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KINETIC STUDIES ON FREE RADICAL REACTIONS

II. The Photochemical Reaction between DPPH and Methylmethacrylate

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The reaction between α, α'-diphenyl-β-picrylhydrazyl (DPPH) and methylmethacrylate (MMA) in benzene solution induced by UV irradiation was investigated.

The change of DPPH concentration was photometrically pursued, and electron spin resonance spectra of the solutions in the course of reaction were observed, where the significant influence of dissolved oxygen was found.

In the case of the absence of dissolved oxygen the apparent rate of disappearance of DPPH is of the first order, only corresponding hydrazine being produced. On the other hand, in the presence of dissolved oxygen it is of the zero order and hydrazine, diphenylnitroxide (DPNO) which was identified by ESR spectrum, and a diamagnetic substance which will be produced from the reaction of one DPPH and one peroxy radical, are produced concurrently.

In both cases it was inferred from the view-point of kinetics that DPPH not only acts as a radical scavenger but also its photo-ecxited molecule participates in the step of radical production from MMA molecule.

Introduction

It has been known that the function of dissolved oxygen is complicated in the free radical polymerization reaction of the vinyl compounds.

The mechanisms have ever been discussed by many investigators and the authors also have reported about the influence of dissolved oxygen in the case of the photo-dissociation reaction of azo-bis-isobutyronitrile, using DPPH as a radical scavenger[1].

Bovey and Kolthoff suggested the following mechanism[2], in the emulsion polymerization reaction of styrene initiated by potassium persulfate, from the polarographic studies and from the mesurement of the changes of oxygen pressure during the reaction, that is,

$$\begin{array}{llll} \mathrm{M} & + \mathrm{OH}\cdot(\text{from } \mathrm{K_2S_2O_8}) & \longrightarrow \mathrm{HOM}\cdot & (1) \\ \mathrm{HOM}\cdot & + \mathrm{O_2} & \longrightarrow \mathrm{HOMOO}\cdot & (2) \\ \mathrm{HOMOO}\cdot & + \mathrm{M} & \longrightarrow \mathrm{HOMOOM}\cdot & (3) \\ \mathrm{HOMOOM}\cdot & + \mathrm{O_2} & \longrightarrow \mathrm{HOMOOMOO}\cdot & (4) \\ & & \longrightarrow (\text{—O—O—M—})_n & \end{array}$$

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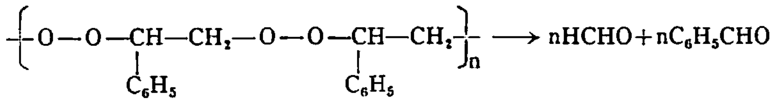
where M represents monomer.

Considering these elementary reactions, they concluded that polymeric peroxide copolymerized with oxygen molecules is produced. They also concluded that in the case of styrene, analogous to the case of phenylstyrene, reported by Staudinger3), benzaldehyde and formaldehyde are produced by the decomposition of polymeric peroxide due to the following reaction,

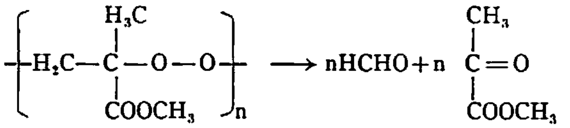


$$\left[-O-O-\underset{C_6H_5}{CH}-CH_2-O-O-\underset{C_6H_5}{CH}-CH_2-\right]_n \longrightarrow nHCHO+nC_6H_5CHO$$

Barnes4), Elofson and Jones5) recognized in the cases of vinyl acetate, methylacrylate and methylmethacrylate that oxygen retards or inhibits the polymerization reactions in whatever photochemical, thermal, or catalyzed, and that a little amount of polymeric peroxide is produced.

In methylmethacrylate (MMA) the final products isolated, are saturated with one mole of hydrogen for five carbons, and show the absorption spectrum indicating methylpyruvate after heated or ultra-violet irradiated.

Hence, in this case also, the polymeric peroxide decomposes into methylpyruvate and formaldehyde.



$$\left[-H_2C-\overset{H_3C}{\underset{COOCH_3}{C}}-O-O-\right]_n \longrightarrow nHCHO+n\,\overset{CH_3}{\underset{COOCH_3}{C}}{=}O$$

In these cases, producing polymeric peroxide, the retardation or inhibition of polymerization reaction by oxygen is explained as follows: the reaction (2) is faster than the propagation reaction;

$$M_n\cdot+M \longrightarrow M_{n+1}\cdot \qquad (5)$$

neverthless the reaction (3) is much slower than the reaction (4). So the rate of polymerization seems to be retarded in the presence of dissolved oxygen.

From these view-points, Mayo and Miller discussed the production of methylpyruvate, formaldehyde and polymeric peroxide in MMA6).

Kerber investigating the rate of consumption of oxygen, concluded that the copolymer of 1 : 1 of MMA to oxygen molecule is produced and discussed the solvent effects on the basis of dielectric constants7).

By means of spectrophotometry and ESR, the authors have elucidated1) that the isobutyronitrile radical produced by the photolysis of AIBN reacts with dissolved oxygen to be peroxy radical, which reacting with DPPH used as a radical scavenger, produces diphenylnitroxide (DPNO) immediately.

This study was performed to prove the existence of peroxy radical, using DPPH as a radical

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1) J. Osugi, M. Sato and M. Sasaki, *This Journal*, **33**, 53 (1963)

2) F. A. Bovey and I. M. Kolthoff, *J. Am. Chem. Soc.*, **69**, 2143 (1947)

3) H. Staudinger, *Ber.*, **58**, 1075 (1925)

4) C. E. Barnes, *J. Am. Chem. Soc.*, **67**, 217 (1945)

5) C. E. Barnes, R. M Elofson and G. D. Jones, *ibid*, **72**, 210(1950)

6) F.. R. Mayo and A. A. Miller, *ibid*, **80**, 2493 (1958)

7) R. Kerber, *Makromol. Chem.* **40**, 25 (1960)

scavenger, and to obtain some informations about the reaction mechanism of the inhibition of DPPH, by means of spectrophotometry and electron spin resonance.

DPPH in benzene solution does not change if ultra-violet irradiation is done, but when MMA added, the absorbance of DPPH at 520 mμ disappears with irradiation time and faster in the presence of dissolved oxygen than in deaerated solution. Studing the rate of disappearance of DPPH, the authors concluded that the initiation step is not from MMA itself but the reaction that DPPH photoexcited, reacts with MMA to produce monomer radical and hydrazine (DPPH–H) by hydrogen abstraction. The existence of peroxy radical or peroxide has been verified, though indirectly, since DPNO is produced in the solutions with dissolved oxygen during the irradiation.

Experimental

Materials ;

DPPH, Benzene : The purifications are the same as previously reported.

MMA : Commercial monomer was repeatedly washed with 5% sodium hydroxide ; it was then washed with water followed by two washings with a saturated solution of sodium bisulfite in water. Then it was washed twice more with water, dried over sodium sulfate and then was fractionally distilled under argon at reduced pressure, only the middle cut being obtained, b. p. 24°C (32 mmHg), 39°C (73mmHg), 43°C (90 mmHg). It was stored at about 7°C and was redistilled just before each experiment in vacuum.

Apparatus ;

The general sets are the same as those in the previous paper, but were displaced simple photometer, for a photomultiplier (Hitachi P–1 type) and a recorder to follow the change of absorption with irradiation time, and a couple of filters, cupric chloride in aqueous solution (5 g/50m*l*, 28 mm thickness) and Waltz Wol filter were inserted between the light source (tungsten lamp) and a reaction cell. The wave length transmitted is from 520 to 600 mμ and obeyed Beer's law up to about 1×10^{-4} mole/*l* of DPPH concentration.

Light source for irradiation : Matsuda 500 W high pressure mercury lamp (3650 Å) with a filter of cupric sulfate solution (100g/*l*).

Procedure ;

A chloroform solution of DPPH (2.5×10^{-4} mole/*l*) was first prepared and taking a certain volume of this solution (0.25～1.0 m*l*) to the reaction cell, the solvent only without heating was vaporized ; after vaporizing completely, a mixture of benzene and MMA is transferred. The procedure to eliminate the dissolved oxygen is the same as in the previous paper. The electron spin resonance spectra were observed at room temperature.

Results

Results with the deaerated solution

Ultra-violet, visible spectra

The spectrum of DPPH in MMA is illustrated in Fig. 1 (a), the absorption band of MMA existing at shorter weve length than 300 mμ. Adding benzene (benzene : 90 vol. %), no change was recognized in the spectrum of DPPH, and neither the leaving of this solution in dark for about a day nor the irradiation of light in visible region (520~600 mμ) did not change its spectrum. But by ultra-viotet irradiation it changes as shown in Fig. 1 (b), where the spectrum was recorded with the solution diluted to one half after irradiation.

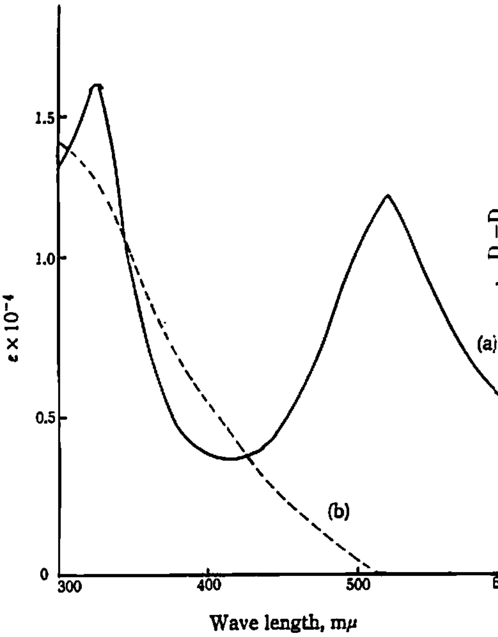

Fig. 1 Absorption spectra of DPPH
(a): not irradiated (in MMA)
(b): 150 minutes irradiated in deaerated MMA

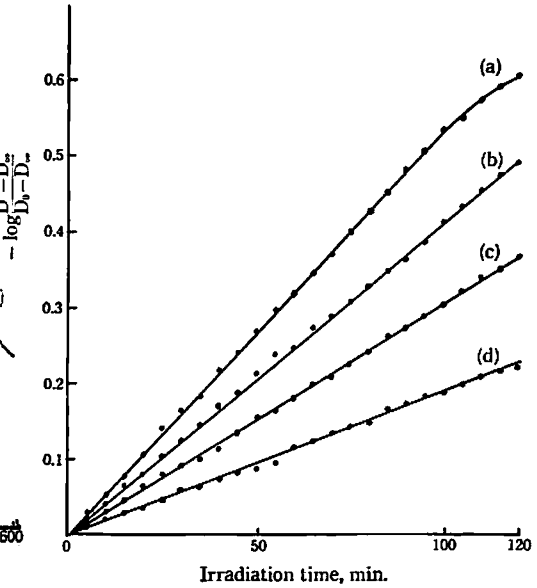

Fig. 2 First-order plots of change of DPPH according to irradiation in deaerated solutions
D : concentration of DPPH at any time during irradiation
D_0 : initial concentration of DPPH
D_∞ : concentration of DPPH after long irradiation
(a) ; D_0 : 1.01×10^{-4} (mole/l), MMA : 100 vol.%
(b) ; D_0 : 1.16×10^{-4} (mole/l), MMA : 40 vol.% in benzene
(c) ; D_0 : 1.05×10^{-4} (mole/l), MMA : 20 vol.% in benzene
(d) ; D_0 : 1.00×10^{-4} (mole/l), MMA : 10 vol.% in benzene

The rates of disappearance of DPPH were measured in benzene solutions of various concentrations of DPPH and MMA, which were of the first order with respect to the concentration of DPPH so that the plots of $-\log\{(D-D_0)/(D_0-D_\infty)\}$ vs time are linear as shown in Fig. 2. The slopes obtained from such plots are written in the fourth column of Table 1 for the various concentrations of DPPH and MMA.

Table 1 Results obtained from first-order plots at various concentrations of DPPH and MMA in benzene solutions

concentration of MMA in benzene (vol. %)	initial concentration of DPPH ($\times 10^4$mole. l^{-1})	k' (slope) ($\times 10^3$ min.$^{-1}$)	$1/k$ ($1/2.303k'$) ($\times 10^{-2}$min.)
100	0.50	5.25	0.80
40	0.47	4.00	1.01
20	0.37	2.86	1.52
10	0.41	1.85	2.34
100	1.01	5.32	0.82
40	1.16	4.12	1.05
20	1.05	3.06	1.42
10	1.00	1.90	2.30
100	0.26	5.35	0.80
60	0.26	4.44	0.98
40	0.26	3.90	1.11
20	0.30	2.89	1.50
10	0.30	1.93	2.25

Electron Spin Resonance spectra

In the course of irradiation of the solution of DPPH in MMA, the intensity of DPPH only decreased monotonously with irradiation time, the solution coming to be yellow after long irradiation, being immediately converted to be violet by treating with a small quantity of solid lead peroxide. The substance thus oxidized by lead peroxide showed the same ultra-violet, visible and ESR spectra as DPPH. In the course of irradiation the absorbances both before and after oxidation were measured and shown in Table 2, from which it is said that for each reaction time the concentration of DPPH after oxidation is equal to the initial concentration, so in deaerated solution, all DPPH come to be corresponding hydrazine (DPPH-H).

Table 2 The concentrations of DPPH before and after treatment with lead peroxide analyzed by measuring the optical density
initial concentration of DPPH ; 1.09 10^{-4} mole/l
MMA ; 100vol.%

irradiation time (min.)	[DPPH] ($\times 10^4$mole. l^{-1}.)	[DPPH]+oxidizable products ($\times 10^4$ mole. l^{-1}.)
0	1.09	1.09
10	0.97	1.00
20	0.86	1.09
30	0.75	1.09
40	0.67	1.13
50	0.59	1.10
60	0.53	1.08
70	0.46	1.07
100	0.30	1.10
120	0.26	1.12
∞	0.002	1.11

Results with the solution containing dissolved oxygen

Ultra-violet and visible spectra

DPPH itself is rather stable in the solution containing dissolved oxygen, but it has been known that vinyl compounds such as MMA are autoxidized8), though rather slowly, and it has been found that a small amount of polymeric peroxide is produced in thermal or photo-initiated polymerization in solution with dissolved oxygen2)-7).

About MMA only, the authors could recognize no difference in the ultra-violet, infrared spectra and viscosity before and after irradiation. Moreover, DPPH in MMA solution ($\simeq 10^{-4}$ mole/*l*) showed no change if being left in dark. Though Barnes, Elofson and Jones reported that when polymeric peroxide of MMA is irradiated, methylpyruvate indicating absorption band between 340 ~360 mμ appears5), the authors did not recognized any absorption in this region.

The solution of DPPH in MMA came to be orange after long irradiation, only part of which was converted to DPPH by being treated with solid lead peroxide.

The ultra-violet and visible spectra of solutions of DPPH in MMA at some intervals during irradiation are shown in Fig. 3.

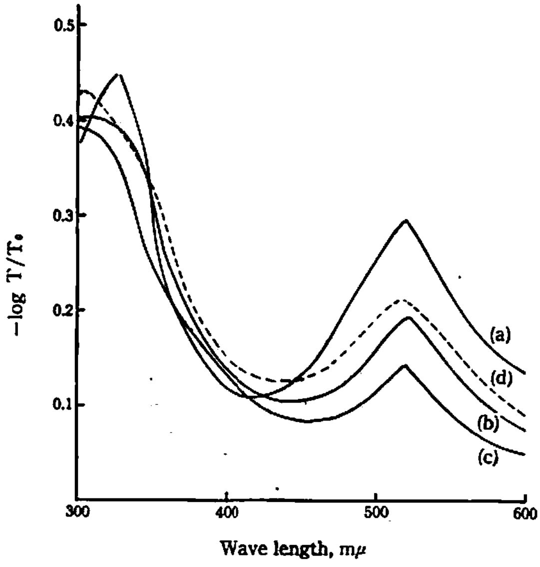

Fig. 3 Change of absorption spectrum of DPPH in MMA with dissolved oxygen
$[\mathrm{DPPH}]_0$; 3.50×10^{-5} (mole/*l*)
Irradiation time (min.);
(a): 24, (b): 36, (c): 55, (d): (b) shaken with PbO_2

The rates of disappearance of DPPH were observed for various concentrations of DPPH and MMA in benzene. DPPH decreases linearly with irradiation time as shown in Fig. 4. The slopes obtained from such plots are written in Table 3.

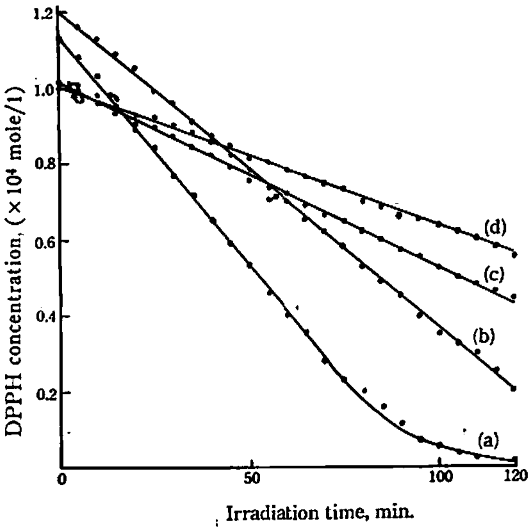

Fig. 4 Change of DPPH according to irradiation in solution containing dissolved oxygen

(a); $[DPPH]_0$: 1.13×10^{-4} (mole/l), MMA: 100 vol. %

(b); $[DPPH]_0$: 1.20×10^{-4} (mole/l), MMA: 40 vol. % in benzene

(c); $[DPPH]_0$: 1.01×10^{-4} (mole/l), MMA: 20 vol. % in benzene

(d); $[DPPH]_0$: 1.00×10^{-4} (mole/l), MMA: 10 vol. % in benzene

Table 3 Results obtained from zero-order plots at various concentrations of DPPH and MMA in benzene solutions

concentration of MMA in benzene (vol.%)	initial concentration of DPPH ($\times 10^4$mole. l^{-1})	k'' (slope) ($\times 10^7$mole.l^{-1}. min.$^{-1}$)	$1/k''$ ($\times 10^{-6}$mole.$^{-1}$ l.min.)
100	1.13	12.51	0.80
40	1.20	8.33	1.20
20	1.01	5.52	1.81
10	1.00	3.50	2.85
100	0.66	12.30	0.81
40	0.59	9.09	1.10
100	0.45	10.50	0.95
40	0.50	9.43	1.06
20	0.49	5.32	1.88
10	0.57	3.64	2.75
100	0.24	11.10	0.90
60	0.26	10.70	0.93
40	0.27	8.54	1.17
20	0.25	6.06	1.65
10	0.26	3.45	2.90

Electron spin resonance spectra

Fig. 5 shows the change of ESR spectra of the solution of DPPH in MMA (5×10^{-5} mole/l) with irradiation time, where irradiation was made with the solution containing dissolved oxygen but the observations of ESR spectra were done after eliminating dissolved oxygen by the usual way. After 30 minutes' irradiation the spectrum began to deform from the typical quintet of DPPH, and finally came to be triplet and proton hyperfine structure appeared (Fig. 5 (d), (e)). This spectrum corresponds to DPNO, where $a_N=9.65$ gauss and $g=2.0050$. When the solution indicating the ESR spectrum as in Fig. 5 (d) was shaken with lead peroxide and rapidly filtered, the spectrum shown in Fig. 5 (f) was observed, which shows, neverthless DPNO remains, clearly part of the products being converted to DPPH.

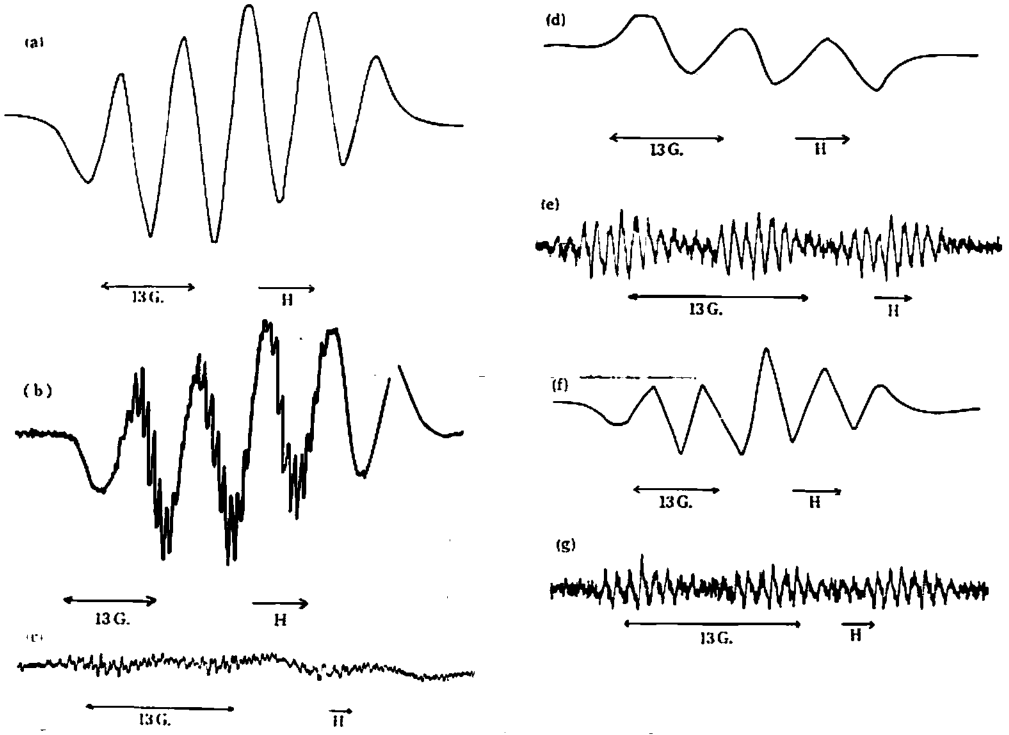

Fig. 5 Change of ESR spectrum of the solution of DPPH (5×10^{-5} mole/l) in MMA according to irradiation (The sample solutions were irradiated in the presence of dissolved oxygen but the spectra were observed after elimination of dissolved oxygen.) Irradiation time (min.); (a): 0, (b) and (c): 30, (d) and (e): 60, (f) and (g): (d) shaken with PbO_2

In the case of a mixture of AIBN and DPPH in benzene, when dissolved oxygen is present, isobutyronitrile radical produced by the photo-dissociation of AIBN reacts immediately with dissolved oxygen, producing peroxy radical, which attacks DPPH and breaks its N–N bond to produced two kinds of free radicals[1]. Moreover it is known that when *tert*-butylhydroperoxide is dropped in DPPH in solution, DPNO only is immediately observed[9,10]. Hence in the case of MMA also, it is suggested that peroxy radical or hydroperoxide compounds will be produced in the presence of dissolved oxygen. The smaller value of a_N in MMA than in benzene may be due to the solvent effects.

Discussion

Results with the deaerated solution

The rate of decrease of DPPH is of the first order with respect to DPPH concentration, as shown in Fig. 2. This fact cannot be explained by the photo-initiation of MMA itself and it does not support the photo-initiation of MMA that MMA has absorption band only below 300 mμ, since the wave length of the light source for irradiation is above 300 mμ.

The slopes of these first-order plots are independent of the initial concentrations of DPPH but dependent on the concentrations of MMA as found from Table 1. The plots of $1/k$ vs $1/[\mathrm{M}]_0$ are linear as shown in Fig. 6, where the concentrations of MMA (mole/l) are determined by mearsuring its density.

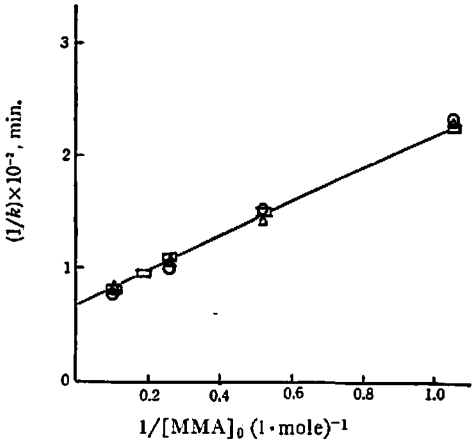

Fig. 6 The dependence of the slopes of first-order plots (Fig. 2) on initial concentrations of MMA

$[\mathrm{DPPH}]_0$: ○: $(0.44\pm0.06)\times 10^{-4}$ (mole/l)

△: $(1.08\pm0.08)\times 10^{-4}$ (mole/l)

□: $(0.28\pm0.02)\times 10^{-4}$ (mole/l)

From these results, the rate of decrease of DPPH is represented as follows.

$$-\frac{d[\mathrm{DPPH}]}{dt}=\frac{\mathrm{A}[\mathrm{M}]_0}{\mathrm{B}[\mathrm{M}]_0+\mathrm{C}}[\mathrm{DPPH}] \qquad (6)$$

where A, B and C are constants.

Considering that the product is only hydrazine (DPPH-H) and that the rate of decrease of DPPH is of the first order, it is suggested that the photo-excitation of DPPH is concerned in the reaction mechanism, hence the following is proposed as the reaction scheme.

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8) C. Walling, "Free Radicals in Solution" Wiley (1957) p. 397

9) H. Ueda, Z. Kuri and S. Shida, *J. Chem. Phys.*, **36**, 1676 (1962)

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

$$\begin{array}{lll}
\mathrm{DPPH} \xrightarrow{h\nu} \mathrm{DPPH}^* & k_1 & \text{(i)} \\
\mathrm{DPPH}^* + (\mathrm{S}) \longrightarrow \mathrm{DPPH} + (\mathrm{S}) & k_2 & \text{(ii)} \\
\mathrm{DPPH}^* + \mathrm{M} \longrightarrow \mathrm{DPPH\text{-}H} + \mathrm{M}\cdot & k_3 & \text{(iii)} \\
\mathrm{M}\cdot \ + \mathrm{M} \longrightarrow \mathrm{M}_1\cdot & & \\
\mathrm{M}_n\cdot \ + \mathrm{M} \longrightarrow \mathrm{M}_{n+1}\cdot & k_p & \\
\mathrm{DPPH} + \mathrm{M}_n\cdot \longrightarrow \mathrm{DPPH\text{-}H} + \mathrm{M}' & k_4 & \text{(iv)}
\end{array}$$

where DPPH*, M and M′ represent the excited state of DPPH, MMA and some diamagnetic substance (i. e. polymer) from MMA respectively, and (S) represents solvent or MMA in large excess and step (ii) means the deactivation of DPPH* by these substance.

DPPH exists sufficient compared with stationary concentration of $\mathrm{M}_n\cdot$ which reacts with DPPH, so the recombination reaction of $\mathrm{M}_n\cdot$ may not be considered.

Assumining a stationary state with respect to $[\mathrm{M}_n\cdot]$ and $[\mathrm{DPPH}^*]$,

$$\frac{d[\mathrm{M}_n\cdot]}{dt} = k_3[\mathrm{M}][\mathrm{DPPH}^*] - k_4[\mathrm{DPPH}][\mathrm{M}_n\cdot] = 0 \tag{7}$$

$$\frac{d[\mathrm{DPPH}^*]}{dt} = k_1[\mathrm{DPPH}] - k'_2[\mathrm{DPPH}^*] - k_3[\mathrm{M}][\mathrm{DPPH}^*] = 0\cdot\dagger \tag{8}$$

From equation (8),

$$[\mathrm{DPPH}^*] = \frac{k_1[\mathrm{DPPH}]}{k'_2 + k_3[\mathrm{M}]}. \tag{9}$$

Since overall reactions are (iii) and (iv), using equations (7) and (9)

$$\begin{aligned}
-\frac{d[\mathrm{DPPH}]}{dt} &= k_3[\mathrm{DPPH}^*][\mathrm{M}] + k_4[\mathrm{DPPH}][\mathrm{M}_n\cdot] \\
&= \frac{2k_1k_3[\mathrm{M}]}{k'_2 + k_3[\mathrm{M}]}[\mathrm{DPPH}] \\
&= k[\mathrm{DPPH}].
\end{aligned} \tag{10}$$

[MMA] exists in large excess compared with [DPPH], so [MMA] may be equal to $[\mathrm{MMA}]_0$, hence

$$k = \frac{2k_1k_3[\mathrm{M}]_0}{k'_2 + k_3[\mathrm{M}]_0} \tag{11}$$

$$-\log\left(\frac{[\mathrm{DPPH}]}{[\mathrm{DPPH}]_0}\right) = \frac{kt}{2.303} = k't \tag{12}$$

$$\frac{1}{k} = \frac{1}{2.303k'} = \frac{k'_2}{2k_1k_3}\frac{1}{[\mathrm{M}]_0} + \frac{1}{2k_1}. \tag{13}$$

So the plots of $1/k$ vs $1/[\mathrm{M}]_0$ are linear, from Fig. 6 the following values are obtained.

$$\left.\begin{aligned}
&k_1 = (0.73 \pm 0.1) \times 10^{-2}\ (\mathrm{min.}^{-1}) \\
&\frac{k'_2}{2k_1k_3} = (1.66 \pm 0.15) \times 10^{2}\ (\mathrm{mole.}\ l^{-1}.\ \mathrm{min.}) \\
\text{Hence}\quad &k'_2/k_3 = 2.32 \pm 1.1\ (\mathrm{mole.}\ l^{-1}.)
\end{aligned}\right\} \tag{14}$$

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† k'_2 is defined as k_2 (S) at the deactivation step (ii).

11) J. Soma, T. Komatsu, H. Kashiwabara and T. Seguchi, 2nd Symposium on ESR, Kyoto, Japan (1963)

The viscosity of MMA solution containing DPPH after long irradiation is not different from that of pure MMA before irradiation, so $M_n\cdot$ radical concerning the step (iv) will be either monomer radical or polymer radical with very low degree of polymerization, and the reaction between those radicals and DPPH is much faster than the propagation reaction of polymer radicals.

The radical produced at the step (iii) in the case of MMA may be as what Soma et al observed in ultra-violet irradiation at low temperature by ESR[11], who suggested the following radical initiation,

$$H_2C=C(CH_3)COOCH_3 \xrightarrow{h\nu} H_2C=C(CH_3)COOCH_2\cdot + H\cdot$$

Results with the solution containing dissolved oxygen

ESR spectra show the production of DPNO after irradiation, which is rather stable and the amount of DPNO increases with irradiation time.

When the end products are treated with lead peroxide, only part of them is converted to DPPH. Though the authors could not identify the substance which is not oxidized by lead peroxide, it is inferred that the substance may be produced from the reaction between one peroxy radical and one DPPH melecule, from the rate equations described below. That substance is represented as X.

Measuring the DPPH concentration at any time during the irradiation, determing the DPPH-H concentration by treating with lead peroxide, and ignoring DPNO concentration because of its small amount (less than 2×10^{-6} mole/l), the following relationship is given,

$$[X]=[DPPH]_0-[DPPH]-[DPPH\text{-}H] \qquad (15)$$

and so it is possible to calculate the amount of X. The values obtained are written in the fourth column of Table 4.

From Fig. 4 the rate of decrease of DPPH is of the zero order, so

$$-\frac{d[DPPH]}{dt}=k'' \qquad (16)$$

The plots of $1/k''$ vs $1/[M]_0$ are linear as shown in Fig. 7,

$$\frac{1}{k''}=\frac{P}{[M]_0}+Q \qquad (17)$$

Table 4 Comparison of the quantities of products observed with those calculated

concentration of MMA in benzene (vol. %)	initial concentration of DPPH ($\times10^4$ mole.l^{-1}.)	irradiation time (min.)	products (obs.) ($\times10^4$ mole.l^{-1}.) X	DPPH-H	DPPH	products (calc.) ($\times10^4$ mol.l^{-1}.) DPPH-H	DPPH
40	1.20	25	0.11	0.10	0.99	0.12	0.97
40	1.20	50	0.24	0.18	0.78	0.15	0.81
40	1.20	100	0.47	0.37	0.36	0.36	0.37
100	1.13	25	0.16	0.11	0.86	0.16	0.81
100	1.13	40	0.25	0.23	0.65	0.24	0.64
10	1.00	30	0.05	0.17	0.78	0.06	0.89
10	1.00	100	0.20	0.24	0.56	0.15	0.65
40	0.50	30	0.19	0.16	0.15	0.08	0.23
20	0.49	75	0.33	0.13	0.03	0.09	0.07

and the values P and Q are found,

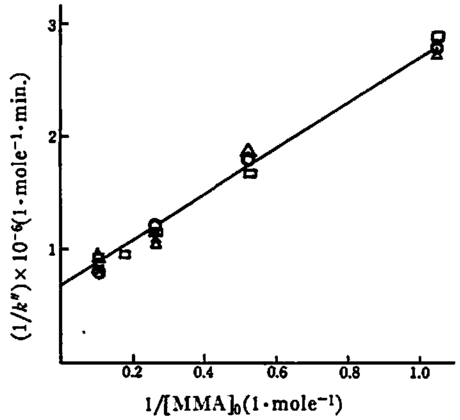

Fig. 7 The dependence of the slopes of zero-order plots (Fig. 4) on initial concentrations of MMA
$[\mathrm{DPPH}]_0$; ○ : $(1.10\pm0.1)\times10^{-4}$ (mole/l)
× : $(0.62\pm0.03)\times10^{-4}$ (mole/l)
△ : $(0.51\pm0.06)\times10^{-4}$ (mole/l)
□ : $(0.25\pm0.10)\times10^{-4}$ (mole/l)

$$Q=(0.68\pm0.08)\times10^{6}\ (l.\ \mathrm{mole.}^{-1}\mathrm{min.})$$
$$P=(1.98\pm0.10)\times10^{6}\ (\mathrm{min.})$$

Compared these values with those of (14),

$$\left.\begin{array}{l} Q=0.99\times10^{4}\ (l/2k_1) \\ P=1.19\times10^{4}\ (k'_2/2k_1k_3) \end{array}\right\} \qquad (18)$$

hence regarding these two coefficients as equal,

$$\frac{1}{k''}=R\left\{\frac{k'_2}{2k_1k_3}\frac{1}{[\mathrm{M}]_0}+\frac{1}{2k_1}\right\}. \qquad (19)$$

So equation (16) can be rewritten,

$$-\frac{d[\mathrm{DPPH}]}{dt}=\frac{1}{\mathrm{R}}\cdot\frac{2k_1k_3[\mathrm{M}]_0}{k_2'+k_3[\mathrm{M}]_0}. \qquad (20)$$

It seems to be explained by the initiation step of MMA itself only if the rate of decrease of DPPH is of the zero order, but equation (20) can not be derived from that mechanism. Moreover leaving the solution of DPPH in MMA in dark, the concentration of DPPH did not change. So the autoxidation reaction does not occur. DPPH in benzene solution without MMA showed no change if being irradiated. Hence it is said that the influence of dissolved oxygen is to produce peroxy radical or peroxide compounds in the course of irradiation, and not to DPPH itself directly.

As the general scheme of this reaction, it is reasonable to consider those steps, that DPPH is first photo-excited as in the case of the absence of dissolved oxygen (i), then the reaction of this excited molecule, DPPH*, with MMA produces a MMA monomer radical (iii), which, reacting with dissolved oxygen immediately, produces a peroxy radical. The peroxy radical will react with DPPH successively to produce a diamagnetic substance, X.

$$\begin{array}{llllll}
\mathrm{DPPH} & & & \xrightarrow{h\nu} \mathrm{DPPH^*} & k_1 & (\mathrm{i}) \\
\mathrm{DPPH^*} & + & (\mathrm{S}) & \longrightarrow \mathrm{DPPH}+(\mathrm{S}) & k_2 & (\mathrm{ii}) \\
\mathrm{DPPH^*} & + & \mathrm{M} & \longrightarrow \mathrm{DPPH{-}H}+\mathrm{M}\cdot & k_3 & (\mathrm{iii}) \\
\mathrm{M}_n\cdot & + & \mathrm{O_2} & \longrightarrow \mathrm{M}_n\mathrm{O_2}\cdot & k_5 & (\mathrm{v}) \\
\mathrm{M}_n\mathrm{O_2}\cdot & + & \mathrm{M} & \longrightarrow \mathrm{M}_n\mathrm{O_2M}\cdot & k_6 & (\mathrm{vi}) \\
\mathrm{M}\cdot & + & \mathrm{M} & \longrightarrow \mathrm{M_2}\cdot & \rbrace\, k_p & \\
\mathrm{M}_n\cdot & + & \mathrm{M} & \longrightarrow \mathrm{M}_{n+1}\cdot & & \\
\mathrm{M}_n\mathrm{O_2}\cdot & + & \mathrm{M} & \longrightarrow \mathrm{M}_n\mathrm{O_2H}+\mathrm{M}\cdot & k_7 & (\mathrm{vii}) \\
\mathrm{M}_n\cdot & + & \mathrm{DPPH} & \longrightarrow \mathrm{DPPH{-}H}+\mathrm{M}' & k_4 & (\mathrm{iv}) \\
\mathrm{M}_n\mathrm{O_2H} & + & \mathrm{DPPH} & \longrightarrow \mathrm{DPNO} & k_8 & (\mathrm{viii}) \\
\mathrm{M}_n\mathrm{O_2}\cdot & + & \mathrm{DPPH} & \longrightarrow \mathrm{X} & k_9 & (\mathrm{ix}) \\
\mathrm{M}_n\mathrm{O_2}\cdot & + & \mathrm{M}_n\mathrm{O_2}\cdot & \longrightarrow \mathrm{U} & & \\
\mathrm{M}_n\mathrm{O_2}\cdot & + & \mathrm{M}_n\cdot & \longrightarrow \mathrm{V} & \rbrace\, k_t & (\mathrm{x}) \\
\mathrm{M}_n\cdot & + & \mathrm{M}_m\cdot & \longrightarrow \mathrm{W} & &
\end{array}$$

The step (vi) is much slower than the step (vii), and so being ignored[12),13)].

$[\mathrm{M}_n\cdot]$ and $\mathrm{M}_n\mathrm{O_2}]$ are so small compared with [DPPH] that the termination reactions (x) can be ignored compared with those of (iv) and (ix).

Assuming the stationary states with respect to $[\mathrm{M}_n\cdot]$, $[\mathrm{M}_n\mathrm{O_2}\cdot]$ and $]\mathrm{M}_n\mathrm{O_2H}]$ respectively,

$$d[\mathrm{M}_n\cdot]/dt=k_3[\mathrm{DPPH^*}][\mathrm{M}]-k_5[\mathrm{O_2}][\mathrm{M}_n\cdot]+k_7[\mathrm{M}][\mathrm{M}_n\mathrm{O_2}\cdot]-k_4[\mathrm{M}_n\cdot][\mathrm{DPPH}]=0, \tag{21}$$

$$d[\mathrm{M}_{n2}\cdot]/dt=k_5[\mathrm{O_2}][\mathrm{M}_n\cdot]-k_7[\mathrm{M}][\mathrm{M}_n\mathrm{O_2}\cdot]-k_9[\mathrm{M}_n\mathrm{O_2}\cdot][\mathrm{DPPH}]=0, \tag{22}$$

$$d\mathrm{M}_n\mathrm{O_2H}]/dt=k_7[\mathrm{M}_n\mathrm{O_2}\cdot][\mathrm{M}]-k_8[\mathrm{M}_n\mathrm{O_2H}][\mathrm{DPPH}]=0. \tag{23}$$

From equation (22)

$$[\mathrm{M}_n\mathrm{O_2}\cdot]/[\mathrm{M}_n\cdot]=\frac{k_5[\mathrm{O_2}]}{k_7[\mathrm{M}]+k_9[\mathrm{DPPH}]}. \tag{24}$$

Considering that $k_7\simeq 10^{-1}\sim 10$ (l. mole^{-1}. sec^{-1}.), and $k_t\simeq k_9\simeq 10^6$ (l. mole^{-1}. sec^{-1}.)[8)] because these two rate constants are of the recombination of two radicals, equation (24) is reduced to

$$[\mathrm{M}_n\mathrm{O_2}\cdot]/[\mathrm{M}_n\cdot]=\frac{k_5[\mathrm{O_2}]}{k_9[\mathrm{DPPH}]}(\equiv\kappa). \tag{25}$$

From equations (25), (21) and $k_4[\mathrm{DPPH}]\gg k_5[\mathrm{O_2}]>k_7\ \kappa[\mathrm{M}]$

$$[\mathrm{M}_n\cdot]=\frac{k_3[\mathrm{M}][\mathrm{DPPH^*}]}{k_5[\mathrm{O_2}]+k_4[\mathrm{DPPH}]-k_7\kappa[\mathrm{M}]}\simeq\frac{k_3[\mathrm{M}][\mathrm{DPPH^*}]}{k_4[\mathrm{DPPH}]}. \tag{26}$$

Using equations (25) and (26),

$$[\mathrm{M}_n\mathrm{O_2}\cdot]\simeq\frac{k_3k_5[\mathrm{O_2}][\mathrm{M}]}{k_4k_9[\mathrm{DPPH}]^2}[\mathrm{DPPH^*}] \tag{27}$$

and from equation (23)

$$[\mathrm{M}_n\mathrm{O_2H}]=\frac{\kappa k_3k_7[\mathrm{M}]^2[\mathrm{DPPH^*}]}{k_4k_8[\mathrm{DPPH}]^2}. \tag{28}$$

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12) J. L. Bolland, *Quart. Rev.*, **3**, 1 (1949)

13) L. Bateman, *ibid.*, **8**, 147 (1954)

The overall reaction rate with respect to DPPH, is

$$-\frac{d[\mathrm{DPPH}]}{dt}=k_1[\mathrm{DPPH}]-k'_2[\mathrm{DPPH^*}]+k_4[\mathrm{M}_n\cdot][\mathrm{DPPH}]+k_8[\mathrm{M}_n\mathrm{O_2H}][\mathrm{DPPH}]+k_9[\mathrm{M}_n\mathrm{O_2}\cdot][\mathrm{DPPH}]$$

and using equations (8), (25), (26), (27) and (28),

$$-\frac{d[\mathrm{DPPH}]}{dt}=2k_3[\mathrm{M}][\mathrm{DPPH^*}]+\frac{\kappa k_3k_7[\mathrm{M}]^2[\mathrm{DPPH^*}]}{k_4[\mathrm{DPPH}]}+\frac{k_3k_5[\mathrm{O_2}][\mathrm{M}][\mathrm{DPPH^*}]}{k_4[\mathrm{DPPH}]}$$

recalling equation (9) for DPPH*,

$$-\frac{d[\mathrm{DPPH}]}{dt}=\frac{2k_1k_3[\mathrm{M}]}{k_2'+k_3[\mathrm{M}]}[\mathrm{DPPH}]+\frac{k_1k_3k_5k_7[\mathrm{O_2}][\mathrm{M}]^2}{k_4k_9[\mathrm{DPPH}]\{k'_2+k_3[\mathrm{M}]\}}+\frac{k_1k_3k_5[\mathrm{O_2}][\mathrm{M}]}{k_4\{k'_2+k_3[\mathrm{M}]\}}\,. \qquad (29)$$

Being known that $k_7 \ll k_4$, k_9, the third term can be neglected compared with the second. And assuming $k_5[\mathrm{O_2}]/k_4 \gg [\mathrm{DPPH}]$ ($\leqq 10^{-4}$), the first term also can be neglected in the apparent reaction and since [M] is approximately constant and equal to $[\mathrm{M}]_0$.

$$-\frac{d[\mathrm{DPPH}]}{dt}=\frac{k_5[\mathrm{O_2}]}{2k_4}\left\{\frac{2k_1k_3[\mathrm{M}]_0}{k'_2+k_3[\mathrm{M}]_0}\right\}=\frac{k_5[\mathrm{O_2}]}{2k_4}k=k^{\prime\prime},$$

$$\frac{1}{k^{\prime\prime}}=\frac{2k_4}{k_5[\mathrm{O_2}]}\left\{\frac{k_2'}{2k_1k_3}\frac{1}{[\mathrm{M}]_0}+\frac{1}{2k_1}\right\} \qquad (30)$$

where k is given in equation (11), and $k^{\prime\prime}$ in equation (16).

Thus equation (19) has been derived and $\mathrm{R}=2k_4/k_5[\mathrm{O_2}]$. The value R is obtained from equation (18), averaging Q and P, thus

$$\left.\begin{aligned}\mathrm{R}=\frac{2k_4}{k_5[\mathrm{O_2}]}&=(1.09\pm0.10)\times10^4\ (l.\ \mathrm{mole}^{-1}),\\ \frac{k_4}{k_5[\mathrm{O_2}]}&=(0.55\pm0.05)\times10^4\ (l.\ \mathrm{mole}^{-1}).\end{aligned}\right\} \qquad (31)$$

The values of k_4 and k_5, which are the rate constants of radical recombination reactions, have known to be the order of 10^6 ($l.$ mole^{-1}. sec^{-1}.) and the solubility of oxygen in air to water is about 10^{-4}mole./l[14], so the value of R obtained above seems to be reasonable.

The experiments have been performed in open so that oxygen is always supplied in the course of reaction and so $[\mathrm{O_2}]$ is expected to be constant during the reaction.

The viscosity after the reaction is over completely, shows no difference from that of monomer, and so it may be said that the reaction (vi) and the propagation reaction procced little in amount, and that, peroxy radicals with very low degree of polymerization react with DPPH to produce some unknown substance, X.

The quantitative relationship between [X], [DPPH], and [DPPH–H], also can be accounted for by the reaction scheme described above, that is,

$$\frac{d[\mathrm{DPPH\text{-}H}]}{dt}=k_3[\mathrm{DPPH^*}][\mathrm{M}]+k_4[\mathrm{M}_n\cdot][\mathrm{DPPH}], \qquad (32)$$

$$\frac{d[\mathrm{X}]}{dt}=k_9[\mathrm{M}_n\mathrm{O_2}\cdot][\mathrm{DPPH}]. \qquad (33)$$

Using equation (25), the following equation is derived,

$$\frac{d[\mathrm{DPPH\text{-}H}]}{d[\mathrm{X}]}=\frac{2k_4}{k_5[\mathrm{O_2}]}[\mathrm{DPPH}]. \qquad (34)$$

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[14] J. W. Moore, "Physical Chemistry" Prentice-Hall Inc., New York (1956) p.123.

Since [DPNO] and [DPPH*] can be neglected compared with [DPPH], [DPPH-H] and [X], the relationship (15) can be applied,

$$\begin{aligned}\frac{d[\mathrm{DPPH\text{-}H}]}{d[\mathrm{X}]} &= \frac{2k_4}{k_5[\mathrm{O_2}]}\{[\mathrm{DPPH}]_0-[\mathrm{DPPH\text{-}H}]-[\mathrm{X}]\} \\ &= R\ \{[\mathrm{DPPH}]_0-[\mathrm{DPPH\text{-}H}]-[\mathrm{X}]\}\end{aligned} \tag{35}$$

and integrating this equation with the initial conditions,

$$[\mathrm{X}]_{t=0}=0,\ [\mathrm{DPPH\text{-}H}]_{t=0}=0,$$

the following relationship is derived,

$$[\mathrm{DPPH\text{-}H}]=\left\{[\mathrm{DPPH}]_0+\frac{1}{R}\right\}\{1-e^{-R[\mathrm{X}]}\}-[\mathrm{X}]. \tag{36}$$

The calculated values of [DPPH-H], using the value R, obtained previously, [DPPH] and [X] observed, are shown at the last column in Table 4, and agree rather well with those observed. The authors have not been able to elucidate the chemical composition of the substance, X, but inferred from the kinetic study that it is to be what is produced by the reaction of one DPPH molecule and one peroxy radical.

In Fig. 4, the observed values sometimes do not lie on the straight line at the initial stage, which will be due to the incorrectness of the assumption, $k_5[\mathrm{O_2}]/k_4 \gg [\mathrm{DPPH}]$, and so in that stage the three terms in the rate equation (29) must be considered as the overall reactions.

Summary

In benzene solutions, the photo-induced reaction between DPPH with MMA has been studied from the view-point of kinetics both in the presence and absence of dissolved oxygen, by means of spectrophotometry and electron spin resonance, and reaction mechanisms in both cases have been elucidated.

It has been found that DPPH acts not only as a radical scavenger but its photo-excited molecule participates in the step of radical production from MMA molecule.

From the view-point of kinetics the following conclusions have been drawn.

1) In the deaerated solution the reaction proceeds according to a simple scheme that one monomer radical or one small polymer radical reacts with one DPPH molecule to produce only one corresponding hydrazine molecule (DPPH-H).

2) In the presence of dissolved oxygen, a monomer radical will be first produced from the hydrogen abstraction reaction from MMA by a photo-excited molecule of DPPH and reacting with dissolved oxygen will be produced a peroxy radical, which moreover will produce a radical from monomer by hydrogen abstraction, so on, and peroxides will be produced.

These peroxides attack DPPH and break the N-N bond of DPPH. Hence in this case, the following three reactions will proceed concurrently, that is, the reaction of one monomer or one small polymer radical with one DPPH molecule to produce one hydrazine, the reaction of one hydroperoxide with one DPPH to produce diphenylnitroxide (DPNO) and perhaps the reaction of one peroxy radical with one DPPH to produce a diamagnetic substance, the chemical composition of which

has not been clarified, but has been inferred from the kinetic treatments of the experimental results.

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