A. H. EWALD

The rate of dissociation of PPE at 70° C was calculated from the slope of the linear portion of a plot of the optical density at 500 mμ against time, by using eqn. (2). The mean of the rate constants found at 1 atm was $2.5 \pm 0.25 \times 10^{-5}$ sec^{-1} which is rather lower than the value found by Bachmann[9] in xylene (5.8×10^{-5} sec^{-1}). Although the spread of the rate constants found in different runs was rather great the ratios k_p/k_1 calculated from different runs were in much better agreement. These ratios are shown in fig. 3.
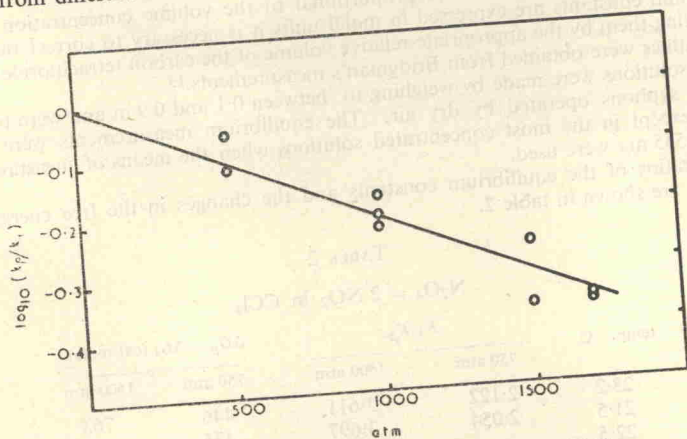

FIG. 3.—The dissociation of PPE in toluene at 70° C.

NITROGEN TETROXIDE

Nitrogen tetroxide was prepared by heating dried lead nitrate to 450° C in a current of dry oxygen. The gas was passed through two U-tubes packed with Raschig rings and phosphorus pentoxide and was condensed in a tube cooled in an ice + salt mixture. It was once more distilled through phosphorus pentoxide before use.

The carbon tetrachloride used to make the solutions had to be very pure and absolutely dry in order to obtain reasonably stable solutions. A.R. carbon tetrachloride was therefore fractionally distilled immediately before use and was exposed to air and light as little as possible.

The dissociation constant of nitrogen tetroxide is given by

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{2\alpha^2 m_0}{1 - \alpha}, \tag{3}$$

where α is the degree of dissociation and m_0 the total concentration of nitrogen oxides expressed as moles NO$_2$/kg. Nitrogen dioxide in CCl$_4$ has a strong absorption band with a maximum at 435 mμ and a pronounced shoulder at 550-555 mμ, while nitrogen tetroxide is quite transparent in this spectral region. Unfortunately it was not possible to find the molecular absorption coefficient of nitrogen dioxide because of the instability of the very dilute solutions required in order to extrapolate to zero concentration and complete dissociation. The dissociation constant of 12.35×10^{-4} (molal) found by Attwood and Roleffson[14] at 25° C, however, shows that α becomes very small in approximately 0.1 m solutions. If, then, $\alpha \ll 1$ we can write (3) as

$$K = 2\alpha^2 m_0, \tag{3'}$$

and the optical density of the solution is given by

$$D = \epsilon_{NO_2} l \, \alpha m_0. \tag{4}$$

Combining these two equations we find

$$D \propto m_0^{\frac{1}{2}}, \tag{5}$$

and this relation was found to apply within the range of 0.3 to 1.0 m solution which was used in the equilibrium measurements.

From eqn. (3′) and (4) we also find that

$$K_1/K_p = D_1^2/D_p^2$$

(6)

and the change of the free energy of dissociation with pressure is then given by

$$\Delta G_p - \Delta G_1 = RT \ln (K_1/K_p) = RT \ln (D_1^2/D_p^2).$$

(7)

Since the optical densities are proportional to the volume concentration while the equilibrium constants are expressed in molal units it is necessary to correct the densities by dividing them by the appropriate relative volume of the carbon tetrachloride solutions. These values were obtained from Bridgman's measurements.[15]

The solutions were made by weighing to between 0·1 and 0·9 m and were transferred through syphons operated by dry air. The equilibrium measurements were made at 435 mµ except in the most concentrated solutions when the means of measurements at 550 and 555 mµ were used.

The ratios of the equilibrium constants and the changes in the free energy of dissociation are shown in table 2.

TABLE 2

$$N_2O_4 \rightleftharpoons 2\ NO_2 \text{ in } CCl_4$$
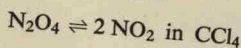
temp. °C	K_1/K_p		$\Delta G_p - \Delta G_1$ (cal/mole)	
	750 atm	1500 atm	750 atm	1500 atm
23·2	2·122			
21·5	2·054	3·611	446	763
22·5		3·697	425	771
23·1		4·025		825
		3·775		788
mean 22	2·08		435	
		3·77		787
51	2·48		588	
52	2·13	4·35	421	953
		3·77		863
mean 51·5	2·30		540	
		4·06		908

DISCUSSION

Although it has been shown that the Stearn-Eyring [16] theory does not correctly describe the effect of pressure on ionic reactions [1] it could be expected to apply more nearly to the homolytic bond fissions occurring in free-radical dissociations.

In the dissociation of AZBN the first bond broken is a C—N bond.[5] If we assume a 10 % stretching of this bond and a constant cross-section of the molecule in passing from the initial to the activated state, we can calculate from a crude molecular model, using covalent radii for the bond lengths and van der Waals radii for the atoms, that the volume of activation should be $\Delta V^{\ddagger} = 4\cdot3$ cm³/mole. From the equation

$$\frac{d \ln k}{dp} = -\frac{\Delta V^{\ddagger}}{RT}$$

(8)

and from the values of the rate constants shown in table 1 we find from the direct measurements $\Delta V^{\ddagger} = 3\cdot8$ cm³/mole and from the scavenger measurements $\Delta V^{\ddagger} = 9\cdot36$ cm³/mole.

If we make a similar rough calculation of the volume of activation of the dissociation of PPE we find a value of $\Delta V^{\ddagger} = 10\cdot5$ cm³/mole, while the measured values of the rate of dissociation at 1 and 1000 atm give a value of $\Delta V^{\ddagger} = 13\cdot1$ cm³/mole.

It is thus apparent that even in this crude form the assumption that the effect of pressure is purely a volume effect and that in the activated state there is a 10 % extension of the reacting bond gives the right sort of answer for these reactions.

The much larger effect of pressure on the rate of dissociation of AZBN found by the iodine scavenger method must be attributed to changes in the " cage effect "