# The Kinetics and Mechanism of the Photo-oxidation of *N,N'*-Diphenyl-*p*-phenylenediamine. Electron-transfer from the Upper Excited Singlet State to Oxygen

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The photo-oxidation of *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) has been studied spectrophotometrically. The quantum yield for the diimine formation, Φ, in aerated cyclohexane at 2537 Å and 20°C did not change with variations of the irradiation time, the concentration of DPPD, or the light intensity. However, the Φ values increased, as did the decrease in the fluorescence quantum yields, as the excitation energies increased. The dissolved oxygen had the optimum concentration ($1.2\times10^{-4}$M), giving the maximum value of Φ in aerated cyclohexane at 2537 Å, and none of the product, the diimine, was obtained in the degassed system. When about 0.13M of ethanol or methanol was added to aerated cyclohexane, the maximum value of Φ was measured, and the addition of a highly-polar solvent, acetonitrile or $H_2O$, decreased regularly in Φ. On the basis of these results, it can be said that the photo-oxidation of DPPD originates from the Franck-Condon state of the upper excited singlet state, $^1(RH_2)_n$. It seems that, in the primary processes of the reaction, the electron transfers take place from the Franck-Condon state of $^1(RH_2)_n$ directly to the oxygen molecule ($^3\Sigma_g^-$) and to the solvent, resulting in a trapped electron which immediately jumps into the oxygen molecule. Then, the $(RH_2)^+O_2^-$ ion pair may be formed, and subsequently the intermediate, $(RH_2)^+O_2^-$, may be converted to the product or the starting materials. The dissolved oxygen and the polar solvents are responsible for the electron-transfer processes, but they deactivate the ion pair, resulting in the decrease in Φ.

It is known that aromatic amine derivatives give rise photochemically to many interesting reactions, such as photoionization, photocyclization, rearrangement, photo-oxidation, and decomposition.

The photoionizations of aromatic amines can be classified as follows: (1) The photo-ionization in a polar solvent *via* the singlet exciplex formed by the interaction between the lowest excited singlet state of the amines (the electron donor) and the ground state of the electron acceptor, or *vice versa*, was originally shown by Leonhardt and Weller.1) Similar results for organic donor-acceptor systems have been reported by Tsubomura *et al.*2,3) and by Koizumi *et al.*4,5) The exciplex formation has been extensively studied by Mataga *et al.*6–10) and by Weller *et al.*11,12) (2) The photo-ionization in a rigid matrix at the temperature of nitrogen by a two-step excitation *via* the lowest triplet states of the amines has been well accomplished by several workers2,13–16) since the pioneering work of Lewis and Lipkin.17) The photo-ionization in fluid media by the two-step excitation *via* the lowest triplet states has also been studied by means of a flash technique.2,18–20) (3) It has been reported by Potashnik *et al.* that the photo-ionization may occur through a CT triplet state of an electron-donor-acceptor pair in a polar matrix.21) (4) Of course, the direct photo-ionization is induced by excitation energies larger than those of the ionization potentials of the molecules.

The photocyclization of diphenylamines has been preliminarily reported by Bowen and Eland,22) and by Linschitz *et al.*23) The reaction mechanism of the photocyclization of diphenylamines has been kinetically studied by Shizuka *et al.*24): the photo-cyclization of

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1) H. Leonhardt and A. Weller, *Z. Phys. Chem.*, *N. F.*, **29**, 277 (1961): *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

2) Y. Nakato, N. Yamamoto, and H. Tsubomura, This Bulletin, **40**, 2480 (1967).

3) K. Kawai, N. Yamamoto, and H. Tsubomura, *ibid.*, **42**, 369 (1969).

4) K. Kaneta and M. Koizumi, *ibid.*, **40**, 2254 (1967).

5) H. Yamashita, H. Kokubun, and M. Koizumi, *ibid.*, **41**, 2312 (1968).

6) N. Mataga, K. Ezumi, and K. Takahashi, *Z. Phys. Chem.*, *N. F.*, **44**, 250 (1965).

7) N. Mataga, T. Okada, and H. Oohari, This Bulletin, **39**, 2563 (1966).

8) N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).

9) N. Mataga and O. Tanimoto, *Theor. Chim. Acta*, **15**, 111 (1969).

10) T. Okada, H. Oohari, and N. Mataga, This Bulletin, **43**, 2750 (1970).

11) H. Knibbe, K. Röllig, F. P. Schäffer, and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967).

12) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968).

13) K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965).

14) G. E. Johnson and A. C. Albrecht, *ibid.*, **44**, 3162 (1966); *ibid.*, **44**, 3179 (1966).

15) J. Joussot-Dubien and R. Lesclaux, *Compt. Rend.*, **258**, 4260 (1964).

16) W. A. Gibbons, G. Porter, and M. I. Savadatti, *Nature*, **206**, 1355 (1965).

17) G. N. Lewis and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 2801 (1942).

18) E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, **57**, 1885 (1961).

19) N. Yamamoto, Y. Nakato, and H. Tsubomura, This Bulletin, **39**, 2603 (1966).

20) K. Kawai, N. Yamamoto, and H. Tsubomura, *ibid.*, **43**, 2266 (1970).

21) R. Potashnik, M. Ottolenghi, and R. Bensasson, *J. Phys. Chem.*, **73**, 1912 (1969).

22) E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.* (London), 202 (1963).

23) K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963). H. Linschitz and K. H. Grellmann, *ibid.*, **86**, 303 (1964).

24) H. Shizuka, Y. Takayama, I. Tanaka, and T. Morita, *ibid.*, **92**, 7270 (1970); H. Shizuka, Y. Takayama, T. Morita, S. Matsumoto, and I. Tanaka, *ibid.*, **93**, 5987 (1971).

diphenylamines originates from the lowest triplet state, and subsequently the triplet transient leads to the formation of the intermediate, M (11,12-dihydrocarbazole, whose two central hydrogens are in the *cis*-configuration), competing with the triplet deactivation processes; then M converts to the corresponding carbazoles, with and without oxygen, or to the ground state of the original substance.

The photo-Fries rearrangements of benzene derivatives (acetanilide, phenylacetate, *N*-acetyl diphenylamine, *N*-acetyl carbazole, *etc.*) in the liquid phase occur *via* the predissociative intersystem crossing ${}^3\sigma_0$(N–C)$\leftarrow S_1(\pi\pi^*)({}^1B_2)$ or ${}^3\sigma_0$(O–C)$\leftarrow S_1(\pi\pi^*)({}^1B_2)$, thus forming the pair radicals; these radicals recombine efficiently in a solvent cage into the original substance and *ortho*- and *para*-isomers, as has been studied by Shizuka *et al.*[25] In general, the predissociation of the benzene derivative occurs at a $\beta$-bond *via* the ${}^1B_2$ state.[25] The photolysis of hydrazobenzene[26] also occurs *via* the predissociative intersystem crossing ${}^3\sigma_0$(N–H)$\leftarrow S_1(\pi\pi^*)$, involving the $\beta$-bond fission of the benzene derivative and subsequent disproportionation between *N,N'*-diphenylhydrazyl radicals, giving, as products, azobenzene and the starting material. If oxygen is dissolved in the system, the radical intermediate reacts with oxygen, thus forming azobenzene and the $HO_2$ radical. A similar photo-decomposition of acetanilide in the vapor phase may occur *via* the predissociation at the $\beta$-bond, as has been reported by Shizuka and Tanaka.[27]

Recently, the flash photolysis of aniline derivatives in various solutions has been studied by Hori, Itoi, and Tsubomura.[28] The initial yield of the cation formed in an oxygenated solution is proportional to the intensity of the flash light, indicating that the photo-ionization is a one-photon process; they suggested that the charge-transfer states are formed between the aromatics and the oxygen molecule, either by direct excitation or *via* the interaction of excited anilines and the ground state of oxygen, and the charge-transfer states then lead to the solvated cations and anions in highly-polar solvents.

The photo-oxdiation of *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) has been predicted by Linschitz *et al.*[29] However, little mechanistic work has yet been reported. In addition to the photochemical processes described above, several processes in the photo-oxidation of DPPD have been considered: the reaction of the lowest excited singlet state of DPPD with the ground state of oxygen (${}^3\Sigma_g^-$), the reaction of the ground state of DPPD with the singlet oxygen (${}^1\Delta_g$),[30] and an electron transfer from the upper excited singlet state of DPPD to the ground state of oxygen. Furthermore, it is unknown whether or not the photochemical reaction of DPPD is accompanied by a photocyclization similar to that of diphenylamine.

This paper will report in some detail on the kinetics and mechanism of the photo-oxidation of DPPD.

## Experimental

*Materials.* The *N,N'*-Diphenyl-*p*-phenylenediamine (DPPD) and *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine (CPPD) were Seiko Chem. Co., Ltd., reagent-grade products and were purified by repeated recrystallizations from ethanol and from ligroin respectively. The corresponding diimines, prepared by the chromic-acid oxidation of DPPD or CPPD in glacial acetic acid,[31] were recrystallized several times from ethanol and cyclohexane. The photoproducts were identified by UV and IR spectroscopy and by thin-layer chromatography. The cyclohexane was a Tokyo Kasei Co. G.R.-grade product; it was purified by passing it through a silica-gel column and by distillation. The acetonitrile was a Tokyo Kasei Co. G.R.-grade product; it was dried over calcium chloride, refluxed repeatedly over phosphorus pentoxide until no color appeared on the oxide, distilled into freshly-fused potassium carbonate, distilled from it, and finally fractionally distilled.[32] The ethanol and methanol were Kanto Chemical Co. G.R.-grade products and were used without further purification.

*Light Source and Actinometry.* A low-pressure mercury resonance lamp with a Vycor glass filter was used as the 2537 Å radiation source, while a xenon lamp (an Ushio 150 W UXL-150D-SS), equipped with a diffraction grating, was used as the 2400—3200 Å range radiation source. The diffraction grating admitted only a narrow band of light wavelengths (±70 Å). Actinometry was carried out using a ferric oxalate solution.[33] The fluorescence quantum yields of DPPD and CPPD were obtained by comparison with the relative fluorescence intensity of naphthalene, whose fluorescence quantum yield is 0.21 in ethanol.[34]

*Degassing Procedure and Measurement of the Oxygen Concentration.* The solution was thoroughly degassed on a high-vacuum line by the freeze-pump-thaw method. The concentration of dissolved oxygen was adjusted by flushing with nitrogen at room temperature, and was determined by the method of Munck and Scott.[35]

*Analysis.* The amounts of the photoproducts (diimines) were determined spectrometrically. The ultraviolet and visible absorption spectra were measured by Hitachi 139 and 124 spectrophotometers. The fluorescence and phosphorescence spectra were taken with a Hitachi MPF-2A fluorescence spectrophotometer. The $\mu$-second flash apparatus was an ordinary one.

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[25] H. Shizuka and I. Tanaka, This Bulletin, **41**, 2343 (1968). H. Shizuka, *ibid.*, **42**, 52 (1969); **42**, 57 (1969). H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *ibid.*, **42**, 1831 (1969). H. Shizuka, M. Kato, T. Ochiai, K. Matsui, and T. Morita, *ibid.*, **43**, 67 (1970).

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[27] H. Shizuka and I. Tanaka, This Bulletin, **42**, 909 (1969).

[28] M. Hori, H. Itoi, and H. Tsubomura, *ibid.*, **43**, 3765 (1970).

[29] H. Linschitz, M. Ottolenghi, and R. Bensasson, *J. Amer. Chem. Soc.*, **89**, 4592 (1967).

[30] *E.g.* B. Stevens and B. E. Algar, *J. Phys. Chem.*, **72**, 3468 (1968); **73**, 1711 (1969); **74**, 3029 (1970). W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969). W. S. Gleason, A. D. Broadbent, E. Whittle, and J. N. Pitts, Jr., *ibid.*, **92**, 2068 (1970).

[31] J. Picard, *Ber.*, **46**, 1853 (1913).

[32] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents", Interscience Publishers, Inc., New York, (1955), p. 435.

[33] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, (London), **A235**, 518 (1956).

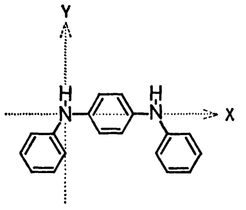
[34] C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **62**, 2785 (1966).

[35] A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956). The molar extinction coefficient of contact CT band between cyclohexane and oxygen was 109 $l\,mol^{-1}cm^{-1}$ at 220 nm.

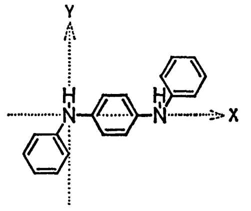
## Method of Calculation

The $\pi$ electronic structure of DPPD was studied by the variable $\beta$, $\gamma$ procedure of the semiempirical SCF-MO method in combination with singly-excited CI calculation. The parameters were taken to be as was proposed by Nishimoto and Forster.[36] The one-center repulsion integrals, $\gamma_{\mu\mu}$, were estimated from the corresponding valence-state ionization potentials ($I_\mu$) and electron affinities ($A_\mu$) by the Pariser-Parr approximation.[37] The values of $I_\mu$ and $A_\mu$ were found in the paper of Hinze and Jaffé.[38] The two-center electron-repulsion integrals, $\gamma_{\mu\nu}$, were estimated by the use of the Nishimoto-Mataga approximation.[39] The corresponding bond-order ($P$)/bond-length ($r$) relations[36] are $r_{CC}(\text{Å})=1.517—0.180P$ for C–C bonds and $r_{CN}(\text{Å})=1.451—0.180P$ for C–N bonds. The two-center core-resonance integrals, $\beta_{\mu\nu}$, were evaluated by the Nishimoto-Forster approximation.[36] The geometries of DPPD were assumed to be as follows:

GEOMETRIES OF DPPD



*cis*-form.



*trans*-form.

The C–C and C–N bond lengths were assumed to be 1.39 and 1.38 Å respectively. All the bond angles were assumed to be 120°. The computation was carried out by means of a HITAC 5020E located at the Computer Center, The University of Tokyo.

## Results

*(1) Absorption and Emission Spectra.* In order to study the behavior of DPPD in electronically-excited states, the absorption and emission spectra of DPPD were measured. Figure 1 shows the absorption and emission spectra of DPPD. Several quantities for the electronically-excited states of DPPD and those calcu-

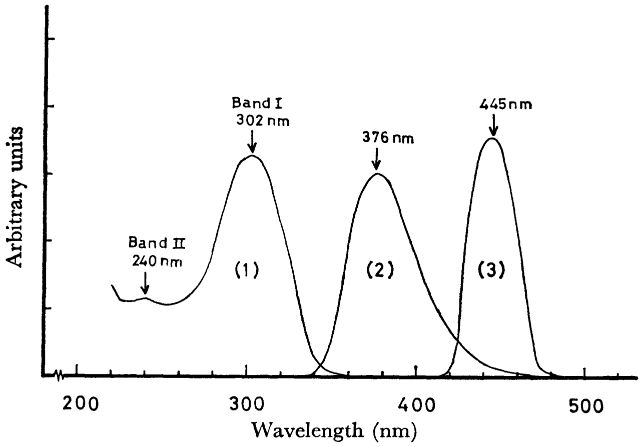


Fig. 1. Absorption and emission spectra of DPPD: (1) absorption spectrum in cyclohexane at 20°C, (2) fluorescence spectrum by the excitation of the 2537 Å light in cyclohexane at 20°C, (3) phosphorescence spectrum by the excitation of the 3000 Å light in methylcyclohexane at 77°K.

TABLE 1. SEVERAL QUANTITIES FOR THE ELECTRONICALLY EXCITED STATES OF DPPD

| Substance | Excited state | Transition energy eV | | Transition moment | | Oscillator strength | |
|---|---|---|---|---|---|---|---|
| | | Obsd | Calcd | X | Y | Obsd | Calcd |
| DPPD *cis*-form | Singlet | 4.11 | 4.135 | 0.000 | −0.273 | | 0.027 |
| −309.7794eV$^a$ | | (Band I) | 4.444 | −0.451 | 0.000 | | 0.079 |
| | | | 4.451 | 0.000 | −0.067 | | 0.002 |
| | | | 4.607 | 1.233 | 0.000 | 0.576 | 0.613 |
| | | | 5.269 | 0.000 | 1.040 | 0.298 | 0.499 |
| | | 5.17 | 5.556 | 0.099 | 0.000 | | 0.005 |
| | | (Band II) | 5.781 | −0.610 | 0.000 | | 0.188 |
| | | | 5.784 | 0.000 | −0.021 | | 0.000 |
| | Triplet | 2.81 | 2.659 | | | | |
| DPPD *trans*-form | Singlet | 4.11 | 4.145 | 0.055 | 0.334 | | 0.041 |
| −309.7802eV$^a$ | | (Band I) | 4.429 | 0.429 | −0.010 | | 0.071 |
| | | | 4.449 | 0.000 | 0.000 | | 0.000 |
| | | | 4.611 | −1.262 | −0.737 | 0.576 | 0.862 |
| | | | 5.234 | 0.000 | 0.000 | | 0.000 |
| | | 5.17 | 5.627 | −0.458 | −0.553 | 0.298 | 0.254 |
| | | (Band II) | 5.783 | −0.562 | 0.178 | | 0.176 |
| | | | 5.791 | 0.000 | 0.000 | | 0.000 |
| | Triplet | 2.81 | 2.533 | | | | |

Where a denotes total $\pi$ electonic energy, and the values of the $^1(RH_2)_n \leftarrow RH_2$ and $^3(RH_2) \leftarrow RH_2$ transition energies are estimated by those of absorption and phosphorescence spectra respectively.

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36) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965); **4**, 155 (1966).

37) R. Pariser and P. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

38) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

39) K. Nishimoto and N. Mataga, *Z. Phys. Chem.*, **12**, 335 (1957); **13**, 140 (1957).

lated by the semiempirical SCF–MO–CI method are summarized in Table 1. In the case of CPPD, similar results were obtained.

*(2) Quantum Yields for the Diimine Formations.* Aerated solutions of DPPD and CPPD are stable at room temperature for several hours. Therefore, the amounts of the corresponding diimines produced by thermal reactions can be neglected.

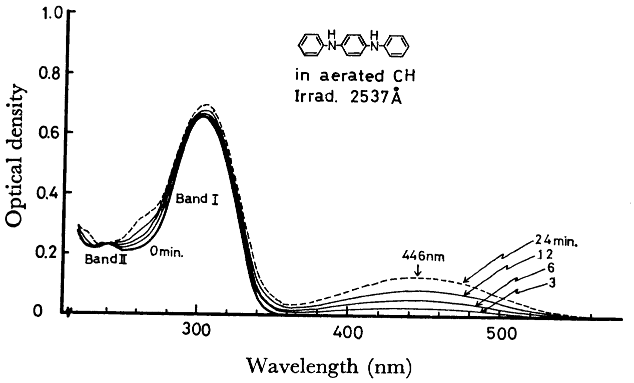
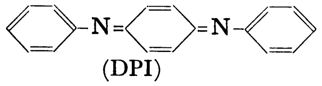
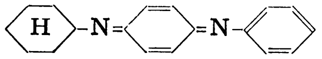


Fig. 2. Spectral change of DPPD in aerated cyclohexane upon irradiation with the 2537 Å light. Numbers refer to time at measurement in minutes.

The spectrum of the aerated cyclohexane solution of DPPD changed upon irradiation with the 2537 Å light, as is shown in Fig. 2. A new band with a maximum at 446 nm appeared; the spectral change showed the formation of *N,N'*-diphenyl-*p*-quinonediimine (DPI). The photoproduct was separated by column chromatography and was identified by UV and IR spectroscopy and by thin-layer chromatography. The photo-oxidation of CPPD also occurred in aerated cyclohexane. However, no photochemical diimine formation was observed in the degassed system in either case, and no photocyclization such as that of diphenylamines took place in the photochemical reactions of DPPD and CPPD. Table 2 shows the molar extinction coefficients of the diimines.

Table 2. The molar extinction coefficients of the diimines

| Substance | Solvent | $\lambda_{max}$ nm | $\varepsilon_{max}(\times 10^{-4})$ $l mol^{-1} cm^{-1}$ |
|---|---|---|---|
|  (DPI) | CH | 304 | 2.83 |
| | | 446 | 0.63 |
| | EtOH | 304 | 2.71 |
| | | 443 | 0.67 |
|  (CPI) | CH | 296 | 2.84 |
| | | 428 | 0.30 |

Where CH and EtOH denote cyclohexane and ethanol respectively, and, where CPI denotes *N*-cyclohexyl-*N'*-phenyl-*p*-quinonediimine.

The quantum yields for the product formation ($\Phi^{\lambda}$) were measured spectrophotometrically. Figure 3 shows the quantum yields for DPI formation under various conditions at 2537 Å. The quantum yields in aerated cyclohexane did not change with any variations in the irradiation time, the concentration of DPPD, or the light intensity. However, the effects of the excitation wavelength, dissolved oxygen, and polar solvents on $\Phi^{\lambda}$ were measured. Similar results were obtained in the case of CPPD. The quantum yields ($\Phi_0^{2537}$) of DPPD and CPPD in aerated cyclohexane at 2537 Å and 20°C were 0.033 and 0.041 respectively.

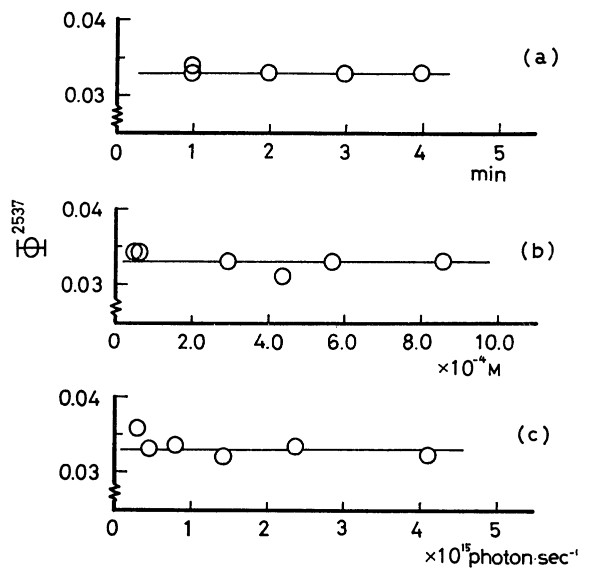


Fig. 3. Dependence of quantum yields for DPPD in cyclohexane solutions at 2537 Å and 20°C: (a) on irradiation time with initial concentration of $5.6\times10^{-4}$M, (b) on concentration, (c) on light intensity.

*(3) Effects of the Excitation Wavelength on the Quantum Yields for the Product Formation ($\Phi^{\lambda}$) and on the Fluorescence Quantum Yields ($\Phi^{\lambda}_{f}$).* The dependence of the excitation wavelength (3200—2400 Å) on $\Phi^{\lambda}$ and $\Phi^{\lambda}_{f}$ in aerated cyclohexane at 20°C was measured using a xenon lamp with a diffraction grating filter. The results are shown in Fig. 4. The $\Phi^{\lambda}$ values increased as a function of the excitation energy. In contrast, the $\Phi^{\lambda}_{f}$ values decreased gradually as the excitation energy increased. The $\Phi^{\lambda}_{f}$ values became constant in the 3000—3200 Å range, where scarcely any photo-oxidation took place.

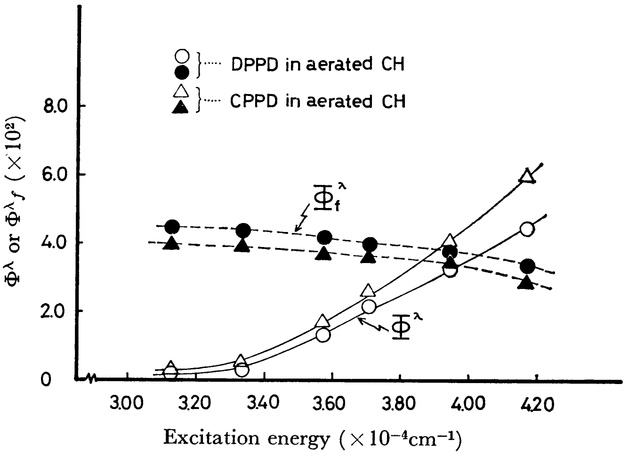


Fig. 4. Dependence of quantum yields $\Phi^{\lambda}$ for the diimine formation and of fluorescence quantum yields $\Phi^{\lambda}_{f}$ on excitation energy in aerated cyclohexane at 20°C.

○: $\Phi^{\lambda}$ of DPPD ●: $\Phi^{\lambda}_{f}$ of DPPD
△: $\Phi^{\lambda}$ of CPPD ▲: $\Phi^{\lambda}_{f}$ of CPPD

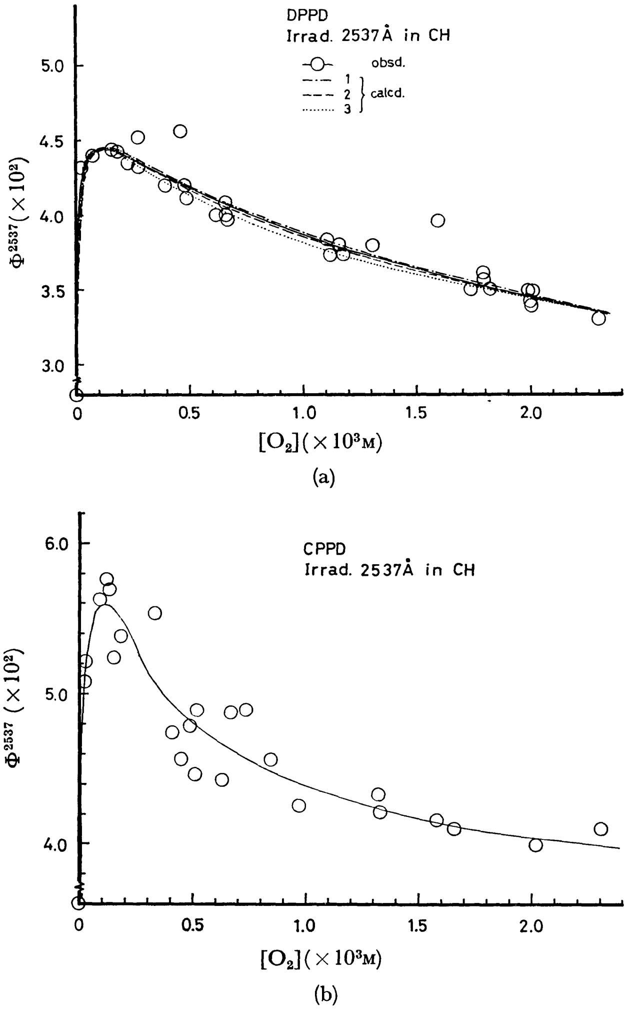


Fig. 5. Dependence of quantum yields $\Phi^{2537}$ on oxygen dissolved in cyclohexane at 2537 Å and 20°C: (a) for DPPD; -○- observed values, (1)—(3) calculated values. See Table 4. (b) for CPPD; -○- observed values.

*(4) Effect of Dissolved Oxygen on $\Phi^{2537}$.* The dependence of dissolved oxygen on $\Phi^{2537}$ in cyclohexane at 2537 Å and 20°C was measured by the method described above. The results are shown in Fig. 5(a) and (b). The $\Phi^{2537}_{max}$ value of DPPD (0.044) was measured at $[O_2]=1.2\times10^{-4}$M. This shows that the dissolved oxygen has the optimum concentration ($1.2\times10^{-4}$M), giving the maximum value of $\Phi^{2537}$ in the photo-oxidation of DPPD. The oxygen effect on the $\Phi^{2537}$ of DPPD was in good accordance with the simulation calculated kinetically, as will be discussed later. Similar experimental results were obtained in the case of CPPD, as is shown in Fig. 5(b).

*(5) Effects of the Addition of Polar Solvents on $\Phi^{2537}$.* The effects of polar solvents on $\Phi^{2537}$ in the aerated system at 2537 Å and 20°C were measured. The mixed solvents used were prepared by the addition of a small amount of polar solvents to cyclohexane, except in the case of $H_2O$. The polar solvents used were ethanol, methanol, acetonitrile, and $H_2O$. Figure 6 shows the dependence of the relative quantum yields ($\Phi^{2537}/\Phi_0^{2537}$) on the addition of polar solvents to cyclohexane in the aerated system at 2537 Å and 20°C. The photo-oxidation of DPPD was considerably affected by the addition of a small amount of polar solvents to cyclohexane. When about 0.13M of ethanol or methanol was added to cyclohexane, the maximum value of $(\Phi^{2537}/\Phi_0^{2537})_{max}$ was measured.

In the cyclohexane and ethanol system, the addition of ethanol increased the $\Phi^\lambda$ values; the values then decreased gradually, passing through the maximum value ($\Phi^{2537}_{max}=0.050$) at [EtOH]=0.13M. However, the addition of a highly polar solvent, acetonitrile or $H_2O$, immediately decreased those values, as is shown in Fig. 6.

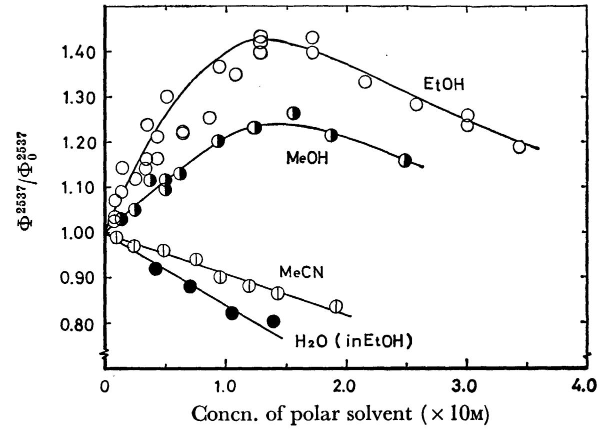


Fig. 6. Effects of the addition of polar solvents on $\Phi^{2537}$ for DPPD at 2537 Å and 20°C, where EtOH, MeOH, and MeCN denote ethanol, methanol, and acetonitrile. A small amounts of polar solvents, except $H_2O$, added to aerated cyclohexane, and in the case of $H_2O$ the aerated EtOH solution was used.

Figure 7 shows the excitation-wavelength effect on the $\Phi^\lambda$ of DPPD in the mixed solvent (cyclohexane and ethanol). At every excitation wavelength, similar results were obtained, as is shown in Fig. 7.

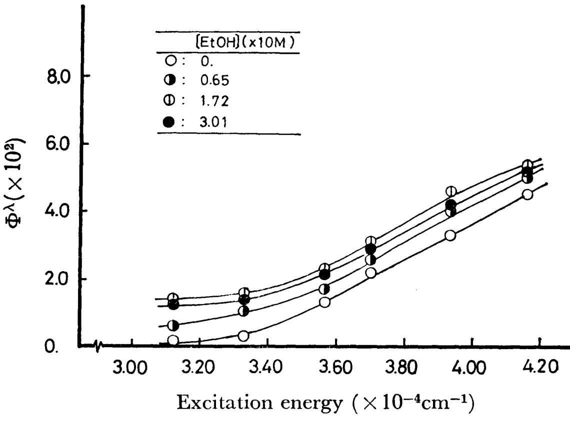


Fig. 7. Dependence of quantum yield $\Phi^\lambda$ for DPPD on excitation energy in the mixed solutions of cyclohexane and ethanol.

On the other hand, no intermediate of the photo-oxidation in aerated and degassed cyclohexane or in ethanol was observed by a $\mu$-second flash technique.

## Discussion

The results on the excitation-wavelength, dissolved-oxygen, and polar-solvent effects on the quantum yields of the reaction and the fluorescence can be accounted for by the following schemes:

$$\mathrm{RH_2} + \mathrm{h}\nu \xrightarrow{I_a} {}^1(\mathrm{RH_2})_n \tag{0}$$

$$^1(\mathrm{RH_2})_n \xrightarrow{k_1} {}^1(\mathrm{RH_2})_1 \tag{1}$$

$$^1(\mathrm{RH_2})_n + \mathrm{O_2} \xrightarrow{k_2^{\lambda}} \mathrm{RH_2}^+ \cdots \mathrm{O_2}^- \xrightarrow{k_2'} (\mathrm{RH_2})^+\mathrm{O_2}^- \tag{2}$$

$$\begin{tikzcd}
^1(\mathrm{RH_2})_n + \mathrm{CH} \arrow[r, "k_3^{\lambda}"] & \mathrm{RH_2}^+ + \mathrm{e}_{\mathrm{solv}}^{\mathrm{CH}} \arrow[r, "{k_{3e}[\mathrm{O_2}]}"] \arrow[d, "k_{3q}"] & {} \\
 & \mathrm{RH_2} + \mathrm{CH} &
\end{tikzcd}$$

$$\mathrm{RH_2}^+ + \mathrm{O_2}^- + \mathrm{CH} \xrightarrow{k_{3p}} (\mathrm{RH_2})^+\mathrm{O_2}^- + \mathrm{CH} \tag{3}$$

$$\begin{tikzcd}
^1(\mathrm{RH_2})_n + \mathrm{EtOH} \arrow[r, "k_4^{\lambda}"] & \mathrm{RH_2}^+ + \mathrm{e}_{\mathrm{solv}}^{\mathrm{EtOH}} \arrow[r, "{k_{4e}[\mathrm{O_2}]}"] \arrow[d, "k_{4q}"] & {} \\
 & \mathrm{RH_2} + \mathrm{EtOH} &
\end{tikzcd}$$

$$\mathrm{RH_2}^+ + \mathrm{O_2}^- + \mathrm{EtOH} \xrightarrow{k_{4p}} (\mathrm{RH_2})^+\mathrm{O_2}^- + \mathrm{EtOH} \tag{4}$$

$$(\mathrm{RH_2})^+\mathrm{O_2}^- \xrightarrow{k_5} \mathrm{R} + (\mathrm{H_2O_2}) \tag{5}$$

$$(\mathrm{RH_2})^+\mathrm{O_2}^- \xrightarrow{k_6} \mathrm{RH_2} + \mathrm{O_2} \tag{6}$$

$$(\mathrm{RH_2})^+\mathrm{O_2}^- + \mathrm{O_2} \xrightarrow{k_7} \mathrm{RH_2} + 2\mathrm{O_2} \tag{7}$$

$$(\mathrm{RH_2})^+\mathrm{O_2}^- + \mathrm{EtOH} \xrightarrow{k_8} \mathrm{RH_2} + \mathrm{O_2} + \mathrm{EtOH} \tag{8}$$

$$^1(\mathrm{RH_2})_1 \xrightarrow{k_s} \mathrm{RH_2} \tag{9}$$

$$^1(\mathrm{RH_2})_1 \xrightarrow{k_f} \mathrm{RH_2} + \mathrm{h}\nu_{\mathrm{f}} \tag{10}$$

$$^1(\mathrm{RH_2})_1 \xrightarrow{k_{isc}} {}^3(\mathrm{RH_2}) \tag{11}$$

$$^1(\mathrm{RH_2})_1 + \mathrm{O_2} \xrightarrow{k_d} \mathrm{RH_2} + \mathrm{O_2} \tag{12}$$

$$^3(\mathrm{RH_2}) \xrightarrow{k_t} \mathrm{RH_2} \tag{13}$$

$$^3(\mathrm{RH_2}) \xrightarrow{k_p} \mathrm{RH_2} + \mathrm{h}\nu_{\mathrm{p}} \tag{14}$$

$$^3(\mathrm{RH_2}) + \mathrm{O_2} \xrightarrow{k_d} \mathrm{RH_2} + \mathrm{O_2} \tag{15}$$

where $\mathrm{RH_2}$, $^1(\mathrm{RH_2})_1$, $^1(\mathrm{RH_2})_n$, and $^3(\mathrm{RH_2})$ are the ground state, the lowest excited singlet state, the upper excited singlet state, and the lowest triplet state of *p*-phenylenediamines (DPPD and CPPD) respectively, where R is the diimine, where f and p denote the fluorescence and the phosphorescence respectively, where $\mathrm{e}_{\mathrm{solv}}^{\mathrm{CH}}$ and $\mathrm{e}_{\mathrm{solv}}^{\mathrm{EtOH}}$ denote solvated electrons trapped by CH and by EtOH respectively, where CH and EtOH are cyclohexane and ethanol respectively, and where $\lambda$ denotes the excitation wavelength.

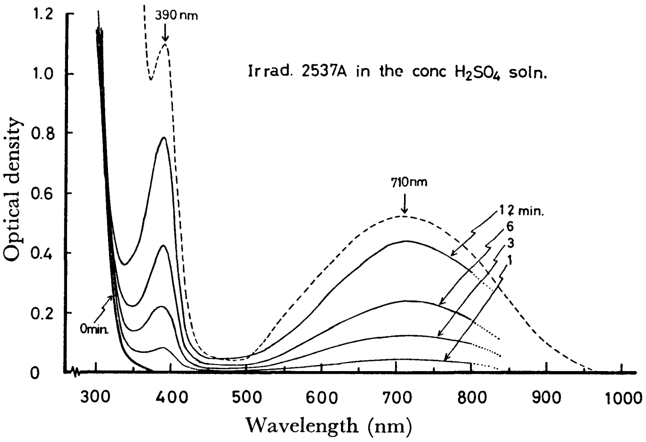


Fig. 8. The spectral change of DPPD upon irradiation with the 2537 Å light in the mixed solution of ethanol and $\mathrm{H_2SO_4}$ in proportions 2 : 1 at 20°C. Numbers refer to time at measurement in minutes. The broken line denote the absorption spectrum for the cation radical $\mathrm{RH_2}^+$ as has been reported by Linschitz *et al.*[29,40]

The effects of the excitation wavelength on $\Phi^{\lambda}$ and $\Phi^{\lambda}{}_f$ show that the photo-oxidation of *p*-phenylenediamines originates from the upper excited singlet state, $^1(\mathrm{RH_2})_n$. Furthermore, it seems, considering the continuously increasing and decreasing of $\Phi^{\lambda}$ and $\Phi^{\lambda}{}_f$ shown in Fig. 4, that the primary processes of the reaction occur from the Franck-Condon state of the upper excited singlet state. Thus, the primary processes of the reaction have very high rate constants, $\sim 10^{11}\,\mathrm{sec}^{-1}$; the rate constants of the processes should be comparable to those of the internal conversion, $^1(\mathrm{RH_2})_n \rightarrow {}^1(\mathrm{RH_2})_1$, whose rate constants are of the order of $10^{12}$—$10^{13}\,\mathrm{sec}^{-1}$. These processes can be accounted for by the ionization processes; one is the long-range electron-transfer process from $^1(\mathrm{RH_2})_n$ to the ground state of $\mathrm{O_2}(^3\Sigma_g^-)$, while the other is the electron-transfer process from $^1(\mathrm{RH_2})_n$ to the solvent. Polar solvents such as ethanol promote the latter process, since the electron-trapping ability in a polar solvent is larger than that in a nonpolar solvent.[2,14] In addition to this, the polar solvents dissolve the intermediate in the reaction, resulting in a decrease in $\Phi^{2537}$ as shown in Fig. 6. Therefore, it seems that the intermediate is an ion pair $(\mathrm{RH_2})^+\mathrm{O_2}^-$ formed by the processes described in Eqs. (2)—(4). This assumption is supported by the fact that the spectrum of DPPD in the concd. $\mathrm{H_2SO_4}$ solution at 2537 Å and 20°C was the same as that of the corresponding cation radical, as is shown in Fig. 8. The UV-V absorption spectrum of the DPPD cation radical has been reported by Linschitz *et al.*[29,40] The ESR absorption spectrum of the cation radical in acetic acid has also been measured.[40] In an acidic solution, the cation radical is very stable. Of course, in a highly polar solvent, no ion pair $(\mathrm{RH_2})^+\mathrm{O_2}^-$ is formed because of the high dielectric constant. The photoionization processes in the photo-oxidation of DPPD and CPPD differ from that of the Weller-type ionization.[1] The Weller-type photoionization occurs through the exciplex (DA)* formed by the interaction between the lowest excited singlet state of the donor and the ground state of the acceptor, or *vice versa*, in a highly polar solvent. The electron transfer between oxygen and aromatic anilines *via* the exciplex formation has been proposed by Hori, Itoi, and Tsubomura;[28] they have also shown that the photoionization is mainly a single-photonic process. In the present work, the electron transfer occurs from the Franck-Condon state of the upper excited state $^1(\mathrm{RH_2})_n$. Since $\Phi^{2537}$ is not dependent

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[40] H. Linschitz, J. Rennert, and T. M. Korn, *J. Amer. Chem. Soc.*, **76**, 5839 (1954).

on the light intensity (Fig. 3(c)), the photoionization is a single-photonic process.

The possibility of a predissociative β-bond fission (N–H bond), such as that of hydrazobenzene,[26] can be disregarded, since the reactive state of DPPD was not the lowest excited singlet state, but the upper excited singlet state, since the $\Phi^{2537}$ values did not depend on the light intensity, and since no diimine formation was observed in the degassed system. The possibility that complex formation between DPPD and $O_2$ in the ground states is responsible for this photo-oxidation was shown to be unlikely by the fact that the spectral intensities and the positions of the aerated solution were identical with those of the degassed solution.

From the steady-state approximation, the following equations are obtained:

$$\frac{\mathrm{d}[(\mathrm{RH_2})^+\mathrm{O_2}^-]}{\mathrm{d}t} = k_2{}^\lambda[{}^1(\mathrm{RH_2})_n][\mathrm{O_2}] + (k_{3p}+k_{4p})[\mathrm{RH_2}^+][\mathrm{O_2}^-] - (k_5+k_6+{}_7[\mathrm{O_2}] + k_8[\mathrm{EtOH}])[(\mathrm{RH_2})^+\mathrm{O_2}^-] = 0 \tag{16}$$

$$[(\mathrm{RH_2})^+\mathrm{O_2}^-] = \frac{k_2{}^\lambda[{}^1(\mathrm{RH_2})_n][\mathrm{O_2}]+(k_{3p}+k_{4p})[\mathrm{RH_2}^+][\mathrm{O_2}^-]}{k_5+k_6+k_7[\mathrm{O_2}]+k_8[\mathrm{EtOH}]} \tag{16'}$$

$$\Phi^\lambda = \frac{\mathrm{d}[\mathrm{R}]/\mathrm{d}t}{I_a} = \frac{k_5[(\mathrm{RH_2})^+\mathrm{O_2}^-]}{I_a} = \left\{\frac{k_2{}^\lambda[\mathrm{O_2}]+\dfrac{k_3{}^\lambda[\mathrm{CH}]k_{3e}[\mathrm{O_2}]}{k_{3e}[\mathrm{O_2}]+k_{3q}[\mathrm{RH_2}^+]}+\dfrac{k_4{}^\lambda[\mathrm{EtOH}]k_{4e}[\mathrm{O_2}]}{k_{4e}[\mathrm{O_2}]+k_{4q}[\mathrm{RH_2}^+]}}{k_1+k_2{}^\lambda[\mathrm{O_2}]+k_3{}^\lambda[\mathrm{CH}]+k_4{}^\lambda[\mathrm{EtOH}]}\right\} \times\frac{k_5}{k_5+k_6+k_7[\mathrm{O_2}]+k_8[\mathrm{EtOH}]} \tag{17}$$

where:

$$[{}^1(\mathrm{RH_2})_n] = \frac{I_a}{k_1+k_2{}^\lambda[\mathrm{O_2}]+k_3{}^\lambda[\mathrm{CH}]+k_4{}^\lambda[\mathrm{EtOH}]}$$

$$[\mathrm{RH_2}^+] = \frac{\{k_3{}^\lambda[\mathrm{CH}]+k_4{}^\lambda[\mathrm{EtOH}]\}[{}^1(\mathrm{RH_2})_n]}{k_{3q}[\mathrm{e}^{\mathrm{CH}}_{\mathrm{solv}}]+k_{4q}[\mathrm{e}^{\mathrm{EtOH}}_{\mathrm{solv}}]+(k_{3p}+k_{4p})[\mathrm{O_2}^-]}$$

$$[\mathrm{O_2}^-] = \frac{\{k_{3e}[\mathrm{e}^{\mathrm{CH}}_{\mathrm{solv}}]+k_{4e}[\mathrm{e}^{\mathrm{EtOH}}_{\mathrm{solv}}]\}[\mathrm{O_2}]}{(k_{3p}+k_{4p})[\mathrm{RH_2}^+]}$$

$$[\mathrm{e}^{\mathrm{CH}}_{\mathrm{solv}}] = \frac{k_3{}^\lambda[\mathrm{CH}][{}^1(\mathrm{RH_2})_n]}{k_{3e}[\mathrm{O_2}]+k_{3q}[\mathrm{RH_2}^+]}$$

and

$$[\mathrm{e}^{\mathrm{EtOH}}_{\mathrm{solv}}] = \frac{k_4{}^\lambda[\mathrm{EtOH}][{}^1(\mathrm{RH_2})_n]}{k_{4e}[\mathrm{O_2}]+k_{4q}[\mathrm{RH_2}^+]}$$

If [EtOH]=0, Eq. (17′) is derived from Eq. (17).

$$\Phi^\lambda = \left\{\frac{k_2{}^\lambda[\mathrm{O_2}]+\dfrac{k_3{}^\lambda[\mathrm{CH}]k_{3e}[\mathrm{O_2}]}{k_{3e}[\mathrm{O_2}]+k_{3q}[\mathrm{RH_2}^+]}}{k_1+k_2{}^\lambda[\mathrm{O_2}]+k_3{}^\lambda[\mathrm{CH}]}\right\}\frac{k_5}{k_5+k_6+k_7[\mathrm{O_2}]} = \left\{\frac{a^\lambda[\mathrm{O_2}]+\dfrac{b^\lambda c[\mathrm{O_2}]}{c[\mathrm{O_2}]+1}}{1+a^\lambda[\mathrm{O_2}]+b^\lambda}\right\}\frac{1}{1+d+e[\mathrm{O_2}]} \tag{17'}$$

where:

$$a^\lambda = \frac{k_2{}^\lambda}{k_1},\quad b^\lambda = \frac{k_3{}^\lambda}{k_1}[\mathrm{CH}],\quad c = \frac{k_{3e}}{k_{3q}[\mathrm{RH_2}^+]}$$

$$d = \frac{k_6}{k_5},\ \text{and}\ e = \frac{k_7}{k_5}$$

On the other hand, the fluorescence quantum yield, $\Phi^\lambda{}_f$, is given by:

$$\Phi_f{}^\lambda = \frac{k_1}{k_1+k_2{}^\lambda[\mathrm{O_2}]+k_3{}^\lambda[\mathrm{CH}]}\cdot\frac{k_f}{k_s+k_f+k_{isc}+k_d[\mathrm{O_2}]} \tag{18}$$

Scarcely any photo-oxidation of DPPD occurred upon irradiation with the 3200 Å light, as is shown in Fig. 4. Therefore, Eq. (19) holds approximately:

$$\Phi_f{}^{3200} = \frac{k_f}{k_s+k_f+k_{isc}+k_d[\mathrm{O_2}]} \tag{19}$$

where $k_1 \gg k_2^{3200}+k_3^{3200}[\mathrm{CH}]$. The relative fluorescence quantum yield, $\Phi_f{}^{3200}/\Phi^\lambda{}_f$, is obtained from Eqs. (18) and (19):

$$\frac{\Phi_f{}^{3200}}{\Phi_f{}^\lambda} = 1 + \frac{k_2{}^\lambda[\mathrm{O_2}]+k_3{}^\lambda[\mathrm{CH}]}{k_1} = 1 + a^\lambda[\mathrm{O_2}] + b^\lambda \tag{20}$$

where $[\mathrm{O_2}]=2.3\times10^{-3}$M.[24] The $\Phi_f{}^{3200}/\Phi^\lambda{}_f$ values are listed in Table 3.

TABLE 3. THE $\Phi_f{}^{3200}/\Phi_f{}^\lambda$ VALUES OF DPPD IN AERATED CYCLOHEXANE

| Excitation wavelength Å | Excitation energy eV | $\Phi^\lambda\times10^2$ | $\Phi_f{}^{3200}/\Phi_f{}^\lambda$ |
|---|---|---|---|
| 2400 | 5.17 | 4.5 | 1.33 |
| 2537 | 4.88 | 3.3 | $1.19_3$ |
| 2700 | 4.59 | 2.2 | 1.12 |
| 2800 | 4.43 | 1.33 | 1.07 |
| 3000 | 4.13 | 0.28 | 1.02 |
| 3200 | 3.87 | 0.18 | 1.00 |

The following values can be estimated:

$$a^{2537}[\mathrm{O_2}] + b^{2537} = 0.19_3 \tag{21}$$

where $[\mathrm{O_2}]=2.3\times10^{-3}$M. Then, the simulation of $\Phi^{2537}$ as a function of $[\mathrm{O_2}]$ was carried out using Eqs. (17′) and (21).

The $(\Phi^{2537}_{\mathrm{calcd}})$ values of DPPD are in accordance with those obtained experimentally, as is shown in Fig. 5(a). The appropriate values of the $a^{2537}$, $b^{2537}$, $c$, $d$, and $e$ parameters are listed in Table 4. From the results of the calculations, the two rates, $k_2^{2537}[\mathrm{O_2}]$ and $k_3^{2537}[\mathrm{CH}]$, in the electron-transfer processes (Eqs. (2) and (3)) can be said to be nearly equivalent in aerated cyclohexane, where $[\mathrm{O_2}]=2.3\times10^{-3}$M, and at 2537 Å, because the $(2.3\times10^{-3}a^{2537})/b^{2537}$ ratio is approximately equal to unity.

TABLE 4. THE APPROPRIATE VALUES OF THE PARAMETERS

| No. of plot in Fig. 5 (a) | $a^{2537}$ $\times10^{-1}$ | $b^{2537}$ $\times10$ | $c\times10^{-5}$ | $d$ | $e\times10^{-3}$ |
|---|---|---|---|---|---|
| 1 | 3.35 | 1.16 | 3.00 | 1.22 | 1.12 |
| 2 | 4.20 | $0.96_5$ | 3.00 | $0.86_5$ | 1.28 |
| 3 | 5.04 | 0.77 | 3.00 | $0.51_1$ | 1.44 |

Thus, Eq. (22) is obtained:

$$k_2{}^{2537} = 4\times10^3 k_3{}^{2537} \tag{22}$$

If $n$ molecules of oxygen are randomly distributed around a DPPD molecule in a certain volume, $V$, the radius $(\bar{r})$ between the DPPD molecule and the nearest-neighbor oxygen molecule can be evaluated by the following equation, derived by Yamamoto, Nakato, and

Tsubomura:[41)]

$$\bar{r} = (V/2\pi n)^{1/3}$$

or

$$\bar{r} = 6.42[O_2]^{-1/3}\text{Å} \qquad (23)$$

The calculated $\bar{r}$ value is 49 Å in aerated cyclohexane ($[O_2]=2.3\times10^{-3}$M) at 2537 Å and 20°C. The large $\bar{r}$ value shows the long-range electron transfer from the Franck-Condon state of the $^1(RH_2)_n$ state to dissolved oxygen. The rate constant of the long-range electron transfer, $k_2^{2537}$, is very much larger than that of the electron transfer to the solvent (cyclohexane), as is shown in Eq. (22).

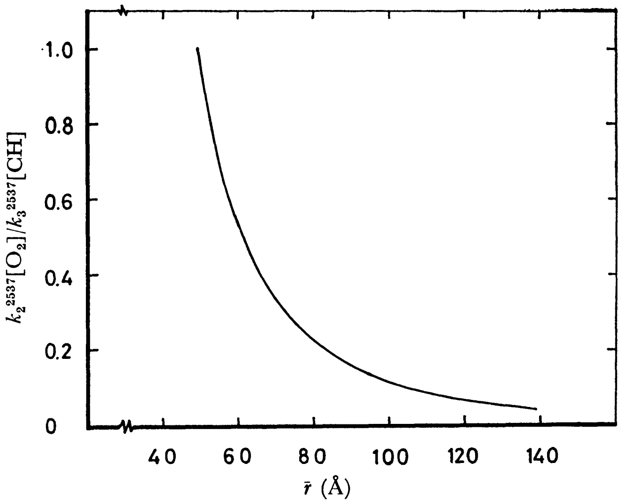

Fig. 9. The ratio $k_2^{2537}$ $[O_2]/k_3^{2537}[CH]$ as a function of $\bar{r}$.

The plot of the $k_2^{2537}[O_2]/k_3^{2537}[CH]$ ratio as a function of $\bar{r}$ is shown in Fig. 9. It can be understood that the $k_2^{2537}[O_2]/k_3^{2537}[CH]$ values significantly decrease as the $\bar{r}$ values increase. The dissolved oxygen in cyclohexane acts as an electron-trapping center in the primary processes of the photo-oxidation and also deactivates the intermediate $(RH_2)^+O_2^-$, as is shown in Eq. (7). In the electron-transfer processes from $^1(RH_2)_n$ to the solvents, it may be assumed that the $^1(RH_2)_n$ species ejects an electron to the solvents and that subsequently the electron is trapped by the dissolved oxygen, as is shown in Eqs. (3) and (4). Scarcely any photooxidation of DPPD in aerated cyclohexane occurred upon irradiation with the 3200 Å light, which corresponds to the shoulder of the absorption Band I in Fig. 1. The absorption Band I is comprised of several singlet-singlet transitions, as is shown in Table 1, where the calculated data for the *cis*-form are almost the same as those for the *trans*-form. Although the reactive state can not be assigned exactly, the photo-ionization processes described above apparently take place from the upper excited singlet state, $^1(RH_2)_n$. In the secondary processes of the reaction, it seems that the $(RH_2)^+O_2^-$ ion pair is converted to the corresponding diimine (Eq. (5)). This transformation probably involves an intramolecular proton transfer process:

$$(RH_2)^+O_2^- \longrightarrow (RH)(HO_2) \longrightarrow R + H_2O_2 \qquad (24)$$

The $H_2O_2$ formation was identified by iodometry.

Finally, a schematic energy diagram of the photooxidation of DPPD and CPPD is shown in Fig. 10. The detailed reaction schemes can be written as in Eqs. (0)—(15).

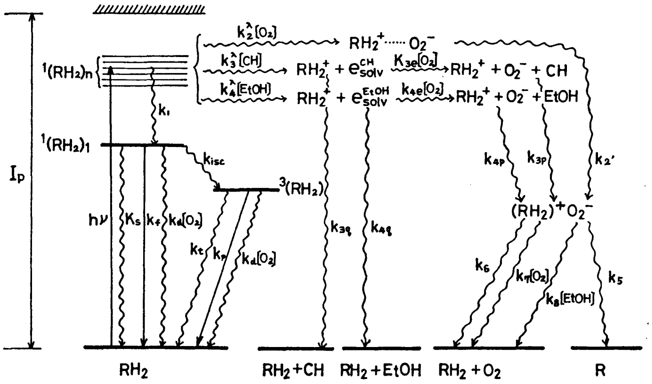

Fig. 10. Schematic energy state diagram for the photooxidation of DPPD.

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[41)] N. Yamamoto, Y. Nakato, and H. Tsubomura, This Bulletin, **40**, 451 (1967).