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EFFECT OF PRESSURE ON THE PHOTOLYSIS OF
AZO-BIS-ISOBUTYRONITRILE IN THE PRESENCE OF
DIPHENYLPICRYLHYDRAZYL

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AIBN was photolyzed in toluene at room temperature at pressures up to 2,000 kg/cm² and the rates of the disappearance of DPPH which was used as a radical scavenger were measured spectrophotometrically. The rate was decreased with increasing pressure and the apparent activation volume was +7.6 cm³/mole.

In comparison with Ewald's results on the thermal dissociation of AIBN, it was considered that an important contribution to the apparent activation volume was due to the change of "cage effect" by pressure and that the retarding effect of pressure on the photodissociation of AIBN would be smaller than on the thermal dissociation of AIBN.

Introduction

The investigation on the photochemical reaction at high pressure has scarcely been reported, but it is an interesting subject. The authors studied the effect of pressure on the rate of disappearance of diphenylpicrylhydrazyl (DPPH) when azo-bis-isobutyronitrile (AIBN) was photolyzed using DPPH as a radical scavenger in toluene at room temperature, at pressures up to 2,000 kg/cm².

Ewald¹⁾ compared the rates of thermal dissociation of AIBN in the absence of a radical scavenger with those in the presence of iodine molecule (used as a radical scavenger), and he suggested that pressure increased "cage effect" of solvent¹⁾. The authors' results were compared with Ewald's.

Experimentals

The apparatus used in this study is shown in Fig 1. The high pressure vessel is provided with three optical windows of sapphire: two for the spectrophotometric measurement and one, placed at the bottom, for photoexciting irradiation. The reaction cell is made of cylindrical quartz (inner diameter: 6 mm). Silicon oil was used as pressure transmitting medium.

Rates of disappearance of DPPH were followed from the decrease of absorption of DPPH at 516

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1) A. H. Ewald, *Discussions Faraday Soc.*, **22**, 138 (1956)

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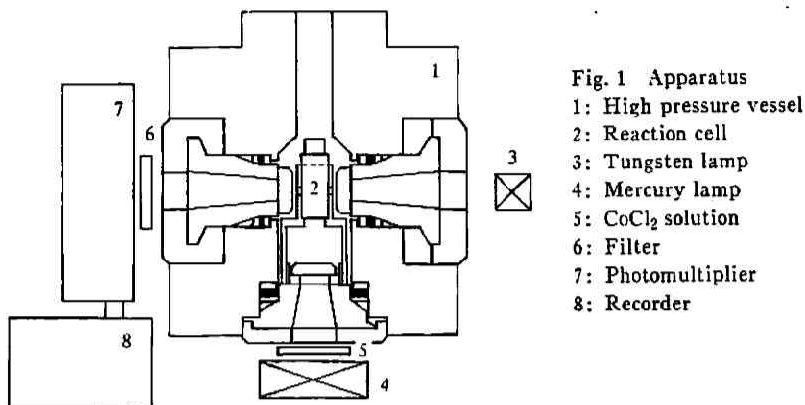


Fig. 1 Apparatus
 1: High pressure vessel
 2: Reaction cell
 3: Tungsten lamp
 4: Mercury lamp
 5: CoCl_2 solution
 6: Filter
 7: Photomultiplier
 8: Recorder

$m\mu$. The transmitting light intensity at the end of reaction was regarded as the referential intensity.

An ultra high pressure mercury lamp (Mazda SHL-200) was used for photoexcitation and the light near $500m\mu$ was filtered off by CoCl_2 solution lest it should interfere with the spectrophotometric measurement.

AIBN (Nakarai Chemicals, Ltd.) was recrystallized from ethanol; mp. 103°C .

DPPH (Nakarai Chemicals, Ltd.) was recrystallized from chloroform-petroleum ether and dried in vacuum at 80°C for 16 hr²⁾.

The reactions were carried out in toluene at room temperature at pressures up to $2,000\text{ kg/cm}^2$. The initial concentration of the reaction solution was $8 \times 10^{-5}\text{ mole/l}$ for DPPH and those for AIBN were varied from $5 \times 10^{-3}\text{ mole/l}$ to $2 \times 10^{-2}\text{ mole/l}$. The dissolved oxygen was eliminated by bubbling with nitrogen gas. The volume contraction of toluene with pressure was measured and the concentrations of solutions were corrected.

Results and Discussions

As shown in Fig. 2, concentrations of DPPH vary linearly with the irradiation time at each pres-

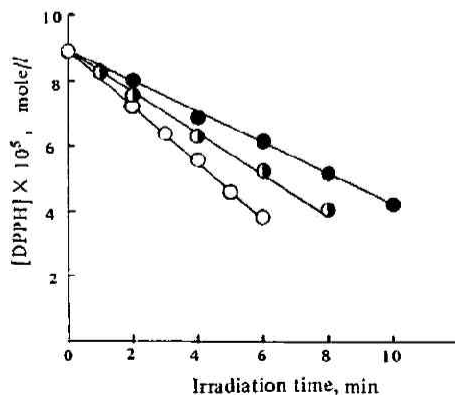


Fig. 2 Change of the concentration of DPPH according to irradiation time
 ($[\text{AIBN}]_0 = 1.5 \times 10^{-2}\text{ mole/l}$)
 ○: 1 kg/cm^2 ,
 ◐: $1,000\text{ kg/cm}^2$,
 ●: $2,000\text{ kg/cm}^2$

2) J. A. Weil and J. K. Anderson, *J. Chem. Soc.*, 1956 5567

sure and at each initial concentration of AIBN. The rate of disappearance of DPPH which obeys zero order rate equations is retarded by pressure.

The relation of the rate of disappearance of DPPH to the initial concentration of AIBN is shown in Fig. 3. The rate is proportional to the initial concentration of AIBN at each pressure.

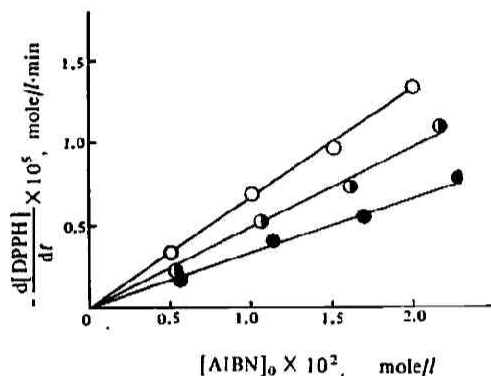
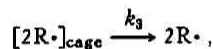
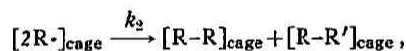
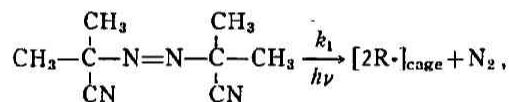


Fig. 3 Dependence of the rate of disappearance of DPPH on the initial concentration of AIBN

○: 1 kg/cm²,
◐: 1,000 kg/cm²,
●: 2,000 kg/cm²

In view of these results, the mechanism of reaction will be represented as follows^{3,4)},



The rate of disappearance of DPPH is given by the following equation:

$$-\frac{d[\text{DPPH}]}{dt} = \frac{2k_1k_3}{k_2+k_3}[\text{AIBN}]_0 = k_{\text{obs}}[\text{AIBN}]_0,$$

where as the extent of the absorption by AIBN is small in the region of wave lengths of photoexcitation, the rate of photodissociation of AIBN is nearly proportional to its concentration. Further, since the amount of AIBN is in much excess of DPPH, the concentration of AIBN is regarded as equal to its initial concentration in the course of reaction.

From the plots of logarithm of the observed rate constant k_{obs} vs pressure, +7.6 cm³/mole was obtained as the apparent activation volume.

Ewald studied the thermal dissociation of AIBN at high pressure by direct measurement of the disappearance of AIBN and by using I₂ as a radical scavenger. He obtained +3.8 cm³/mole as the activation volume for the former and +9.36 cm³/mole for the latter and considered that the difference

3) J. C. Roy, J. R. Nash, R. R. Williams, Jr. and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 519 (1956)

4) C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56**, 815 (1960)

between the two values was due to the pressure effect on "cage effect" of solvent.

According to the reaction scheme given above, $k_3/(k_2+k_3)$ is a measure of "cage effect", which, as Ewald suggested, is decreased with increasing pressure. Considering that "cage effect" depends on the viscosity of the solvent strongly, the increase of the viscosity of the solvent with pressure will be an important cause for the decrease of $k_3/(k_2+k_3)$ ⁵⁾⁶⁾.

The value of the apparent activation volume which the authors obtained is approximately equal to Ewald's one by the scavenger method. It is also considered that in the photochemical reaction an important contribution to the pressure effect on the overall reaction is that on "cage effect". In addition, comparing the apparent activation volume obtained here with those by Ewald, the retarding effect of pressure on the photodissociation of AIBN will be smaller than on the thermal dissociation of AIBN.

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5) C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967)

6) R. C. Neuman, Jr. and J. V. Behar, *J. Am. Chem. Soc.*, **91**, 6024 (1969)