

EXPERIMENTAL

All the reactions were followed by means of a Unicam S.P. 500 spectrophotometer which was modified to accommodate a high-pressure absorption cell.¹¹ At pressures up to 1700 atm (up to 3000 atm in one case) the reactions were carried out directly in this cell and could be observed continuously. For reactions above 3000 atm the reaction mixture was enclosed in either an all-glass or an all-Teflon reaction tube having at one end a well-fitting plug which could slide into the tube to transmit pressure to the reaction mixture. These cells were immersed in oil in a steel bomb of 1-in. int. diam., of the type described by David and Hamann.² At the end of a run the reaction cell was removed from the bomb, chilled, and the contents were then analysed in an ordinary stoppered spectrophotometer cell.

2: 2'-AZO-bis-ISOBUTYRONITRILE

This was prepared by the method of Thiele and Heuser¹² and the final product melted at 104-105° C. A.R. toluene was carefully purified by the usual methods and finally fractionally distilled from sodium and stored over sodium. The solutions for the direct measurements were made up by weighing and were approximately 0.6 M. The rate constants were calculated from the observed optical densities D at 350, 370, 280 $m\mu$ ⁴ by the equation

$$k = - (1/t) \ln (D/D_0). \quad (1)$$

The method of least squares was used to find the best value of k for any one plot of D against time t . The results are quoted in table 1 and are the means of the values found at the three wavelengths.

The reactions using iodine as a scavenger were carried out in the manner of Bawn and Mellish¹⁰ using a 20- to 50-fold excess of AZBN over iodine. The solutions of AZBN in toluene were made up by weight and were freed of oxygen by bubbling purified nitrogen saturated with toluene through them. These solutions were then mixed with similarly deoxygenated solutions of iodine so that the reaction mixtures were approximately 0.001 m in iodine and 0.057 m in AZBN, except in a few cases when half this concentration of AZBN was used in order to check the first-order character of the reaction.

The reaction was followed by measuring the iodine absorption at 500 $m\mu$ at short intervals. In order to eliminate any optical effects due to the pressure applied to the cell the optical density was also measured at 950 $m\mu$ since the reaction mixture was known to be quite transparent at this wavelength. These measurements were used as a correction to the readings at 500 $m\mu$.^{*} A plot of D against time gave straight lines and the reaction rates were calculated from the slope by the equation

$$k = - \frac{1}{\epsilon' l} \frac{dD}{dt} \frac{1}{[AZBN]_0}. \quad (2)$$

Here ϵ' is the molal extinction coefficient of iodine at the temperature and pressure of the particular experiment, l is the optical path length of the absorption cell, and concentrations are expressed in mole/kg. Values of ϵ' were determined in separate experiments using analysed solutions of iodine in toluene.

TABLE 1.—DISSOCIATION OF 2: 2'-AZO-bis-ISOBUTYRONITRILE IN TOLUENE

pressure atm	$k \times 10^5$ (sec ⁻¹) 70° C direct	$k \times 10^5$ (sec ⁻¹) 62.5° C direct	$k \times 10^5$ (sec ⁻¹) 62.5° C scavenger	$\frac{k \text{ (scavenger)}}{k \text{ (direct)}}$
1	5.50	1.87	0.892	0.447
1500	4.47	1.52	0.552	0.363

Some rate constants obtained by the two methods are shown in table 1. The third column of the table gives the rate constant at 62.5° C calculated from the direct measurements at 70° C by using the energy of activation $\Delta E^\ddagger = 31.1$ kcal/mole found by Talât-Erben and Bywater⁵ and confirmed in the present investigation. Further results obtained by the scavenger method are shown in fig. 1. The upper of the two rate constant curves shows the results of a run in which particular care was taken to exclude all oxygen by

* This method of correction was used with all the spectrophotometer measurements.

handling the solutions only in an atmosphere of carbon dioxide. The higher rate constants obtained in this run show the inhibiting effect of oxygen on the scavenging reaction between iodine and the free radicals, although there was no actual induction period as was found in the PPE system. The top curve on fig. 1 shows values of $\log_{10}(k_p/k_t)$ calculated for individual runs. The close agreement in this ratio between different runs shows that it is not affected by the presence of a trace of oxygen.

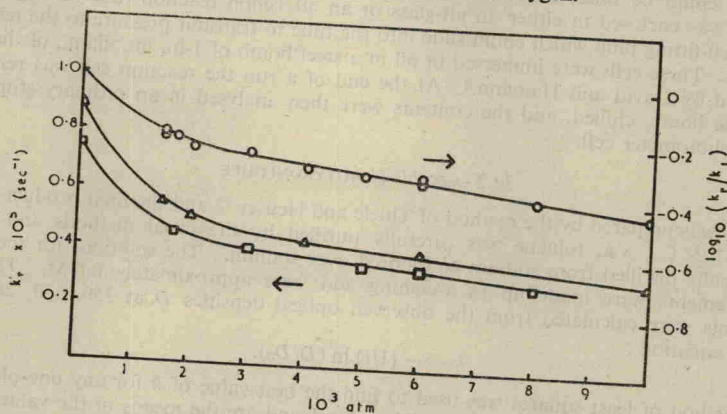


FIG. 1.—The dissociation of AZBN in toluene at 62.5° C.

PENTAPHENYLETHANE

This substance was prepared by coupling diphenylmethyl chloride with triphenylmethyl sodium in the manner of Bachmann and Wiselogle.¹³ The final product melted with decomposition between 168 and 172° C.

The reaction with iodine was carried out in the same manner as for AZBN using solutions 0.001 m in iodine and between 0.015 and 0.025 m in PPE. The reaction, however, seemed to be more sensitive to the presence of oxygen. Although nitrogen was bubbled

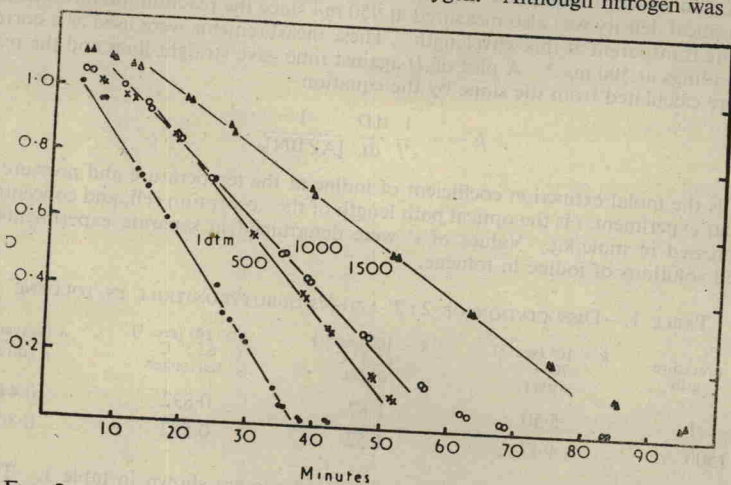


FIG. 2.—Optical density at 500 $m\mu$ of PPE + iodine in toluene at 70° C

through the solutions and these were handled afterwards only in an atmosphere of carbon dioxide, the plots of optical density against time showed an induction period during which iodine disappeared at a slower rate than during the remainder of the reaction. This induction period usually lasted for only a small part of the time during which the reaction was followed. Fig. 2 shows the reaction curves obtained in one series of runs.