

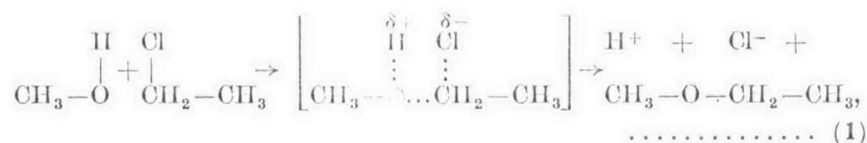
Rate of Reaction

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 manageable slow rate of reaction over the whole pressure range. The reaction proceeds by the first-order S_N2 mechanism (Ingold 1953)



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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TABLE I
EFFECT OF PRESSURE ON THE METHANOLYSIS OF ETHYL CHLORIDE IN PURE METHANOL
AT 65 °C

Pressure, p (atm)	Reaction Time (sec)	Percentage Reaction*	First-Order Rate Constant $10^3 k$ (sec^{-1})	$\frac{k_p^\dagger}{k_1}$
1	57600 \ddagger	4 \ddagger	4.7	1
3000	90000	3	37	7.9
10000	21600	6	290	62
12500	20700	11	510	109
15000	14400	9	630	134
17500	12600	14	1000	210
20000	10800	16	1560	330
23200	3600	8	2300	490
25100	5400	13	2600	550
27500	1800	6	3400	720
30600	1800	10	5700	1210

* Measured as hydrochloric acid.

† This is the ratio of the rate constant at the pressure p to that at 1 atm.

‡ These two columns list typical results, not all the experimental data.

Firstly, the pressure vessel A (Fig. 2) was given external support in the manner devised by Bridgman (1936). It was made in the form of a cone, of very acute angle, fitting closely into a similar conical hole in a steel supporting ring B . The thrust of the piston C not only produced the internal pressure in A

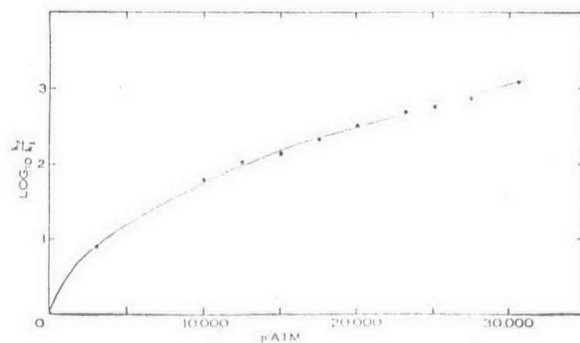


Fig. 1.—The pressure-dependence of the rate of methanolysis of ethyl chloride.

but also forced this vessel into the supporting ring and produced a pressure at its outer surface equal to half the internal pressure.

Secondly, since the limit of the crushing strength of steel is about 25000 atm, it was necessary to make the piston of "Carboloy"* which has a crushing

* "Carboloy" is the trade name for tungsten carbide cemented in cobalt. The grade used was No. 883.

strength of 50000–60000 atm. To ensure that the thrust was applied axially, the piston was mounted in a push-rod *D*, of larger diameter, guided by a cap *E* as used by Poulter (1932). The push-rod was actuated by a 25-ton hydraulic press.

Thirdly, the “unsupported area” seal was modified as suggested by Bridgman (1937*a*), in order to overcome the “pinching-off” effect (Bridgman 1912) in the mushroom stem. Bridgman reported that no difficulty was experienced from failure of the spacing piece *F*, but in our apparatus this proved

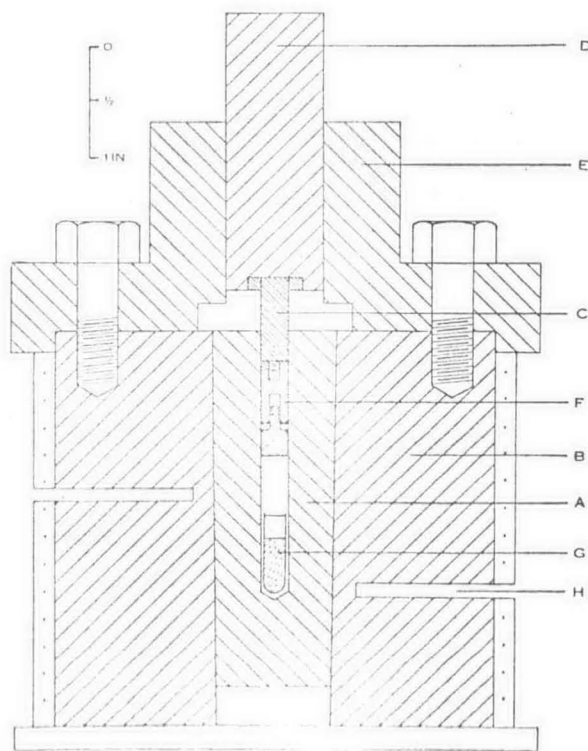


Fig. 2.—The high pressure apparatus.

to be the weakest part. Several types of steel were tried, the most successful being Eagle and Globe “Ultra Capital Plus One” tool steel, heat treated to extreme hardness. Even with this steel, failures occurred above 25000 atm.

The materials used for the other parts of the apparatus were as follows. The pressure vessel *A* and supporting ring *B* were of “Comsteel R4”, the mushroom of “Comsteel R5”, and the push-rod of Eagle and Globe “PRN2” steel. The mushroom was fully hardened and the remaining pieces were quenched from 850 °C and tempered at 200 °C. The tube *G*, containing 0.15 ml of the reaction mixture, was of soda glass sealed by a “Neoprene” plug. It was surrounded by *iso*-propyl alcohol to transmit the pressure from the piston.

The temperature was measured by thermocouples housed in two probe-holes *H*, and was regulated by manual adjustment of the current in a lagged heater wound around the supporting ring. The pressure in *A* was calculated from the oil pressure in the hydraulic press, the relationship between these two pressures being established by some observations, at 23 °C, of the transitions: water (liq.)→ice VI, at 9100 atm (Bridgman 1911) and ice VI→ice VII at 21600 atm (Bridgman 1937*b*).

(*b*) *Procedure*.—The experimental procedure has been described earlier (David and Hamann 1954). The initial concentration of ethyl chloride was about half-molar. The reactions were followed by titrating the hydrochloric acid formed against N/100 barium hydroxide, complete reaction of the 0.15 ml samples, requiring 7.5 ml of the barium hydroxide solution. The measurements at 1 and 3000 atm were made in a much larger apparatus than that shown in Figure 1 and the samples were correspondingly larger.

(*c*) *Results*.—At 1 atm and at 65 °C the reaction proceeded very slowly until, after a week, the concentration of hydrochloric acid reached a steady value equal to about 1 per cent. of the initial concentration of ethyl chloride. The smallness of this yield could mean that the reaction is reversible or that the hydrochloric acid is removed by the possible concurrent reactions:

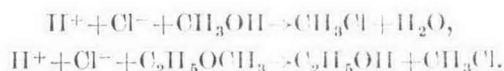


Table I shows that the effect of pressure is to increase enormously both the yield of hydrochloric acid and its rate of formation. The values of the first-order rate constants in Table I are based on the *initial* rate of formation of hydrochloric acid.

References

- BRIDGMAN, P. W. (1911).—*Proc. Amer. Acad. Arts Sci.* **47**: 441.
BRIDGMAN, P. W. (1912).—*Phil. Mag.* **24**: 63.
BRIDGMAN, P. W. (1936).—*Proc. Amer. Acad. Arts Sci.* **72**: 45.
BRIDGMAN, P. W. (1937*a*).—*Proc. Amer. Acad. Arts Sci.* **72**: 157.
BRIDGMAN, P. W. (1937*b*).—*J. Chem. Phys.* **5**: 964.
BUCHANAN, J., and HAMANN, S. D. (1953).—*Trans. Faraday Soc.* **49**: 1425.
DAVID, H. G., and HAMANN, S. D. (1954).—*Trans. Faraday Soc.* **50**: 1188.
INGOLD, C. K. (1953).—“Structure and Mechanism in Organic Chemistry.” p. 310. (Bell and Sons: London.)
POULTER, T. C. (1932).—*Phys. Rev.* **40**: 860.