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The Pressure Dependence of the Activation Volume

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The analysis of the pressure dependence of the activation volume, $(\partial\Delta V^*/\partial P)_T$, in terms of ion-dielectric theory has been performed. The values of $(\partial\Delta V^*/\partial P)_T$ obtained on this basis are in good agreement with those found for the hydrolyses of organic halides. These results further indicate that contributions to $(\partial\Delta V^*/\partial P)_T$ arising from compression of the molecule or ion are by far more important than those arising from electrostriction of the dielectric medium. Also, the effects of quadrupole moments can be very important since the contributions from this are as great as those from dipole moments. Nevertheless it seems that ion-dielectric theory gives only a partial answer to the question of the nature and origin of $(\partial\Delta V^*/\partial P)_T$. Apparently, the contributions from solvent structure, unaccounted for on this model, cannot be ignored.

Une analyse de la dépendance du volume d'activation par rapport à la pression, $(\partial\Delta V^*/\partial P)_T$, a été réalisée en fonction de la théorie ion-diélectrique. Les valeurs de $(\partial\Delta V^*/\partial P)_T$ obtenues sur cette base, sont en bon accord avec celles trouvées pour l'hydrolyse des halogénures organiques. Ces résultats indiquent de plus que les contributions à $(\partial\Delta V^*/\partial P)_T$ provenant de la compression des molécules ou des ions sont de beaucoup plus importantes que celles provenant de l'électrostriction du milieu diélectrique. De plus, les effets des moments quadripolaires peuvent être très importants puisque leurs contributions sont aussi grandes que celles des moments dipolaires. Néanmoins, il semble que la théorie ion-diélectrique ne donne qu'une réponse partielle à la question de l'origine et de la nature de $(\partial\Delta V^*/\partial P)_T$. Apparemment, les contributions dues à la structure du solvant, non interprétées dans ce modèle, ne peuvent être ignorées.

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Recently some attention has been focussed upon finding an analytical function which best expresses the pressure dependence of reaction rates (1-3). This situation is essential since the activation volume, ΔV^* , is pressure dependent (1-7). The pressure dependence of the activation volume, $(\partial\Delta V^*/\partial P)_T$, for the hydrolytic reactions of organic halides usually lies in the range 0 to +10 ml/kbar mol (1-7). This has been attributed to differences in the compression of the ground

state and transition state (1, 4, 9).² However, this does not give as clear a picture of the factors contributing to ΔV^* and the associated parameter $(\partial\Delta V^*/\partial P)_T$ as is desirable. Benson and Berson

²A referee has calculated $(\partial\Delta V^*/\partial P)_T$, assuming the initial and transition state compressibilities to be the same (K), on the following basis

$$(\partial\Delta V^*/\partial P)_T = -\Delta V^* \times K$$

If $\Delta V^* = -15$ ml/mol and $K = 100 \times 10^{-6}$ bar⁻¹, then $(\partial\Delta V^*/\partial P)_T = 1.5$ ml/kbar mol. This is in the range found for the reactions being considered in this paper.

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(8) estimate a 50% change in ΔV^* over a 3 kbar range. This would result in $(\partial\Delta V^*/\partial P)_T$ in the expected range. However, this estimate takes into account only the electrostriction of the solvent and any compression of the cavity containing the initial and transition states is taken to be negligibly small. Walling and Tanner (9) have pointed out that if the transition state is not a volume extremum, pressure displaces the transition state along the reaction-coordinate. A theoretical treatment of the pressure dependence of the activation volume then becomes particularly difficult. They further state that only for a small group of non-ionic reactions will the transition state have compressibility factors of normal molecules. These conclusions have been amply refuted by Benson and Berson (10) who have shown that perturbations of the parameters ΔV^* and ΔF^* are negligibly small in the pressure ranges commonly employed, even for extremely compressible transition states. It seems, therefore, that an estimate of the pressure dependence of the activation volume taking into consideration a larger number of factors is wholly desirable. This will then allow a clearer understanding of the nature and origin of $(\partial\Delta V^*/\partial P)_T$ as well as providing useful information about the transition states involved. Results will be discussed in terms of the hydrolytic reactions of organic halides for which there is by far the largest body of accurate data.

The activation volume may be split up into two terms, $\Delta V^*(r)$ and $\Delta V^*(s)$ (11). $\Delta V^*(r)$ is the change in the van der Waals volume when the transition state is formed, that is the volume change due directly to the changing interaction of the reacting molecules with each other. The main contributions to it are due to changes in bond length, changes in the non-bonded interactions within the molecules, and changes in electron densities around nuclei. $\Delta V^*(s)$ is the volume change due directly to the changing interaction of the reacting molecules with the solvent. These changes are not all localized in the solvent but may also be localized within the molecules (11, 14, 15). As yet there is no adequate molecular theory which is both accurate and detailed enough to treat the interaction of a molecule with its solvent. By far the most applicable is that of Whalley (14). In this model the molecule is considered to be in a spherical cavity in a continuous dielectric medium. The cavity is both expansible and compressible and has a dielectric constant equal to

unity. If the dielectric constant of the medium is very much greater than unity, the electrostatic volume of solvation, $\Delta V^*(s)$, due to the changing electrostatic interaction between the molecule and the dielectric (solvent) is given by eq. 1,

$$\begin{aligned}
 [1] \quad V^*(s) = & (Nz^2e^2/2a_0) [(\partial\epsilon_0^{-1}/\partial P) + \\
 & (1 - 1/\epsilon_0)(\partial \ln a_0/\partial P)] \\
 & + (3N\mu^2/2a_0^3) [(\partial\epsilon_0^{-1}/\partial P) + \\
 & (1 - (3/2\epsilon_0))(\partial \ln a_0/\partial P)] \\
 & + (5Nq^2/2a_0^5) [(\partial\epsilon_0^{-1}/\partial P) + \\
 & (1 - (5/3\epsilon_0))(\partial \ln a_0/\partial P)]
 \end{aligned}$$

for an ion of charge ze , with point dipole (μ) and quadrupole moment (q) at the center. $\Delta V^*(s)$ is the sum of terms due to charge, dipole, and quadrupole. $\Delta V^*(s)$ can be further split up into two terms. These terms are $\Delta V^*(c)$ and $\Delta V^*(e)$. $\Delta V^*(c)$ is the change in volume of the cavity (molecule) caused by the force, resulting from the electrostatic interaction with the dielectric (solvent), exerted on it by the dielectric (solvent) and represented by terms in $(\partial \ln a_0/\partial P)$. These changes are not localized in the solvent but in the cavity (molecule). $\Delta V^*(c)$ is not an electrostriction of the cavity (molecule) which is zero if the dielectric constant is unity. $\Delta V^*(e)$ is the change in the volume of the dielectric (solvent). This change is localized in the solvent and is represented by terms in $(\partial\epsilon_0^{-1}/\partial P)$. According to Whalley's analysis (14) compression of the cavity contributes more to the electrostatic volume of solvation than does electrostriction of the dielectric (2). Whalley was also able to show that quadrupole moments may be important in some reactions.

Let us assume that the part of the activation volume $\Delta V^*(r)$ is not significantly pressure dependent, as would be expected if a critical amount of change in the bond length(s) is needed for reaction. Then the variation of the activation volume with pressure must be explained in terms of the variation of $\Delta V^*(s)$ with respect to pressure. In fact it has long since been recognized that solvation effects can be very important in determining the effects of pressure on reaction rates (13, 16, 17). An estimate of this pressure dependence of the activation volume, $(\partial\Delta V^*/\partial P)_T$, may be obtained by differentiating Whalley's expression for $\Delta V^*(s)$, eq. 1, with respect to pressure. The resulting expression for $(\partial\Delta V^*/\partial P)_T$ ob-

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

$(\partial\Delta V^*/\partial P)_T$ undergoes parallel changes (30). The implication of all this is that solvent structure is playing a part in influencing this kinetic behavior. This has been illustrated in other studies (18, 19, 30). However, at present a quantitative estimate of the extent of this cannot be made.

It is worthwhile to mention that in all of those studies quoted in the previous paragraph involved aqueous-organic solvent mixtures. It is known that the structural nature of these systems is quite complex. This complexity is reflected in the kinetics in these systems. However, when the variation of activation volume with solvent is related to a change from one pure solvent to another (*e.g.* ethanol, methanol, etc.), Eckert and co-workers (31-33) have found that then the variation of ΔV^* with solvent can be explained on the basis of ion-dielectric theory. All of the solvents involved in these studies are structurally similar, so structural influences are ruled out and a less complicated behavior results.

One further conclusion worth mentioning here, is the fact that the contributions to the pressure dependence of the activation volume from quadrupole moments can be quite significant and cannot be ignored. The contribution from quadrupole moments is about equal to that from dipole moments, Table 2.

To summarize, we may say that although these calculations are not very refined mainly because of the rough estimates of the parameters involved, that ion-dielectric, as applied here, does afford a clearer understanding of the nature and origin of the pressure dependence of the activation volume. Valuable information about the transition state can also be extracted on this basis. However, it may be constantly borne in mind that the contribution to ΔV^* and $(\partial\Delta V^*/\partial P)_T$ arising from structural properties of the aqueous binary solvent must be considered.

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1. H. S. GOLINKIN, W. G. LAIDLAW, and J. B. HYNE. *Can. J. Chem.* **44**, 2139 (1966).
2. B. T. BALIGA and E. WHALLEY. *Can. J. Chem.* **48**, 528 (1970).
3. J. KOSKIKALLIO and E. WHALLEY. *Trans. Faraday Soc.* **55**, 813 (1959).
4. K. J. LAIDLAW and R. MARTIN. *Int. J. Chem. Kinet.* **1**, 113 (1969).
5. A. B. LATEEF and J. B. HYNE. *Can. J. Chem.* **47**, 1369 (1969).
6. B. T. BALIGA and E. WHALLEY. *J. Phys. Chem.* **73**, 654 (1969).
7. J. B. HYNE, H. S. GOLINKIN, and W. G. LAIDLAW. *J. Am. Chem. Soc.* **88**, 2104 (1966).
8. SIDNEY W. BENSON and JEROME A. BERSON. *J. Am. Chem. Soc.* **84**, 152 (1962).
9. CHEVES WALLING and DENNIS D. TANNER. *J. Am. Chem. Soc.* **85**, 612 (1963).
10. SIDNEY W. BENSON and JEROME A. BERSON. *J. Am. Chem. Soc.* **86**, 259 (1964).
11. E. WHALLEY. *Adv. Phys. Org. Chem.* **2**, 93 (1964).
12. M. G. EVANS and M. POLANYI. *Trans. Faraday Soc.* **31**, 875 (1935).
13. S. D. HAMANN. *Physicochemical effects of pressure*. Butterworths Scientific Publications, London, 1957.
14. E. WHALLEY. *J. Chem. Phys.* **38**, 1400 (1968).
15. E. WHALLEY. *Ber. Bunsenges. Phys. Chem.* **70**, 957 (1966).
16. A. L. TH. MOESVELD. *Z. Phys. Chem.* **105**, 455 (1923).
17. A. L. TH. MOESVELD and W. A. T DE MEESTER. *Verlag Gevone Vergader Afdell Natuurk. Ned. Akad. Wetenschap*, **36**, 827 (1927).
18. E. M. ARNETT, W. G. BENTRUDE, J. J. BURKE, and P. M. DUGGELBY. *J. Am. Chem. Soc.* **87**, 1541 (1965). E. M. ARNETT, P. McC. DUGGELBY and J. J. BURKE. *J. Am. Chem. Soc.* **85**, 1350 (1963). E. M. ARNETT, W. G. BENTRUDE, and P. McC. DUGGELBY. *J. Am. Chem. Soc.* **87**, 2048 (1965).
19. F. FRANKS and D. J. G. IVES. *Q. Rev.* **20**, 1 (1966).
20. DIGBY D. MACDONALD and J. B. HYNE. *Can. J. Chem.* **48**, 2494 (1970).
21. D. L. GAY and E. WHALLEY. *Can. J. Chem.* **48**, 2021 (1970).
22. B. B. OWEN, R. C. MILLER, C. E. MILLER, and H. L. COGAN. *J. Phys. Chem.* **65**, 2065 (1961).
23. E. A. MOELWYN-HUGHES. *Physical chemistry*. 2nd revised ed. Pergamon Press, N.Y., 1961, pp. 323, 331.
24. C. WALLING and H. S. SCHUGAR. *J. Am. Chem. Soc.* **85**, 607 (1963).
25. K. J. LAIDLAW and D. CHEN. *Trans. Faraday Soc.* **54**, 1026 (1963).
26. J. KISKIKALLIO and E. WHALLEY. *Can. J. Chem.* **37**, 783 (1959).
27. MOYRA J. MACKINNON, A. B. LATEEF, and J. B. HYNE. *Can. J. Chem.* **48**, 2025 (1970).
28. B. T. BALIGA and E. WHALLEY. *Can. J. Chem.* **43**, 1835 (1964).
29. B. T. BALIGA, R. J. WITHEY, and E. WHALLEY. *Trans. Faraday Soc.* **61**, 517 (1965).
30. H. S. GOLINKIN, I. LEE, and J. B. HYNE. *J. Am. Chem. Soc.* **89**, 1307 (1967).
31. R. A. GRIEGER and C. A. ECKERT. *Trans. Faraday Soc.* **66**, 2579 (1970).
32. C. A. ECKERT. *Ind. Eng. Chem.* **59**(9), 20 (1967).
33. J. R. MCCABE, R. A. GRIEGER, and C. A. ECKERT. *Ind. Eng. Chem. Fund.* **9**(1), 156 (1970).