

The Pressure Dependence of the Activation Volume

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Received September 8, 1970¹

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.

Canadian Journal of Chemistry, 49, 3231 (1971)

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.

¹Revision received May 10, 1971.

(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-