

## KINETIC STUDIES ON FREE RADICAL REACTIONS

## I. Reaction of DPPH with Free Radicals formed by the Photolysis of Azo-bis-isobutyronitrile

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The formation of free radicals produced by the photo-dissociation of azo-bis-isobutyronitrile (AIBN) in a benzene solution was investigated by the ultra-violet spectrophotometric and ESR methods using DPPH as radical scavenger.

From the change of the ultra-violet and ESR spectra of DPPH in the course of irradiation, it was found that the influence of dissolved oxygen on the free radical reaction of AIBN is significant. The peroxy free radicals formed by the reaction of free radicals with dissolved oxygen react with DPPH. The intermediate found by ESR is rather stable and consists of two kinds of free radicals. The results obtained by the ESR method show that both free radicals contain an unpaired electron mainly localized on  $N^{14}$  nucleus.

From the view-point of kinetics, the reaction mechanism of DPPH with the free radicals formed in the course of irradiation of AIBN is discussed both in the presence and absence of dissolved oxygen.

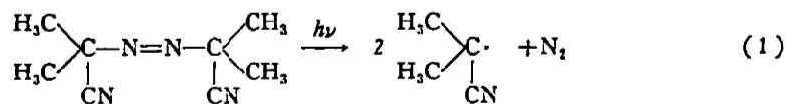
## Introduction

It has been known that the dissolved oxygen acts usually as an inhibitor for the free radical reaction. The formation mechanism of an initiator radical for the radical polymerization is also complex in the presence of dissolved oxygen.

The authors intended to elucidate the further detail of the formation of free radicals from an initiator by photo-dissociation. In this report the photolysis of  $\alpha\alpha'$ -azo-bis-isobutyronitrile (AIBN) in benzene solution was examined both in the presence and absence of dissolved oxygen.

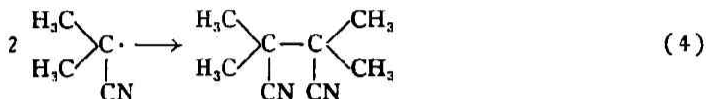
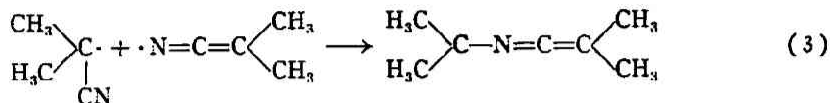
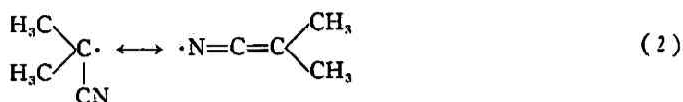
The free radicals thus formed were scavenged by diphenyl-picryl-hydrazyl (DPPH). By measuring the change of the concentration of DPPH in the course of a reaction using a spectrophotometric and ESR methods, the reaction mechanism was discussed.

In the deaerated solution it is known that the decomposition of AIBN proceeds by the following mechanism<sup>1)2)3)4)</sup>.



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- 1) G. S. Hammond, O. D. Trapp, R. T. Keys and D. L. Neff, *J. Am. Chem. Soc.*, **81**, 4878 (1959)
- 2) J. Thiele and K. Hauser, *Ann.*, **290**, 1 (1896)
- 3) G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955)
- 4) M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710 (1955)



In the presence of DPPH the free radicals thus formed react directly with DPPH producing the corresponding hydrazine. The results obtained by the authors agree well with the above cited reaction mechanism.

On the other hand, in the presence of dissolved oxygen it is confirmed that the isobutyronitrile (IBN)-radical reacts rapidly with the oxygen, producing peroxy free radical. In this case the decreasing rate of DPPH is much faster than that in a deaerated solution. From the results obtained by the ESR method, the decomposition of DPPH by the attack of peroxy free radicals was observed. The decomposition intermediate of DPPH showed distinct ESR spectrum consisting of two kinds of rather stable free radicals. The one was ascribed to the diphenyl nitric oxide, the other to the free radicals including the picryl group due to the DPPH.

## Experimentals

### Materials

AIBN: recrystallized twice from ethanol. The melting point was  $104^\circ\text{C} \sim 105^\circ\text{C}$ .

DPPH (G. R. Grade): to eliminate the trace of hydrazine a benzene solution was shaken after adding  $\text{PbO}_2$ , and then dried with anhydrous sodium sulfate.

tert-Butylhydroperoxide (t-BHPO) (C. P. Grade): used without further purification.

Benzene (E.P. Grade): after dried with  $\text{CaCl}_2$  and metallic Na, distilled at  $80.1^\circ\text{C}$  and stored under the atmosphere of argon.

### Apparatus

Absorption spectrophotometer: Hitachi EPU-2 type.

Infrared spectrophotometer: Hitachi EPIS-2 type.

Electron spin resonance spectrophotometer: Japan Electron Optics Co., Ltd. JES-3 type. (X-band with 100 KC modulation;  $\text{TE}_{211}$  cavity).

Light source for the photo-dissociation: Matsuda 500 W high pressure mercury lamp ( $3650 \text{ \AA}$ ) with a filter of cupric sulfate solution (100 g/l).

Photometer: constructed to follow continuously the reaction.

Reaction cell: made of pyrex glass ( $15 \times 13 \times 50 \text{ mm}$ ).

### Procedure

A benzene solution (2.5 ml) of AIBN ( $1 \times 10^{-2} \sim 5 \times 10^{-2}$  mole/l) and DPPH ( $5 \times 10^{-4}$  mole/l) was poured into the reaction cell. The dissolved oxygen was eliminated by repeating the procedure of freezing in a dry ice-ethanol bath, evacuation and melting. The cell was sealed in vacuum and then placed in C (Fig. 1) and exposed to the light of the mercury lamp M. The rate of disappearance of DPPH was measured photometrically using a tungsten lamp and a photo-cell. For the observation of ESR spectra the solution irradiated for a certain time was transferred to a pyrex glass tube ( $\phi=4\text{mm}$ ). After degassing by the above mentioned way, ESR spectra were observed at room temperature.

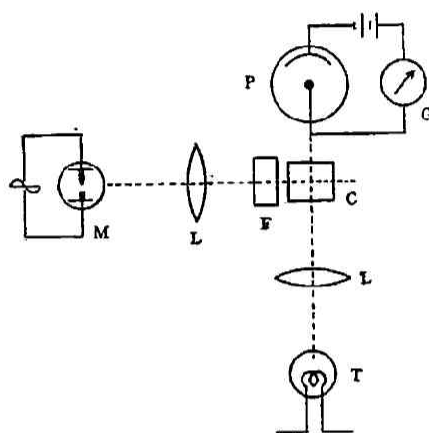


Fig. 1 Apparatus

- M : Mercury lamp
- L : Lens
- F : Filter
- P : Photocell
- G : Galvanometer
- C : Reaction cell
- T : Tungsten lamp

### Results

#### Results with the deaerated solution

##### *Ultra-violet, visible and infrared spectra*

By using a benzene solution of AIBN (initial concentration : 0.01 mole/l) a ultra-violet spectra both before and after irradiation were recorded as shown in Fig. 2. The absorption maximum at  $345\text{ m}\mu$  corresponds to N=N bond of AIBN and the maximum at  $291\text{ m}\mu$  to dimethyl-N-(2-cyanoisopropyl)-keteneimine (DKI). Moreover, from the appearance of a peak of DKI at  $4.91\mu$  in the infrared spectrum after irradiation, it was found that DKI is produced by the photo-dissociation of AIBN<sup>1)4)</sup>.

The ultra-violet and visible spectrum of the mixture of DPPH ( $5 \times 10^{-4}$  mole/l) and AIBN ( $5 \times 10^{-2}$  mole/l) in a benzene solution is shown by a full line of Fig. 3. The spectrum after irradiation for one hour is shown by a dotted line. For the measurement of these spectra, after the irradiation the samples were diluted to one tenth with benzene. The molar extinction coefficient of DPPH at  $345\text{ m}\mu$  is so great, compared with that of AIBN and of DKI, that the absorptions due to AIBN and DKI in these solutions may be negligible. The change of the concentration of DPPH in the course of the irradiation was measured continuously and the results are shown in Fig. 4. It was confirmed that the spectrum of DPPH in a solution without AIBN does not change after irradiation.

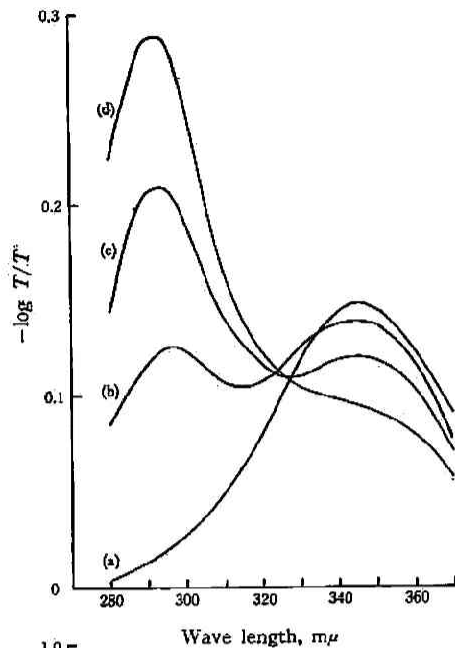


Fig. 2 Absorption spectra of AIBN  
Solvent : deaerated benzene  
Irradiation time (min.);  
(a): 0 (b): 10 (c): 20 (d): 30

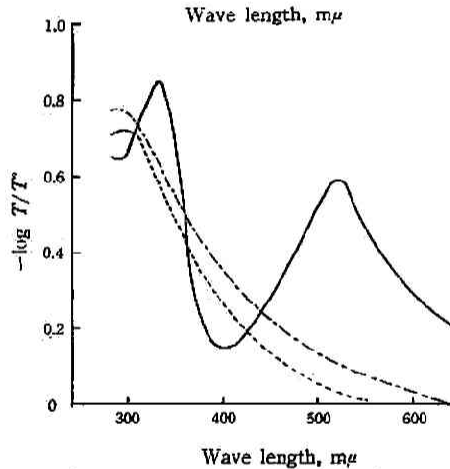


Fig. 3 Absorption spectra of the mixture of  
DPPH and AIBN  
DPPH ;  $5 \times 10^{-4}$  (mole/l)  
AIBN ;  $5 \times 10^{-2}$  (mole/l)  
Irradiation time ;  
———— : 0 hr. (in benzene)  
----- : 1 hr. (in deaerated benzene)  
- · - · - : 1 hr. (in benzene)

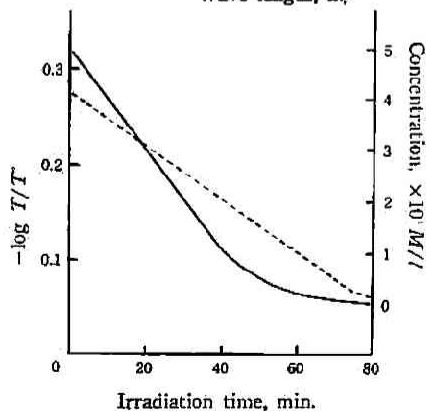


Fig. 4 Change of the concentration of DPPH  
according to the irradiation  
Solvent : deaerated benzene  
———— : DPPH ( $5 \times 10^{-4}$  mole/l)  
          : AIBN ( $5 \times 10^{-2}$  mole/l)  
----- : DPPH ( $4.1 \times 10^{-4}$  mole/l)  
          : AIBN ( $2 \times 10^{-2}$  mole/l)

*ESR spectra*

In the course of the reaction of DPPH with AIBN by irradiation, the change of the intensity of DPPH was observed. The intensity of DPPH decreased monotonously with the irradiation time. Though the color of the sample solution was yellow after irradiation for a long time, it was immediately changed to violet by shaking with solid lead peroxide. The solution thus obtained showed the same ultra-violet and ESR spectra as those of DPPH, but it could not be clarified whether para-substitutions of the diphenyl-group of DPPH are substituted or not.

**Results with the solution containing dissolved oxygen***Ultra-violet, visible and infrared spectra*

By using a benzene solution of AIBN (initial concentration: 0.01 mole/l), the change of a ultra-violet spectra according to irradiation time is shown in Fig. 5, where the absorption maximum corresponding to the existence of DKI does not exist. The ultra-violet and visible spectrum of a mixture of DPPH ( $5 \times 10^{-4}$  mole/l) and AIBN ( $5 \times 10^{-2}$  mole/l) after one hour irradiation is shown in Fig. 3. The color of the sample solution after the irradiation was orange and it was not changed to violet by shaking with a solid lead peroxide. Hence the product in this case is not a corresponding simple hydrazine of DPPH. It was confirmed that the spectrum of DPPH in a benzene solution without AIBN does not change after long irradiation.

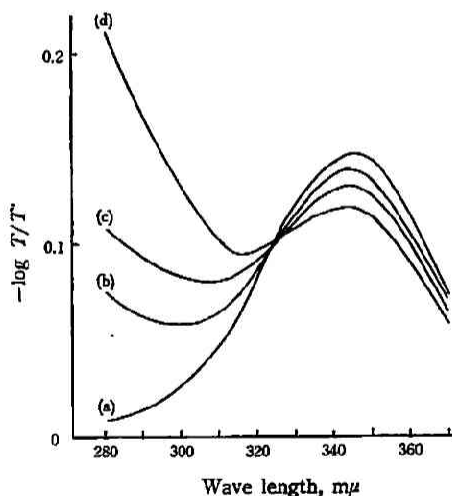


Fig. 5 Absorption spectra of AIBN  
Solvent; benzene without deaeration  
Irradiation time (min.);  
(a): 0 (b): 10 (c): 20 (d): 30

Besides, it was investigated how the rate of disappearance of DPPH depends on the initial concentration of AIBN, and the results are illustrated in Fig. 6, where the initial concentration of DPPH is kept constant ( $5 \times 10^{-4}$  mole/l) and that of AIBN is varied from  $1 \times 10^{-2}$  to  $5 \times 10^{-2}$  mole/l. The disappearance rate of DPPH was not linear with irradiation time, whereas it was linear in the deaerated solution.

*ESR spectra*

By using a mixture of DPPH ( $5 \times 10^{-4}$  mole/l) and AIBN ( $1 \times 10^{-2}$  mole/l), the changes of the ESR

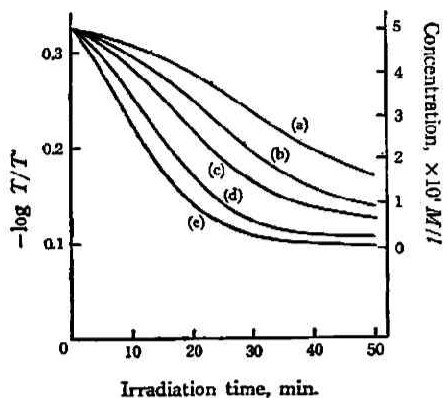


Fig. 6 Change of the concentration of DPPH according to the irradiation  
 Solvent; benzene without deaeration  
 DPPH;  $5 \times 10^{-4}$  (mole/l)  
 AIBN;  $1 \times 10^{-2}$  (mole/l)  
 (a): 1 (b): 2 (c): 3 (d): 4 (e): 5

spectra of DPPH in the course of irradiation are illustrated in Fig. 7. With the irradiation, the spectrum began to deform from a quintet to triplet, and a proton hyperfine structure appears. The intensity of the spectrum decreases corresponding to the changes observed photometrically (Fig. 6). Fig. 7 shows the appearance of two kinds of free radicals. One of these spectra (I) consists of three multiplets due to  $N^{14}$ , each giving resolved proton hyperfine structure, and the triplet splitting constant due to  $N^{14}$  is 9.8 gauss ( $g$ -value: 2.0056). The other spectrum (II) also consists of three multiplets due to  $N^{14}$ , each giving resolved proton hyperfine structure ( $g$ -value: 2.0058). After standing the sample having the spectrum (b) in Fig. 7 for 48 hours in the dark, the spectrum (I) disappeared and (II) was only observed as shown in Fig. 7 (c).

In order to confirm the structure of these two free radicals, the following experiments were performed.

The spectrum of (I) was found to coincide with that obtained with a mixture of DPPH and t-BHPO in a benzene solution as shown in Fig. 8. Moreover, the latter spectrum is the same as that obtained by the reaction of diphenylamine with dissolved oxygen<sup>5)6)</sup>. In this case the spectrum is identified as a diphenyl nitric oxide.

Then the present authors attribute the spectrum (I) to the diphenyl nitric oxide produced by the decomposition of DPPH due to the attack of peroxy free radicals from AIBN.

Though the structure of a spectrum (II) has not yet been identified it would be probable that (II) is produced by the reaction of a peroxy free radical with a picryl group of DPPH, because the intensity of (II) is always equal to that of (I) in the course of a reaction and (II) shows a triplet spectrum due to  $N^{14}$ .

If the above hypothesis is valid, the mixture of AIBN and a derivative of DPPH substituted at para-positions of a diphenyl-group will also give two kinds of free radicals by irradiation; one of which will be the derivative of diphenyl nitric oxide, the other will be the same as (II) produced in the case of DPPH.

In order to confirm the hypothesis  $\alpha\alpha'$ -di-(*p*-nitro)-phenyl- $\beta$ -picryl-hydrazyl ((*p*-NO<sub>2</sub>)<sub>2</sub>-DPPH)

5) J. R. Thomas, *J. Am. Chem. Soc.*, **82**, 5955 (1960)

6) R. H. Hoskins, *J. Chem. Phys.*, **25**, 788 (1956)

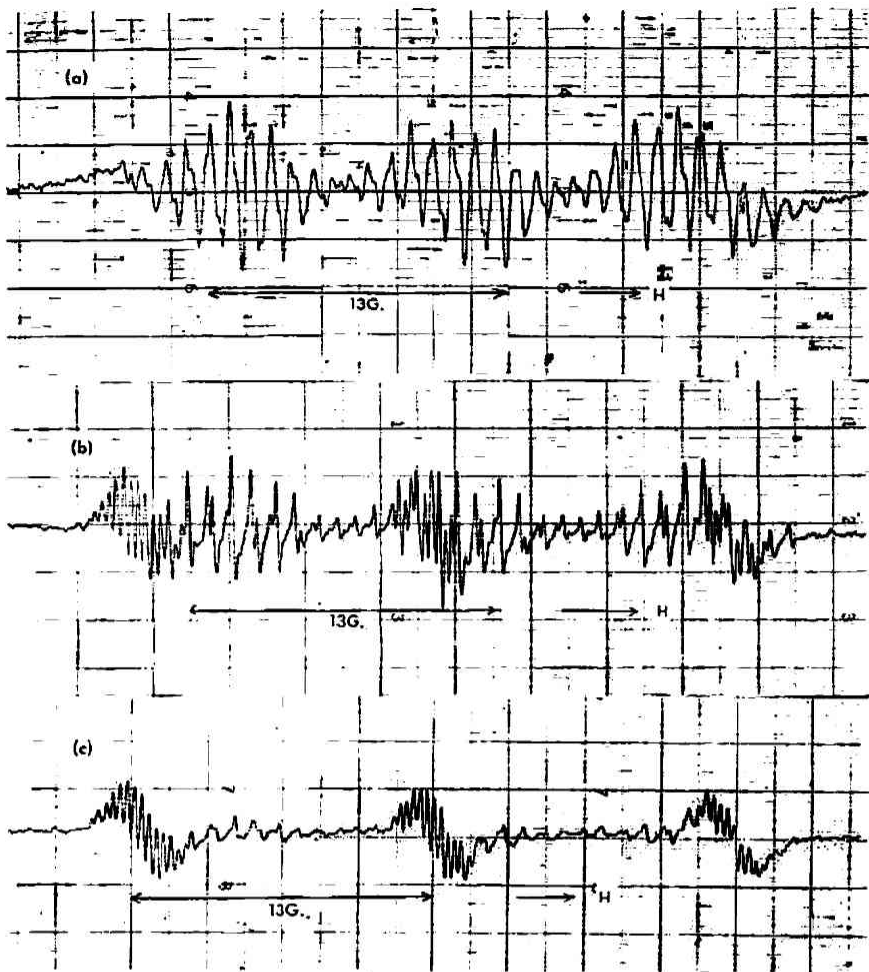


Fig. 7 ESR spectra of the mixture of DPPH and AIBN  
 Solvent ; deaerated benzene (The sample solution was irradiated  
 in the presence of dissolved oxygen.)  
 Irradiation time (min.): (a): 20 (b): 30 (c): (d) after 48hr. standing.

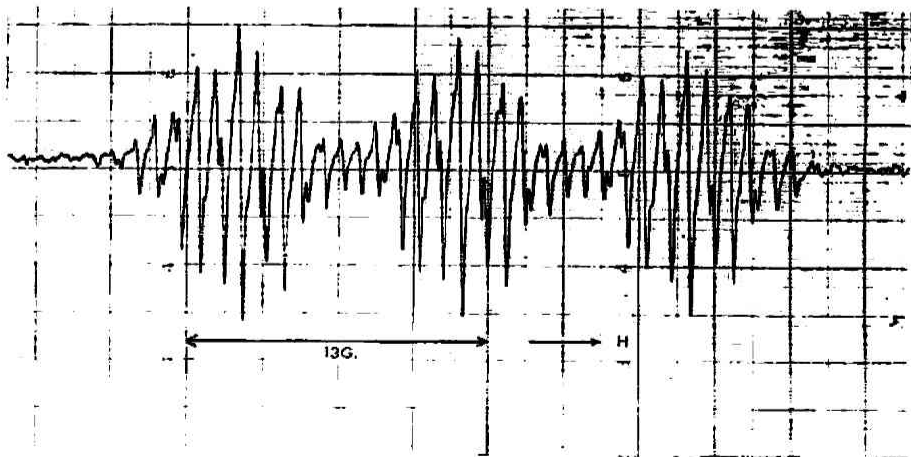
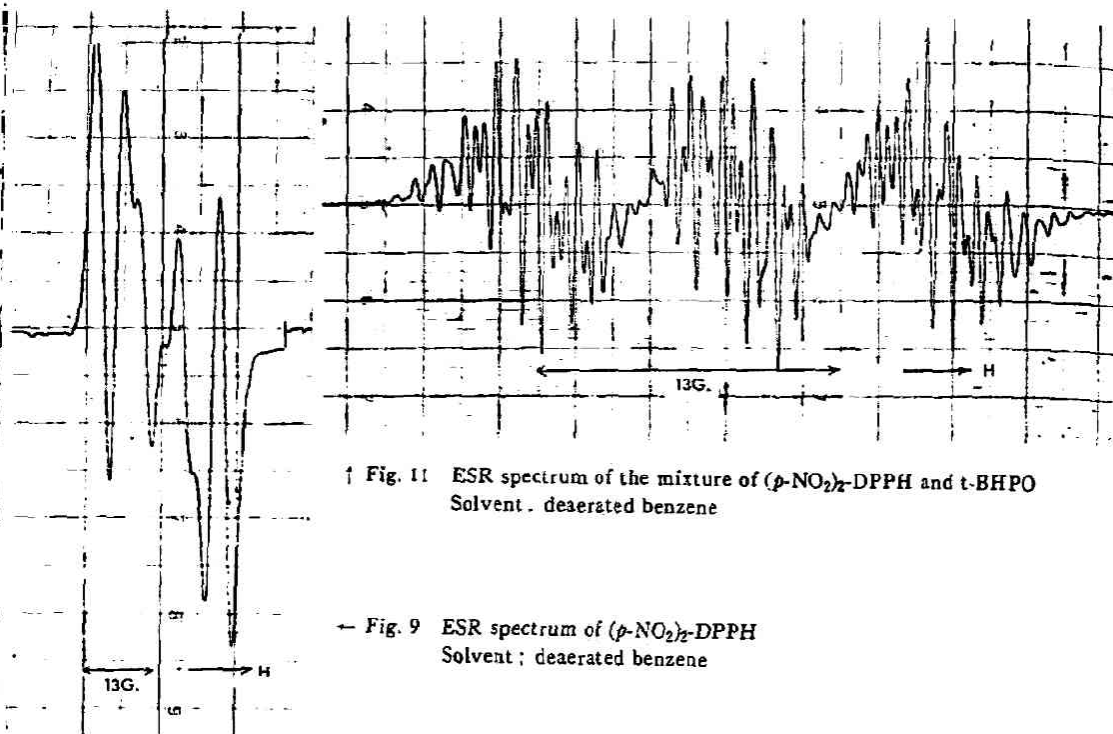


Fig. 8 ESR spectrum of the mixture of DPPH and t-BHPO  
 Solvent ; deaerated benzene



↑ Fig. 11 ESR spectrum of the mixture of  $(p\text{-NO}_2)_2\text{-DPPH}$  and  $t\text{-BHPO}$   
Solvent: deaerated benzene

— Fig. 9 ESR spectrum of  $(p\text{-NO}_2)_2\text{-DPPH}$   
Solvent: deaerated benzene

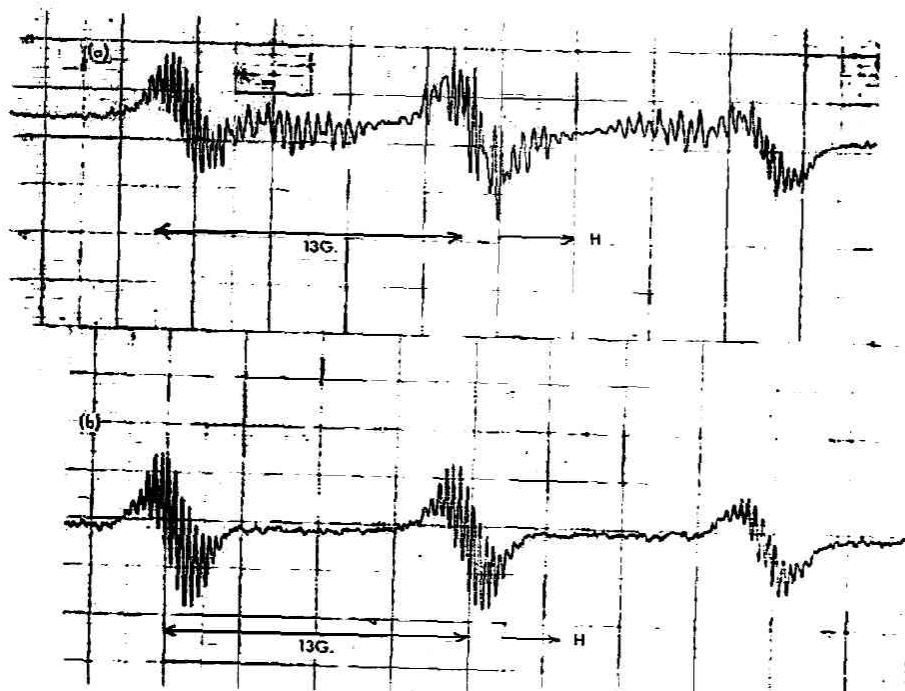


Fig. 10 ESR spectra of the mixture of  $(p\text{-NO}_2)_2\text{-DPPH}$  and AIBN  
Solvent: deaerated benzene (The sample solution was  
irradiated in the presence of dissolved oxygen.)  
(a): Irradiation time: 30 min.  
(b): (a) after 49 hr. standing.



synthesized as a derivative of DPPH<sup>7)8)</sup>. The ESR spectrum of (*p*-NO<sub>2</sub>)<sub>2</sub>-DPPH in a benzene solution agreed exactly with that reported previously<sup>8)9)</sup> (Fig. 9).

By using a mixture of (*p*-NO<sub>2</sub>)<sub>2</sub>-DPPH and AIBN in a benzene solution with dissolved oxygen, the ESR spectrum was observed. The spectrum after half an hour irradiation was shown in Fig. 10, where two kinds of free radicals appear. After standing the irradiated sample for 48 hours in the dark, one of them disappears. The spectrum of one of them coincides with that of (II) obtained in the case of DPPH, and the other (III) has a smaller splitting constant for triplet (9.1 gauss) due to N<sup>14</sup> than that of diphenylnitric oxide.

The identical spectrum with (III) could be obtained by the addition of *t*-BHPO to a benzene solution of (*p*-NO<sub>2</sub>)<sub>2</sub>-DPPH (Fig. 11).

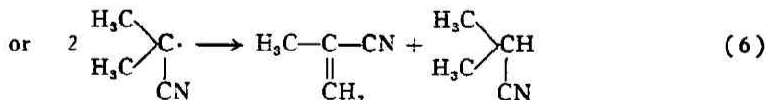
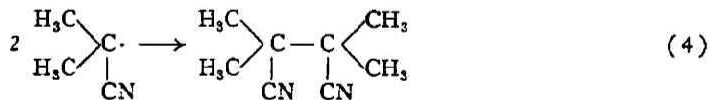
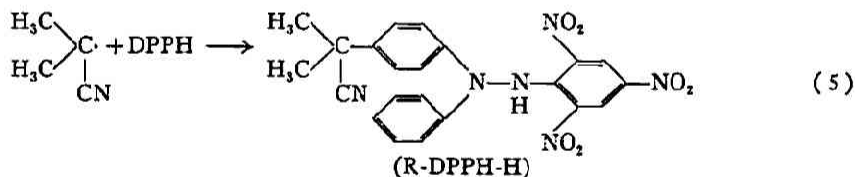
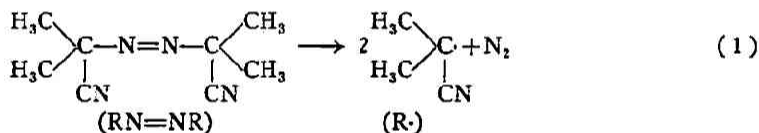
From these results, it was clarified that the N-N bond of DPPH is broken by the attack of a peroxy free radical and two kinds of free radicals are produced.

### Discussion

#### Results with the deaerated solution

It is concluded that the reaction between DPPH and AIBN radical follows the simple mechanism proposed previously by several investigators<sup>3)10)11)</sup>. The following two reaction schemes have been reported.

a) Scheme by Bawn, Mellish and Verdin<sup>10)11)12)</sup>.



7) R. H. Poirier, E. J. Kahler and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952)

8) J. A. Weil, K. V. Sane and J. M. Kinkade, Jr., *J. Phys. Chem.*, **65**, 710 (1961)

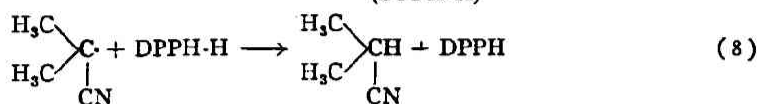
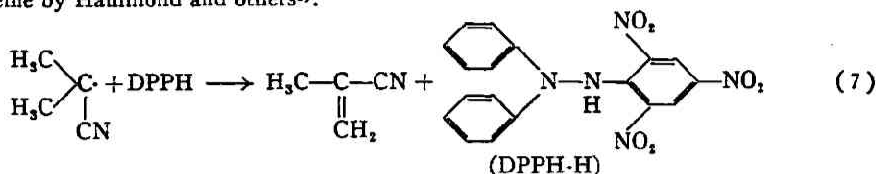
9) M. M. Chen, K. V. Sane, R. I. Walter and J. A. Weil, *J. Phys. Chem.*, **65**, 713 (1961)

10) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951)

11) D. Verdin, *Trans. Faraday Soc.*, **56**, 823 (1960)

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

b) Scheme by Hammond and others<sup>3)</sup>.



From the present results, it is certain that a corresponding hydrazine of DPPH is produced by the reaction between DPPH and IBN radical, but it is not yet clarified whether the para positions of hydrazine is substituted with IBN or not. This question might be solved if the ESR spectra of irradiated solutions gave a proton hyperfine structure after shaking with solid lead peroxide.

The reaction scheme a) better fits the experimental results. Now denoting  $f$  as the efficiency at which the produced radical  $R\cdot$  reacts with DPPH, the following equation (9) is derived from equations (1) and (5).

$$-\frac{d[\text{DPPH}]}{dt} = 2k_1f[\text{RN}=\text{NR}] \quad (9)$$

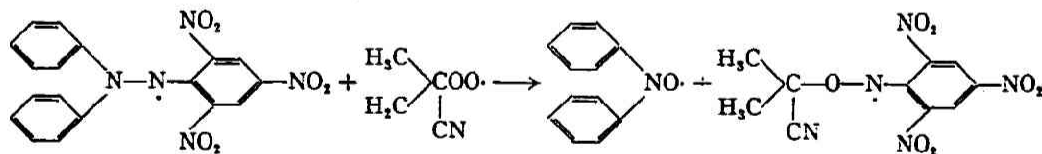
Throughout the experiments, an initial concentration of AIBN,  $[\text{RN}=\text{NR}]_0$  is in large excess compared with that of DPPH, so the instantaneous concentration of AIBN,  $[\text{RN}=\text{NR}]$  may be assumed to equal to  $[\text{RN}=\text{NR}]_0$ . It is possible to calculate  $k_1f$  from Fig. 4 and equation (9).

$$k_1f = 1.76 \times 10^{-6} \text{ (sec}^{-1}\text{)}$$

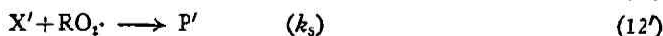
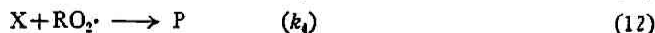
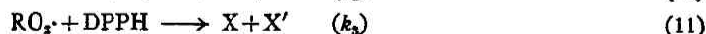
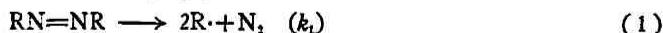
#### Results with the solution containing dissolved oxygen

In this case Verdin stated that the infra-red spectra of the end products don't show the existence of any N-H bond, so it was concluded that a peroxy free radical adds to  $\beta$ -nitrogen atom of DPPH<sup>11)</sup>.

On the contrary, the present results lead to another conclusion that a peroxy free radical breaks the N-N bond of DPPH, producing two kinds of free radicals. The authors propose the following scheme analogous to that stated by Möbius and Schneider<sup>13)</sup>.



As the whole reaction process, the following equation can be written.



13) K. Möbius and F. Schneider, *Z. Naturforsch.*, **18a**, 428 (1963)

where X and X' are the intermediates produced, P and P' are stable end products. When the initial concentration of DPPH is large, the reaction (13) should be negligible and almost  $\text{RO}_2\cdot$  radicals should react with DPPH, X and X'. As it was known that the concentration of X is nearly equal to that of X' in the whole course of reaction, it would be possible to consider that only one of them should contribute to the rate equation. So the following rate equation can be obtained.

$$\frac{d[\text{R}\cdot]}{dt} = 2k_1f[\text{RN}=\text{NR}] - k_2[\text{R}\cdot] \quad (14)$$

$$\frac{d[\text{RO}_2\cdot]}{dt} = k_2[\text{R}\cdot] - k_3[\text{RO}_2\cdot][\text{DPPH}] - k'_4[\text{X}][\text{RO}_2\cdot] \quad (15)$$

$$\frac{d[\text{DPPH}]}{dt} = -k_3[\text{RO}_2\cdot][\text{DPPH}] \quad (16)$$

$$\frac{d[\text{X}]}{dt} = k_3[\text{RO}_2\cdot][\text{DPPH}] - k_4[\text{RO}_2\cdot][\text{X}] \quad (17)$$

Assuming  $[\text{R}\cdot]$  and  $[\text{RO}_2\cdot]$  constant at stationary state, equations (18) and (19) can be derived from equations (14) and (15), respectively.

$$[\text{R}\cdot] = \frac{2k_1f}{k_2}[\text{RN}=\text{NR}] \quad (18)$$

$$[\text{RO}_2\cdot] = \frac{2k_1f[\text{RN}=\text{NR}]}{k_3[\text{DPPH}]_0} \quad (19)$$

where  $[\text{DPPH}]_0$  represents the initial concentration of DPPH. By using equation (19), the term  $[\text{RO}_2\cdot]$  is eliminated in (16) and it becomes as follows:

$$\frac{d[\text{DPPH}]}{dt} = -2k_1f[\text{RN}=\text{NR}] \frac{[\text{DPPH}]}{[\text{DPPH}]_0} = -k'[\text{DPPH}] \quad (20)$$

$$k' = 2k_1f \frac{[\text{RN}=\text{NR}]}{[\text{DPPH}]_0} \quad (\cong \text{constant}) \quad (21)$$

By integrating equation (20), one obtains an expression for  $[\text{DPPH}]$ .

$$[\text{DPPH}] = [\text{DPPH}]_0 e^{-k't} \quad (22)$$

From equations (19), (20) and (22), another expression can be derived for equation (17).

$$\frac{d[\text{X}]}{dt} = k'[\text{DPPH}] - \frac{k_4}{k_3}k'[\text{X}] \quad (23)$$

$$= k'[\text{DPPH}]_0 e^{-k't} - k''[\text{X}] \quad (24)$$

$$k'' = (k_4/k_3)k' \quad (25)$$

By integrating equation (24),  $[\text{X}]$  can be written as follows:

$$[\text{X}] = k'[\text{DPPH}]_0 \frac{e^{-k''t} - e^{-k't}}{k' - k''} \quad (26)$$

The measured value in the photometric method can be assumed to be equal the sum of  $[\text{DPPH}]$  and  $[\text{X}]$ , equation (27) could be derived from equations (22) and (26):

$$[\text{DPPH}] + [\text{X}] = [\text{DPPH}]_0 \frac{k'e^{-k''t} - k''e^{-k't}}{k' - k''} \quad (27)$$

The ratio  $k_4/k_3$  can not be determined experimentally. However, when the ratio is assumed to be 2/3, the values  $[\text{DPPH}] + [\text{X}]$  calculated from equation (27) agree well with the experiments, whereas at the lower concentrations of  $[\text{DPPH}]$ , the assumption that the reaction (13) should be negligible is no more valid, so the discrepancy occurs.

According to equation (26) the concentration of  $[X]$  does not depend appreciably on the initial concentration of AIBN. It was confirmed by the experiments in which the ESR spectra of intermediates were observed with various concentrations of  $[RN=NR]$ , keeping  $[DPPH]$  constant. Moreover, as Verdin stated, the total reaction does not depend appreciably on the concentration of dissolved oxygen; this fact was confirmed by measuring the intensity of ESR spectra of intermediates using a solution saturated with oxygen prior to irradiation.

#### Summary

In a benzene solution the reaction of IBN radicals, produced from AIBN by the photo-dissociation, with DPPH was studied both in the presence and absence of dissolved oxygen. By the results using a spectrophotometric and an ESR methods, it was found that the influence of dissolved oxygen is significant.

From the view-point of reaction kinetics the following conclusions can be drawn.

1) In the deaerated solution the reaction proceeds according to a simple scheme proposed previously in the thermal decomposition of AIBN; one IBN radical reacts with one DPPH molecule, producing one corresponding hydrazine of DPPH.

2) In the presence of dissolved oxygen, IBN radicals produced by the dissociation of AIBN react immediately with dissolved oxygen, forming peroxy free radicals. It breaks the N-N bond of DPPH, producing two kinds of free radicals as intermediates which become more stable end products after further irradiation. From the analysis of ESR spectra, the structures of intermediates are identified; one is as diphenylnitric oxide, the other as a free radical including picryl group due to the decomposition of DPPH.

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