COMMENTS

Comment on “Phantom Activation Volumes”

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It has long been known that chemical reactions in solution are generally accompanied by changes in volume, ΔV, which are called their reaction volumes. Multiplied by the pressure P, these reaction volumes give rise to work terms, $P\Delta V$, which are a part of the free energy change of the reaction

$$\Delta G = \Delta E + P\Delta V - T\Delta S \qquad (1)$$

The free energy term is in turn related to the equilibrium constant for the reaction

$$\Delta G = -RT \ln K \qquad (2)$$

Since $(\partial G/\partial P)_T = V$, we have

$$(\partial \ln K/\partial P)_T = - \Delta V/RT \qquad (3)$$

The validity of eqs 1−3 has never been in dispute. The reaction volume can be determined by appropriate summing of the partial volumes of the participating molecules, by means of dilatometry, or via the effect of pressure on the equilibrium constant. The reaction volume has been determined for innumerable reactions; in many instances, this was done in two or even all three of the possible ways.[1−4]

It has been surmised since the days of van‘t Hoff[5] and shown, first by Röntgen,[6] that the rates of reactions in solution are also subject to pressure effects, for which eq 4 holds

$$(\partial \ln k/\partial P)_T = - \Delta V^*/RT \qquad (4)$$

where ΔV^* is known as the activation volume. This expression was put on a solid basis by Eyring,[7] who deduced it from his equation for absolute rates[8]

$$k = (RT/Nh) \exp(-\Delta G^*/RT) \qquad (5)$$

Eyring’s theory rests on the assumptions that the reactants must surmount a free energy barrier and that the so-called transition state is in equilibrium with the reactants. These theoretical underpinnings have served generations of mechanistic chemists very well. Of course, there are areas in chemistry where Eyring’s assumptions are not justified and where the kinetics must accordingly not be thrust into the framework of absolute rate theory; these areas include, for example, reactions in which tunneling makes an important contribution or in which the barrier is so low that equilibrium between reactants and transition state is no longer a factor relevant in the magnitude of rates.

Unlike the reaction volume, the activation volume can be determined in only one way, namely, by measuring the effect of pressure on the rate constant. The activation volume has been evaluated in this way for several thousand reactions, and the findings have proved to be a useful gauge in the elucidation of reaction mechanisms.[1−3,9]

ΔV^* values can be dissected in terms of several contributions, the most important of which are due to the following:

(a) The breaking and making of bonds. When bonds are broken, the atoms which were previously bound at covalent bond distances now recede to van der Waals separations, and the opposite happens in bond making. A simple example of bond breaking is furnished by the decomposition of peroxides to give free oxy radicals; the rates are retarded by pressure, and substantial, positive activation volumes are found.[9a,10] The propagation step in polymerization is an example of bond making: in that case, the activation volume is negative.[11]

(b) Changes in polarity. The most severe of these changes occur in ionization and neutralization processes. The ions strongly polarize and attract solvent molecules (electrostriction[12]), and the resulting contractions are generally even larger than the expansion due to bond breaking. Thus, solvolysis rates are always enhanced despite the bond cleavage. Very large negative values are encountered when both new bonds and ionic charges are formed, as is the case, for example, in the zwitterion formation from vinyl ethers and TCNE.[13]

(c) Changes in interstitial and thermal expansion volume. The hard sphere model of molecules leaves some fraction of the space available unoccupied, and the thermal expansion tells us that some space is required by molecules to exercise their thermal motions. These changes and their corresponding contributions to ΔV^* have been discussed elsewhere.[14] In recent years, Klärner[15] has attempted to assess them in cycloaddition reactions so as to give a truer picture of the volume changes due to the formation of new bonds. These refinements have not forced any reassignments of mechanism, however.

Changes in viscosity have in certain cases also been observed to affect activation volumes. Prominent among them are those reactions which are diffusion-limited. Since pressure causes a large increase in viscosity, such reactions are very severely retarded by pressure. A well-known example is the termination step in free-radical polymerization.[11] Although a bond is formed and the volume reduced thereby, the highly viscous medium inhibits the encounter of radicals, and the formal value of ΔV^* for this step is therefore large and positive. Furthermore, reactions which are not diffusion-limited under ambient conditions may become so at high pressure. Hamann has described several S_N2 displacement reactions which are subject to normal accelerations at low pressures but which abruptly become severely retarded when the pressure reaches values at which diffusion control begins to limit the rate.[16] It is important to realize that diffusion control is always characterized by a positive contribution to ΔV^*. The mechanistic significance of this in bimolecular reactions is not hard to see; a molecule cannot change its location without open space being made available first. It may be noted that unimolecular reactions are sometimes also found to be affected by viscosity;[17] suffice it here to say that in all of these cases also, the reaction rates are suppressed by increasing viscosity.

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A new proposal concerning viscosity and its role in pressure-induced changes in reaction rates has been published by Firestone.[18] He reports that certain pericyclic reactions conducted in *n*-alkane solvents are mildly accelerated as the number of carbon atoms in the solvent molecules is raised.[19] A similar effect was observed when comparisons of such reactions in various glyme solvents were made.[20] Firestone assumes that these accelerations are a direct consequence of the changes in viscosity and extrapolates further that since pressure raises solvent viscosities, a part of the pressure-induced rate accelerations of these reactions is due to viscosity changes. He calls this part a "phantom activation volume" (PAV) and proceeds to estimate that it can "range up to 61%". His abstract states that ". . . we now demonstrate that high pressure accelerates some bond-making reactions in an additional, nonvolume-related way, through its elevation of solvent viscosity". Earlier, the same Author stated that ". . . activation and reaction volume data are not useful as criteria of the Diels-Alder mechanism" and, hence, that at least part of the evidence claimed[21] as support for the concerted nature of cycloaddition is invalid.

We now state categorically that the conjecture of a pressure effect which is "nonvolume-related" is fundamentally false if the transition state theory is valid. No matter what the origin of the pressure effect on the rate of a reaction may be, the derivative of the free energy with respect to pressure at constant temperature is a volume term, which has the dimension of volume and which is in no way imaginary. The correlation between reaction rate constants and the molecular weights within homologous series of solvents, if true, needs to be studied with a view of finding which solvent property is responsible. Several possibilities come to mind; among them are the dielectric constant, surface tension, conformational population changes, and so on.[22] The most likely responsible factor, in our opinion, is the so-called internal pressure, $(\partial E/\partial V)_T$, a term which is included in the thermodynamic equation of state. There have been occasional suggestions in the literature that this property may be part and parcel of the solvent effects on the rates of many reactions;[23] there is little question that a high internal pressure helps accelerate reactions with negative activation volumes. But even if, indeed, the viscosity is responsible, it would only mean that there is apparently a diffusion process which is facilitated by reduced volume, difficult though that may be to imagine. It would certainly not mean that such a diffusion effect is not represented in the work term ($P\Delta V^*$).

Accepting the PAV conjecture leads to several untenable extrapolations. For example, if a diligent search were to turn up evidence for a similar solvent effect on equilibrium constants, the concept of "phantom volumes" should then presumably have to be extended to reaction volumes as well. The validity of the thermodynamic eq 3 would thus be explicitly rejected. Furthermore, we note that the viscosity of liquids is sensitive not only to pressure but also to temperature: it generally diminishes with rising temperatures. Should we now "correct" the temperature-induced rate accelerations by adding phantom entropies and enthalpies to the values calculated in the traditional way? To sum up, the claim that part of the activation volume is not real implies that the Eyring equation is not valid for any of the pericyclic reactions listed in his Tables 1−4,[19] that the entropy and/or enthalpy of activation also contain a phantom element, and that equilibrium constants must be independent of the type of solvent effects he has encountered in kinetics experiments.

We trust that raising these questions will encourage reconsideration by anyone who thinks of using "phantom activation volumes" to "correct" literature values and use the results as the basis on which to postulate phantom intermediates in pericyclic reactions considered to be concerted hitherto. We hope that these comments, with which we end our concern with the PAV proposal, will help to clarify and illuminate its true nature.

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(23) The melting point might be mentioned here to illustrate the idea that a correlation does not prove cause and effect. Melting points show regular increases with molecular weights within homologous series, and they also rise with pressure. But this hardly means that one should attribute the rising rates of reactions under pressure to the changes in solvent melting point and proceed to "correct" the rate constants accordingly.

(24) For nonpolar liquids such as those used by Firestone, the internal pressure is closely approximated by the cohesive energy density, defined as $\Delta E_{\mathrm{vap}}/V_{\mathrm{M}}$; this term ranges from 1 to 10 kbar. See, for example, ref 9a and Dack, M. J. R. *Chem. Soc. Rev.* **1975**, *4*, 211. We plan to address this matter further in a future publication.