

Some results of investigations of the effect of pressure on the rate of addition of alkyl halides to tertiary amines and pyridine in acetone are given in Table 2¹²⁾.

Table 2

Reaction velocity in acetone at high pressures¹²⁾

Reaction	Temperature (°C)	Pressure p (kg/cm ²)	k _p /k ₀	A ₀
(CH ₃) ₃ N + i-C ₃ H ₇ I	60	3000	16.4	1.87x10 ⁷
(C ₂ H ₅) ₃ N + i-C ₃ H ₇ I	60	3000	16.0	3.76x10 ⁷
C ₅ H ₅ N + CH ₃ I	60	3000	6.78	1.96x10 ⁷
C ₅ H ₅ N + C ₂ H ₅ I	40	2980	6.85	2.13x10 ⁷
		5000	14.7	
		8500	48.0	
C ₅ H ₅ N + n-C ₄ H ₉ Br	60	3000	8.14	1.33x10 ⁷
C ₅ H ₅ N + n-C ₄ H ₉ I	60	3000	6.16	2.66x10 ⁸
C ₅ H ₅ N + i-C ₃ H ₇ I	60	3000	9.60	7.91x10 ⁸
C ₆ H ₅ N(CH ₃) ₂ + i-C ₃ H ₇ I	60	3000	25.5	
		5000	80	
		8500	200	
		12000	493	

From the data of Table 2 it may be seen that the investigated reactions are "slow" (exponential term A₀ ~ 10⁷-10⁸) and strongly accelerated by pressure. In one of the papers quoted¹²⁾, data are given for the value of ΔV (i.e. the volume change) for the reaction of pyridine with ethyl iodide in acetone. Comparison of the values of ΔV given here with values of ΔV[‡] calculated from experimental data by use of equation(III) showed that at 30°C and 1 atm., ΔV[‡] (-20.0 cm³/mole) was 2.7 times less than ΔV (-54.3 cm³/mole). This fact, it would seem, bears witness to the value of the hypothesis that the solvent takes part in the activated complex. However, it was subsequently discovered³⁷⁾ that the indicated difference between the values of ΔV[‡] and ΔV is caused by the solvation of the product (N-ethylpyridine iodide) by acetone, which leads to the large negative value of ΔV. Now if we compare the value of ΔV[‡] with the change in volume during the reaction, calculated from the molar volumes of the original pure liquid components and of the reaction product (see 37)), we find a very close agreement (-20.0 and -20.5 cm³/mole respectively at 30°C and 1 atm.) It has also been shown³⁸⁾ that solvation by acetone does not have a noticeable effect on the value of ΔV[‡]. This is seen from the data cited below on the change of the rate of the investigated reaction with increasing pressure in different solvents.

* k₀ and A₀ are the velocity constant and the pre-exponential term of the Arrhenius equation at atmospheric pressure; k_p is the velocity constant at pressure p.