

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,