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:

$$H^+ + Cl^- + CH_3OH \rightarrow CH_3Cl + H_2O,$$
$$H^+ + Cl^- + C_2H_5OCH_3 \rightarrow C_2H_5OH + CH_3Cl.$$

Table 1 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 1 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.

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