Reprinted from the *Transactions of the Faraday Society*, 54-0031
No. 383, Vol. 50, Part 11, November, 1954

THE CHEMICAL EFFECTS OF PRESSURE

PART 2

BY H. G. DAVID AND S. D. HAMANN
C.S.I.R.O. Division of Industrial Chemistry, High Pressure Laboratory,
Sydney University, Australia

Received 30*th June*, 1954

The rates of a number of liquid-phase reactions have been measured at pressures up to 15,000 atm. Those reactions in which ions were formed were strikingly accelerated by pressure, while a reaction in which ions were removed was retarded. These results support an earlier suggestion that the most important effect of pressure on ionic reactions is to increase the solvation free energy of the ionic charges.

In part 1 of this series [1] the suggestion was advanced that the effects of pressure on liquid-phase ionic reactions are due principally to an enhancement of the ion-solvent interaction forces at high pressures. An increase in hydrostatic pressure should accelerate reactions in which the number of ionic charges is increased, but retard those in which the number of charges is reduced.

To test this hypothesis we have now made some rough measurements to 15,000 atm of the rates of a number of reactions in solution. The types of reactions studied are shown in table 1, where R denotes an alkyl group, R′ is an alkyl group or hydrogen atom, X is a halogen atom.

TABLE 1

reaction	rate-determining step	change in number of ionic charges	expected change in reaction rate with increase in pressure
(*a*) S_N1 solvolyses [2]	$RX \rightarrow R^+ + X^-$	increase	large increase
(*a*) S_N2 solvolyses [2]	$RX + R'OH \rightarrow ROR' + H^+ + X^-$	increase	large increase
(*b*) negative ion substitutions	$RX + OR'^- \rightarrow ROR' + X^-$	no change	small increase
(*c*) formation of urea	$NH_4^+ + NCO^- \rightarrow (NH_2)_2CO$	decrease	decrease

From our earlier discussion of solvation effects [1] and by analogy with the electrically similar reactions observed by Perrin (part 1 of this series, table 1) we expected the pressure effects listed in the last column of table 1.

EXPERIMENTAL

APPARATUS.—The measurements above 3000 atm were made in the apparatus shown in fig. 1. The pressure vessel was a cylinder A of Ni-Cr-Mo steel, 3 in. diam. and $5\frac{1}{2}$ in. in length. A $\frac{1}{4}$ in. diam. hole was drilled and reamed axially into it. This cylinder stood on the bottom (movable) platen of a four-column 7-ton hydraulic press. Attached to the top platen of the press was a piston of glass-hard ball-race steel B with a $2\frac{1}{2}$ in. diam. boss transferring the thrust from the platen. The pressure produced by forcing B into A was sealed by a piston head C of design originated by Bridgman,[3] incorporating an " unsupported area " packing of two mild steel washers D and a rubber ring E. The cylinder was filled with petroleum ether and the reaction mixture was contained in a small glass tube F sealed by a well-fitting Neoprene plug. Under the external pressure the plug moved inwards, transmitting the pressure to the contents of the tube. Tests with a liquid immiscible with petroleum ether showed that no leak took place into or out of the glass tube.