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Rate of Reaction

REACTION KINETICS AT 30000 ATMOSPHERES*

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In this note we describe some measurements of the rate of solvolysis of ethyl chloride in pure methanol at several pressures up to 30000 atm. This pressure is almost twice as great as any hitherto applied in kinetic measurements. We have made the experiments to see whether any new chemical effects appear in the range 15000–30000 atm.

We selected methanol and ethyl chloride as the reactants for the following reasons: (i) it was essential that the reaction mixture should not solidify under compression; methanol is the only highly polar hydroxylic solvent which is still liquid at 30,000 atm, (ii) ethyl chloride is sufficiently unreactive to give a manageably slow rate of reaction over the whole pressure range. The reaction proceeds by the first-order S_N2 mechanism (Ingold 1953)

$$CH_3{-}\overset{|}{O}{-}H \;+\; Cl{-}CH_2{-}CH_3 \rightarrow \left[CH_3{-}O\overset{\delta+}{\cdots}H\cdots\overset{\delta-}{Cl}\cdots CH_2{-}CH_3\right] \rightarrow H^+ + Cl^- + CH_3{-}O{-}CH_2{-}CH_3, \quad \ldots\ldots\ldots\ldots\ (1)$$

with, perhaps, a small amount of side-reaction producing ethylene. The transition state, shown in brackets in (1), is more polar than the initial state, and, from our earlier considerations of the effects of pressure on the solvation free energies of electrically charged groups (Buchanan and Hamann 1953) we expected the reaction to be greatly accelerated by pressure. We found experimentally that it was accelerated by a factor of 1200 at the highest pressure. The results are given in Table 1.

Figure 1 shows that $\log_{10}(k_p/k_1)$ varies smoothly with the pressure, much in the manner of our earlier results to 15,000 atm (David and Hamann 1954). There is no strikingly new behaviour at the higher pressures.

Experimental

(*a*) *Apparatus.*—The pressures were produced by using a hydraulic press to force a piston into a massive steel cylinder containing the pressure fluid. The method was similar to that employed in our earlier measurements to 15000 atm (David and Hamann 1954), but some modifications were needed to reach 30000 atm.

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