THE CHEMICAL EFFECTS OF PRESSURE

PART 2

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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) $\begin{cases} S_N1 \text{ solvolyses [2]} \\ S_N2 \text{ solvolyses [2]} \end{cases}$	$\begin{aligned} RX &\to R^+ + X^- \\ RX + R'OH &\to ROR' + H^+ + X^- \end{aligned}$	increase	large increase
(b) negative ion substitutions	$RX + OR'^- \to ROR' + X^-$	no change	small increase
(c) formation of urea	$NH_4^+ + NCO^- \to (NH_2)_2CO$	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 $5\frac{1}{4}$ 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 $2\frac{1}{4}$ 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.

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Frictional effects were too great to permit calculation of the pressure in the cylinder directly from the piston area and the applied thrust. A manganin resistance gauge (ref. (3), p. 70) was therefore used to determine the pressu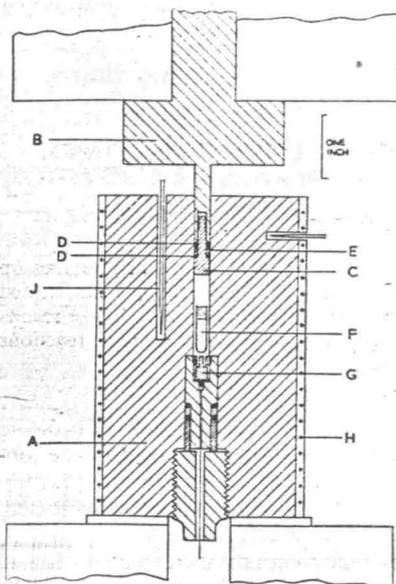re for selected values of the thrust on the piston. The electrical connection G to this gauge was of the type designed by Poulter.[4] The gauge coil (not shown in the diagram) was a small bundle of 40-gauge manganin wire, of about 100-ohms resistance. In a subsidiary experiment pressures up to 3000 atm, developed by an oil pump, were applied through a lens-ring seal at the mouth of the cylinder and the gauge constant was determined by comparison with a Bourdon gauge. This constant was then assumed to apply over the whole pressure range to 15,000 atm.[5]

A lagged heater H was wound around the cylinder to maintain it above room temperature. Chromel-alumel thermocouples in probe-holes J were used to determine the temperature distribution through the cylinder and it was found that a good indication of the temperature in the axial hole was given by a thermocouple in a probe-hole parallel to, and about $\frac{1}{2}$ in. distant from it. The temperature was maintained to within $\pm \frac{1}{2}°$ C of the desired value by manual adjustment of the heater current.

FIG. 1.—High-pressure reaction vessel.

Because of the friction between piston and cylinder the pressures in this apparatus were rather uncertain below 5000 atm. For that reason the measurements from 500 to 3000 atm were made in an apparatus resembling that described in part 1.[1]

MATERIALS.—All the chemicals were of the highest purity available and the organic halides were further purified by drying and distillation. Dry methanol was purified by the method of Lund and Bjerrum.[6] Sodium methoxide solutions were made by dissolving metallic sodium in pure methanol and were standardized against hydrochloric acid. Ammonium cyanate was prepared in the manner described by Warner and Stitt.[7]

PROCEDURE.—The reactions were: I, the unimolecular neutral solvolysis of *tert.*-butyl chloride in 80 % ethanol (20 volumes of water added to 80 volumes of ethanol); II, the unimolecular neutral solvolysis of *tert.*-butyl chloride in pure methanol; III, the bimolecular neutral solvolysis of ethyl bromide in 80 % ethanol; IV, the bimolecular neutral solvolysis of ethyl bromide in methanol; V, the bimolecular neutral solvolysis of ethyl iodide in methanol; VI, the bimolecular alkaline solvolysis of methyl bromide by sodium hydroxide in 80 % ethanol; VII, the bimolecular alkaline solvolysis of ethyl bromide by sodium methoxide in methanol; VIII, the conversion of ammonium cyanate to urea in water.

For each reaction an approximately N/2 solution of the reactants was made up at a low temperature and 0·2 ml of this was transferred to a small soda glass reaction tube F (fig. 1). The tube was quickly stoppered by a Neoprene plug and dropped into pre-heated petroleum ether in the pressure vessel A. Pressure was then applied to the petroleum ether as described in an earlier section. After a known time, usually several hours, the pressure was released and the reaction tube removed, rapidly cooled, broken, and washed with cold alcohol. The contents of the tube and the alcohol washings were titrated to find the extent of reaction. In reactions I-V the hydrogen halide was estimated by titration with standard barium hydroxide; in reactions VI and VII the unchanged alkali was titrated with hydrochloric acid, and in VIII the unchanged ammonium cyanate titrated in excess ethanol with standard mercurous nitrate, using eosin as an indicator.

At 1 atm and at the highest pressure the reactions were measured over several time intervals and gave consistent rate constants for different reaction times. Because of the tedium of the experimental procedure and the strictly limited life of the pressure vessel, many of the reactions at intermediate pressures were observed over only a single time interval.

In reactions I-V and VII the predominant nucleophilic replacement of the halogen atom X was probably accompanied by a small amount of olefin-forming elimination of HX. But since the transition states for the two reactions are electrically similar (for I and II they are identical) no effort was made to separate the rate constants for the two processes.

RESULTS

The inaccuracies of titration together with the uncertainty of the pressures, temperatures and times of reaction could cause errors of 30 % in the rate constants; the results are therefore more of qualitative than of quantitative significance. The first-order rate constants for reactions I-V and the second-order constants for VI-VIII were worked out by the usual formulae. The second-order constants have been corrected for the contraction of the solutions under pressure.

The results are given below.

I, neutral (S_N1) solvolysis of $C(CH_3)_3Cl$ in 80 % ethanol at 25° C

p (atm)	1	1500	3000	6000	9000	12000	15000
$10^6 k$ (sec^{-1})	8·4	21	41	74	134	170	240

II, neutral (S_N1) solvolysis of $C(CH_3)_3Cl$ in methanol at 36° C

p (atm)	1	5000	10000	15000
$10^6 k$ (sec^{-1})	3·1	38	74	140

III, neutral (S_N2) solvolysis of C_2H_5Br in 80 % ethanol at 55° C

p (atm)	1	1000	2000	3000	5000	10000	15000
$10^6 k$ (sec^{-1})	1·4	2·4	3·9	5·7	9·5	23	46

IV, neutral (S_N2) solvolysis of C_2H_5Br in methanol at 65° C

p (atm)	1	500	1000	1700	3000	6000	9000	12000	15000
$10^6 k$ (sec^{-1})	1·49	2·3	3·5	5·6	8·1	21	44	66	90

V, neutral (S_N2) solvolysis of C_2H_5I in methanol at 65° C

p (atm)	1	750	1700	3000	6000	9000	15000
$10^6 k$ (sec^{-1})	1·14	2·2	3·5	5·4	8·4	12·1	21·3

A considerable amount of free iodine was produced in this reaction, possibly from oxidation of the hydrogen iodide. The rate constants may therefore be too low.

VI, alkaline (S_N2) solvolysis of CH_3Br with NaOH in 80 % ethanol at 0° C*

p (atm)	1	1000	2000	3000
$10^6 k$ (sec^{-1} mole^{-1} l.)	5·7	7·8	9·8	12·5

* These measurements were made by Mr. W. Strauss.

VII, alkaline (S_N2) solvolysis of C_2H_5Br with $NaOCH_3$ in methanol at 30° C

p (atm)	1	3000	6000	9000	12000	15000
$10^5 k$ (sec^{-1} mole^{-1} l.)	3·8	10·0	14·2	22·1	26·1	33·2

VIII, conversion of NH_4NCO into $(NH_2)_2CO$ in water at 60°C

p (atm)	1	1500	3000	6000	9000	12000	15000
$10^3 k$ (sec^{-1} mole^{-1} l.)	1·62	1·01	0·60	0·43	0·34	0·31	0.29

DISCUSSION

For convenience the results listed in the last section are summarized in table 2, where the symbols k_p represent the rate constants at the pressures p (atm). In fig. 2 the rate constants have been plotted on a logarithmic scale to give an indication of the change of activation free energies with pressure.

It is evident that the three classes of reactions show the pressure effects which were predicted in the introduction. A point which calls for comment, however,

is that the curves of $\log_{10} k_p/k_1$ against p for the negative ion replacements (b) lie much closer to those of the reactions (a) which produce ions, than to that of the reaction (c) which removes ions. There is some evidence from activation entropies [8] that the transition states for these negatives ion substitutions may resemble (1) rather than (2):

$$X^- + R\!-\!Y \rightarrow (X^-R^+Y^-) \rightarrow X\!-\!R + Y^-, \tag{1}$$

$$X^- + R\!-\!Y \rightarrow (X^{-\delta} \ldots R \ldots Y^{-\delta}) \rightarrow X\!-\!R + Y^-, \tag{2}$$

so that, although the net charge of the system does not change, the transition state may be more highly polar than the initial state. We should then expect an acceleration of these reactions with an increase in pressure.

TABLE 2

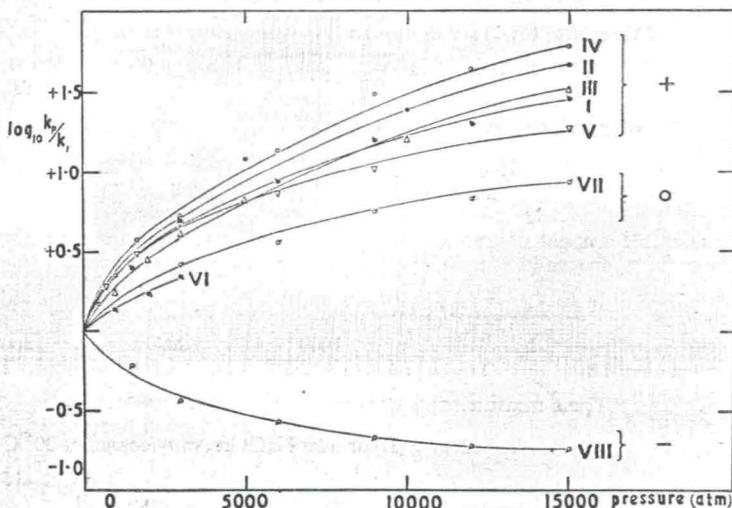| reaction		solvent	temperature °C	$\dfrac{k_{3000}}{k_{2}}$	$\dfrac{k_{1500}}{k_1}$
(a) S_N1 solvolyses	I. $C(CH_3)_3Cl$	80 % ethanol	25	4·9	29
	II. $C(CH_3)_3Cl$	methanol	36	5·4	45
S_N2 solvolyses	III. C_2H_5Br	80 % ethanol	55	4·1	33
	IV. C_2H_5Br	methanol	65	5·4	60
	V. C_2H_5I	,,	65	4·7	19
(b) VI. $CH_3Br + OH^-(OC_2H_5{}^-)$		80 % methanol	0	2·2	
VII. $C_2H_5Br + OCH_3{}^-$		methanol	30	2·6	8·7
(c) VIII. $NH_4{}^+ + NCO^-$		water	60	0·37	0·18

FIG 2.—Effect of pressure on reaction rates. The Roman numerals refer to the reactions in table 2. The +, O, and — signs indicate that the reactions were accompanied by an increase, no change, and a decrease, respectively, in the number of ionic charges.

[1] Buchanan and Hamann, Trans. Faraday Soc., 1953, 49, 1425.
[2] Ingold, Structure and Mechanism in Organic Chemistry (Bell & Sons, London, 1953), p. 310.
[3] Bridgman, Physics of High Pressure (Bell & Sons, London, 1949), p. 39.
[4] Poulter, Physic. Rev., 1932, 40, 860.
[5] Bridgman, Proc. Amer. Acad. Arts Sci., 1940, 74, 1.
[6] Lund and Bjerrum, Ber., 1931, 64, 210.
[7] Warner and Stitt, J. Amer. Chem. Soc., 1933, 55, 4807.
[8] Evans and Hamann, Trans. Faraday Soc., 1951, 47, 40.