

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 entropies⁸ that the transition states for these negative ion substitutions may resemble (1) rather than (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	$\frac{k_{3000}}{k_1}$	$\frac{k_{15000}}{k_1}$	
(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	

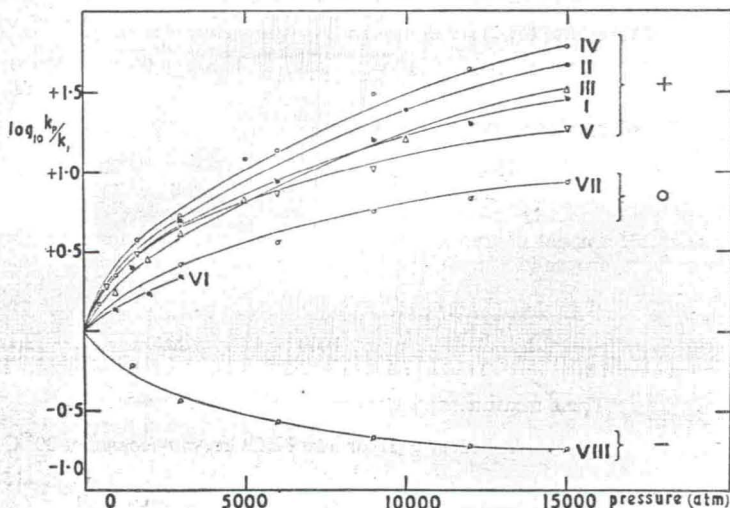


FIG. 2.—Effect of pressure on reaction rates. The Roman numerals refer to the reactions in table 2. The +, O, and - signs indicate that the reactions were accompanied by an increase, no change, and a decrease, respectively, in the number of ionic charges.

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.