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bar^{-2}

0.012 and a highly
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n was fitted with the

^{6} bar^{-1}

$$c = -(146 \pm 8) \times 10^{-9} \quad \text{bar}^{-2}$$

$$d = (19.7 \pm 2) \times 10^{-12} \quad \text{bar}^{-3}$$

with a standard deviation of 0.0028.

The quadratic eq. [11] is clearly not useful. The cubic equation with four parameters fits about as well as eq. [10] with three parameters, and might have slightly more nearly random deviations. Equations [10] and [11] and the cubic equation yield activation volumes of -26.7, -16.7, and -21.6 cm^3 mole^{-1}, respectively. The last value is the only one that is even close to the value of $-21.5 \pm \sim 1$ cm^3 mole^{-1} determined from Fig. 2. The large difference in the values obtained from eq. [10] and the cubic, although both equations are moderately good fits to the original data, cautions against too great reliance on fitted equations. An attempt (33) to use another empirical equation does not give reliable volumes of activation at zero pressure (17).

It is concluded, therefore, that while the power series is not as good as eq. [10] in fitting log k against pressure for the reaction considered provided the same number of parameters is used, it gives a better activation volume if a larger number of parameters is used. It seems likely that the method used in Fig. 2 is the most reliable way of obtaining the activation volume.

Summary

1. The activation volumes for the spontaneous solvolysis of *t*-butyl chloride in 0, 10, 25, and 40% v/v ethanol in water at 0 °C are -2.0, -7.0, -13.2, and -21.5 cm^3 mole^{-1}. In pure water, the small value is a result of the expansion in the transition state due to the lengthening of the C—Cl bond and the opposing contraction due to the changing interaction with the solvent when the transition state is produced. Analogy with the activation volumes for the unimolecular decomposition of ions, and with the volume of formation of zwitter-ions of glycine and other amino acids supports this view.

2. Most of the volume of formation of glycine zwitter-ion, which is -14 cm^3 mole^{-1}, appears to be due to the compression of the zwitter-ion by the dipole–solvent interaction. Electrostriction of the solvent contributes only a small part.

3. The effect of solvent on the activation volume is of course largely caused by the changing interaction with solvent when the transition state is produced. It cannot be accounted for by the solvation of the transition state on the basis of the usual dipole-in-dielectric theory. It is possibly due in part to the effect of solvent on the partial volume of *t*-butyl chloride, by analogy with Golinkin, Lee, and Hyne's analysis of similar effects of solvent on the activation volume for the solvolysis of benzyl chloride. Unfortunately, experimental verification of this speculation will not be easy.

4. At 3 kbar, the activation volume appears to be little dependent on the pressure. The cause of this is not known, although it is possible to speculate that the partial volume of the initial state *t*-butyl chloride depends little on the solvent at this pressure.

5. The minimum in the constant-pressure activation enthalpy and entropy as a function of solvent composition is approximately halved if the constant-volume activation energy and entropy are considered. The minima here do not appear to be entirely an artifact of using constant-pressure conditions, as they do for several other reactions.

6. The rate constant as a function of pressure cannot be represented by a power series of less than third order. If an empirical equation is required, a rational function of the form $\ln k = (a + bp)/(1 + cp)$ appears to be more suitable than a power series with the same number of parameters. However, the rational function gives a poor value of the activation volume at zero pressure. It is concluded that graphical methods are the best for extracting activation volumes from the rate constants.

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