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Effect of pressure on the solvolysis of benzyl chloride in glycerol–water mixtures[1]

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The effect of pressure up to 1.6 kbar on the rate of solvolysis of benzyl chloride in 0 to 75% v/v glycerol–water has been measured at 50 °C. The volume of activation is $-10.7 \pm \sim 0.4$ cm^3 mole^{-1}, essentially independent of solvent composition. Therefore, the partial volumes of both benzyl chloride and the transition state depend on solvent composition in the same way. The constant-volume energy and entropy of activation are simple functions of the solvent composition, and resemble the constant-volume parameters in ethanol–water mixtures. It is concluded that constant-volume conditions are probably more appropriate than constant-pressure conditions for discussing the solvent dependence of these solvolyses.

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Introduction

The constant-pressure enthalpy and entropy of activation for the solvolysis of benzyl chloride vary much less with composition in aqueous glycerol than in aqueous ethanol (1), and in particular, the minima so frequently observed in similar systems are almost absent. The constant-volume energy and entropy of activation for the reaction in aqueous ethanol have no minimum as a function of solvent composition (2), and other reactions behave in similar ways (see ref. 1 for a summary). These and related observations have lead to the suggestion that some of the complexity of the variation of the constant-pressure activation parameters for reactions in aqueous organic solvents is directly connected with the large variation in the thermal expansivity of the solvent with composition. The larger the thermal expansivity, the more the interaction of the initial and transition states with the solvent will change with temperature. This changing interaction with temperature contributes a term to the constant-pressure enthalpy and entropy of activation that is absent in the constant-volume energy and entropy of activation.

The thermal expansivity of aqueous glycerol is almost independent of composition near 50 °C, and consequently there should be no contribution to the composition dependence of the constant-pressure parameters of activation of reactions carried out in it arising from a composition-dependent thermal expansion. This explains why the constant-pressure parameters for the solvolysis of benzyl chloride depend much less on composition in aqueous glycerol than they do in aqueous ethanol (1).

In order to complete this work it is clearly desirable to measure the constant-volume parameters for benzyl chloride in aqueous glycerol, and this paper reports the results.

Experimental

The materials and techniques were those used previously (1) except for the high-pressure techniques. The conductimetric cells were similar to those described by Baliga and Whalley (3) except that they were small enough that two could be fitted into the pressure vessel. They were made of Pyrex glass, about 80 mm long and 20 mm o.d. and had a capacity of about 20 cm^3. The cells had holes at the lower end and were immersed in mercury in a Teflon cup to prevent a short-circuit to ground. Mercury flowed into the cell to transmit the ambient pressure.

Electrode polarization was eliminated by a light deposit of platinum black; the conductance of millimolar hydrochloric acid differed by $\sim 0.02\%$ at 0.4 and 1 kc s^{-1}. The cells were cleaned with hot concentrated nitric acid, washed thoroughly with distilled water, and treated with 0.1 *M* hydrochloric acid at 100 °C until the conductance of millimolar hydrochloric acid at 50 °C remained constant within 0.1% for 2 days. The conductance was measured with a General Radio catalogue number 1680-A automatic capacitance–conductance bridge and digital read-out as described previously (1).

Results

The rate constants are summarized in Table 1 and are plotted in Fig. 1. The volumes of activation were determined both from the slopes of the lines of Fig. 1 and by plotting mean volumes of activation $\Delta V^{\ddagger}$ between two pressures, given by

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