\partial P^2)_T$ are by far the more important in determining the pressure dependence of the activation volume, as is evident from the results in Table 2, then it would be expected that the pressure dependence of the activation volume would be neither temperature nor pressure dependent, if the dielectric constant is very much greater than unity. In this case "a" would not be sensitive to dielectric constant. This lack of sensitivity of $(\partial\Delta V^*/\partial P)_T$ to temperature and solvent is not unknown (5, 20, 21). The temperature sensitivity of this parameter has been discussed earlier. However, the sensitivity of $(\partial\Delta V^*/\partial P)_T$ to solvent may be very large (2, 4, 7, 28), contrary to predictions of ion-dielectric theory as outlined in this paper. Thus it becomes evident that ion-dielectric theory does not totally account for all that is happening in solution under these conditions. Similar conclusions have been reached previously by Baliga and Whalley (2, 28, 29) who observed large variations in the activation volume for reactions which occur without large changes in the interactions with solvent. A detailed analysis of this large variation of the contribution of this interaction with solvent is not known in terms of ion-dielectric theory. Hence most workers have resorted to the approach of Arnett *et al.* (18) and have analyzed the effect of solvent on the activation volume in terms of the solvent effect on initial and transition state partial volumes (2, 20, 21, 32). The result of this approach is that in most cases the variation of partial volume of the initial state is more responsible for the variation of the activation volume with solvent composition than the transition state (2, 20, 30). In some cases the variation of the partial volume of the transition state may be more responsible (20). It also seems likely that when there is no variation of the activation volume with solvent that both the initial and transition state partial volumes are undergoing similar changes as solvent composition changes (21). In all cases