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The Photo-oxygenation Reactions of Diethyl Ether, *p*-Phenylenediamine, and *N*,*N*-Dimethylaniline

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The products of photo-oxygenation reactions of ethyl–ether, *p*-phenylenediamine, and dimethylaniline were studied quantitatively and some radical intermediates were found by ESR measurements. The following quantum yields of the main products of these reactions were obtained: ethyl acetate (for ethyl ether), 0.49; *p*-benzoquinonediimine (for *p*-phenylenediamine), 0.01. As a possible reaction mechanism of the photo-oxygenation reactions of ethyl ether and *p*-phenylenediamine, it is proposed that at least part of the reaction is initiated by the charge transfer from the organic molecule to oxygen, followed by rapid proton detachment, yielding such radicals as $EtO\text{-}\dot{C}HCH_3$ and $\dot{N}HC_6H_4NH_2$ respectively.

In a previous paper, we have studied the photochemical reaction of the triethylamine–O_2 system under irradiation in the region of the charge transfer (CT) band.[1] By use of ESR spectroscopy and chemical analysis of the reaction products, the possible reaction mechanisms leading to various reaction products were speculated upon. This paper will present the results of similar studies of the photo-oxygenation of ethyl ether and some aromatic amines.

Experimental

Materials. Reagent grade diethyl ether was dried overnight with potassium chloride, and fractionally distilled through a Widmer column with Na-K amalgam. Reagent grade *p*-phenylenediamine (PPD) was purified by recrystallization from benzene and sublimed. *N*,*N*-Dimethylaniline (DMA) was dried with sodium hydroxide, vacuum distilled and preserved in a vacuum desiccator. Isopentane, *n*-heptane, and methylcyclohexane were purified by passing them through silica gel columns and then were distilled. Dioxane was dehydrated with sodium wire and then distilled.

ESR Measurements. The ESR measurements were made using a JES-ME-2X spectrometer of Japan Electron-Optics Laboratory Co. in the X-band. The magnetic field was measured by use of the proton magnetic resonance signal. The solution was put into a quartz capillary cell (5 mmϕ). After oxygen gas or air was bubbled into the cell, each sample was irradiated with a Ushio 500 W high pressure mercury lamp through Toshiba glass filters which transmit the light in the region of the CT band.

Analysis of the Photo-oxygenation Products. The reaction products were analyzed by the gas-chromatographic, chemical, IR, and UV techniques.

The analysis of peroxide was made by use of an electrochemical method suggested by Brewer and Milford.[2] The cathode was fine platinum and mercury was used as the anode. The polarizing potential was about 0.3 V and 0.2% KI aq. was used as the working solution.

The quantum yields of the reaction products were obtained with the aid of chemical actinometry using potassium ferrioxalate. A modified method of Hatchard and Parker[3] was used to prepare the actionometer solution. The irradiation was done through the reaction cell into the actinometer solution so that the light transmitted through the former was absorbed completely by the latter. The number of photons absorbed in the reaction cell was calculated as the difference between the number of photons absorbed in the actinometer with and without the presence of the reaction cell.

Results

The O_2–Ether System. No ESR signal was detected by the irradiation, at room temperature, of ether saturated with oxygen or of solutions of ether–O_2 in isopentane, *n*-heptane, and methylcyclohexane. When O_2-saturated ether at 1 atm was irradiated at 77 K with a UV-D25 filter (280—350 nm) for 3 min, a prominent quartet signal with a hyperfine coupling constant (hfs) of 26 G was obtained. This signal may be assigned to either the ethyl or the methyl radical. The former is more probable because of the high hyperfine coupling constant.[4,5] A similar result was obtained even when a mixture of methylcyclohexane and ether (in the vol. ratio of 1 : 1) was used as a solvent (Fig. 1(A)). When the input of the microwave power was raised up to about 100 mW, the quartet signal observed in the ether–O_2 system disappeared owing to saturation. On standing at 77 K, the ESR signal most likely assignable to an alkylperoxy radical appeared and became stronger

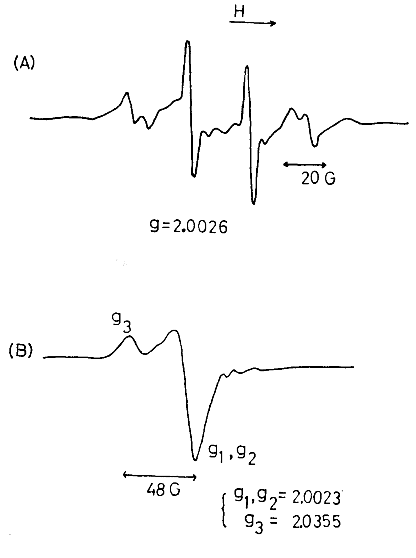

Fig. 1. ESR spectra of the species produced by the UV-irradiation of ether–O_2 at 77 K (A), followed by warming in the dark (B).

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with time. When the sample cell was taken out from liquid nitrogen for several seconds and dipped in again, a different ESR signal with large anisotropic *g*-factor was obtained, as shown in Fig. 1(B). In isopentane, softer than methylcyclohexane at 77 K, an ESR spectrum quite similar to the latter one was observed from the beginning. Upon warming the matrix, the intensity decreased without any change in the spectral shape.

The reaction products were identified by comparison of the retention times of the gas chromatograms, using PEG-6000 as the column packing, with those of the pure products expected. The yields of the reaction products were determined by comparison of the areas under the gas-chromatographic peaks, with benzene used as an internal standard. Then, from the photon intensity measured by chemical actinometry, the quantum yields of the products were calculated; these are shown in Table 1.

Table 1. The quantum yields for the products of ethyl ether photo-oxygenation

Products	Quantum yield
Ethyl acetate	0.49
Ethyl formate	0.23
Acetaldehyde	0.17
Ethanol and/or[a] methanol	0.43

a) We were unable to separate ethanol and methanol in the gas-chromatogram.

*The O_2–*p*-Phenylenediamine–Cyclohexane System.* It is known that PPD in water or alcohol is thermally oxidized at room temperature to produce gradually the brown precipitate of Bandrowski's base.[6] When the cyclohexane or dioxane solution of PPD, more stable than the protic solutions, was irradiated in the region of the absorption band of PPD with bubbling oxygen, it turned to red. No change was observed when the same experiment was done in the deoxygenated state.

The spectrum of 9.54×10^{-5} M cyclohexane solution of PPD saturated with O_2 was shown in Fig. 2, together with the products of irradiation through a UV-D25 filter. The products were separated by thin layer chromatography and elution chromatography, the developing solvent being an acetone (1): benzene (1) solution, and were analyzed by IR, UV, and chemical techniques. The material which absorbs at about 380 nm was identified to be 4,4′-diaminoazobenzene (DAAB) by comparing its IR and UV spectrum with those of the synthesized DAAB. The two absorption bands at about 260 nm are assigned to *p*-benzoquinonediimine from the identity in the UV spectrum with the synthesized material.[7,8] Because of its high reactivity, we could not separate it from the reaction products. The shoulder at 470 nm agrees with the first band of Bandrowski's base,[9] and can most probably be assigned to it. 1.30×10^{-6} M peroxide was produced when a 1.27×10^{-4} M cyclohexane solution of PPD was irradiated.

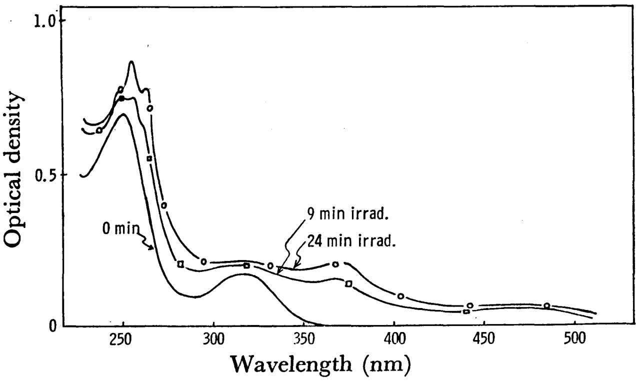


Fig. 2. Electronic spectral change of PPD in cyclohexane saturated with O_2 by the irradiation through a UV-D25 glass filter.

Each of the quantum yields for the reaction products was derived from the peak intensity of the UV absorption spectrum: *p*-benzoquinonediimine 0.01, DAAB 0.003, Bandrowski's base 0.002.

No ESR signal was detected for the dioxane solution irradiated at room temperature. But a weak broad singlet signal with the *g*-value of 2.016 was detected in cyclohexane irradiated at room temperature.

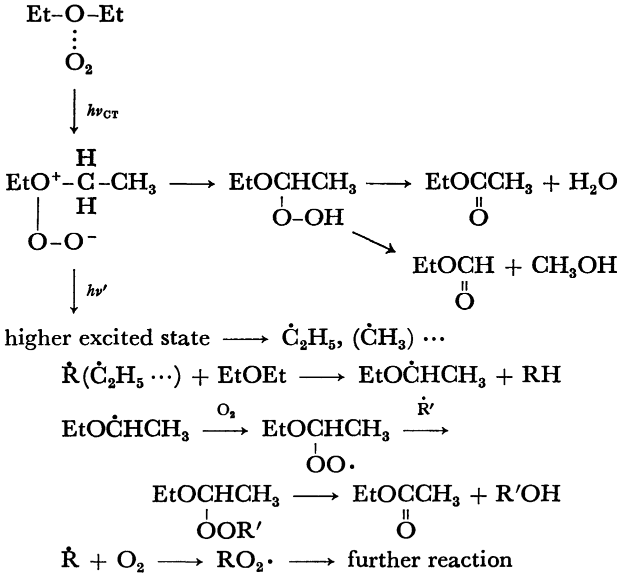
In the case of the cyclohexane solution at 77 K a broad singlet ESR spectrum was obtained. A similar spectrum was obtained for the dioxane solution. The *g*-values were 2.0050 and 2.0036, respectively. The broad singlet ESR bands became stronger with the irradiation time, without change in the shape. As the matrix was warmed, the signal intensity decreased.

The O_2–Dimethylaniline System. The ESR spectrum obtained for this system irradiated through a UV-39 filter at 77 K was a broad singlet. For the case of O_2-saturated DMA at room temperature, the *g*-value was 2.0065, and for the case of DMA (1): cyclohexane (1) at room temperature, the *g*-value was 2.0048. Although it is impossible to determine the species relevant to the ESR signal which appeared by the irradiation at room temperature, it seems reasonable to assign it to *N*-methylanilino radical, because of the fairly large *g*-value and the circumstances of its appearance.

When oxygen gas was bubbled into DMA, it turned to yellow owing to the CT absorption with O_2.[10] The reaction products were analyzed by gas chromatography using PEG 6000+KOH as column packing. No product was identified except for *N*-methylaniline. Its quantum yield could not be obtained because of the poor yield. *N*-Methylaniline was also obtained by the irradiation of deaerated DMA.

Discussion

The Ether–O_2 System. The results obtained indicate that the reaction mechanism in this system is rather similar to that for the triethylamine–O_2 system studied by us.[1] The formation of ethyl (or, less probably, methyl) radical is observed by the ESR studied at 77 K. Upon warming, the ethyl (methyl) radical and possibly a small quantity of some other radicals produced become mobile, and either react with oxygen to form peroxy radicals or abstract hydrogen atoms from ether. Our observed experimental results showed that the peroxy radicals were gradually produced in the ether–O_2 system irradiated at 77 K even if the temperature was kept at 77 K. The formation of ethyl, and possibly other radicals, can be explained by assuming the photo-excitation of the metastable singlet CT state or $\mathrm{EtO\dot{C}HCH_3}$ formed by hydrogen abstraction from ether. The over-all scheme for the formation of the main reaction products can be shown by the following equations:



$$\mathrm{Et{-}O{-}Et} \cdots \mathrm{O_2} \xrightarrow{h\nu_{CT}} \mathrm{EtO^+{-}\overset{H}{\underset{H}{C}}{-}CH_3}\ (\mathrm{O{-}O^-}) \longrightarrow \mathrm{EtO\underset{O{-}OH}{CH}CH_3} \longrightarrow \mathrm{EtO\underset{\overset{\|}{O}}{C}CH_3} + \mathrm{H_2O}$$

$$\mathrm{EtO\underset{O{-}OH}{CH}CH_3} \longrightarrow \mathrm{EtO\underset{\overset{\|}{O}}{C}H} + \mathrm{CH_3OH}$$

$$\xrightarrow{h\nu'} \text{higher excited state} \longrightarrow \mathrm{\dot{C}_2H_5},\ (\mathrm{\dot{C}H_3}) \cdots$$

$$\mathrm{\dot{R}(\dot{C}_2H_5 \cdots)} + \mathrm{EtOEt} \longrightarrow \mathrm{EtO\dot{C}HCH_3} + \mathrm{RH}$$

$$\mathrm{EtO\dot{C}HCH_3} \xrightarrow{O_2} \mathrm{EtO\underset{OO\cdot}{CH}CH_3} \xrightarrow{\dot{R}'}$$

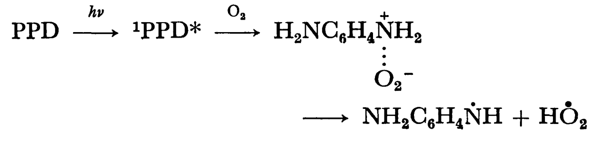
$$\mathrm{EtO\underset{OOR'}{CH}CH_3} \longrightarrow \mathrm{EtO\underset{\overset{\|}{O}}{C}CH_3} + \mathrm{R'OH}$$

$$\mathrm{\dot{R}} + \mathrm{O_2} \longrightarrow \mathrm{RO_2\cdot} \longrightarrow \text{further reaction}$$

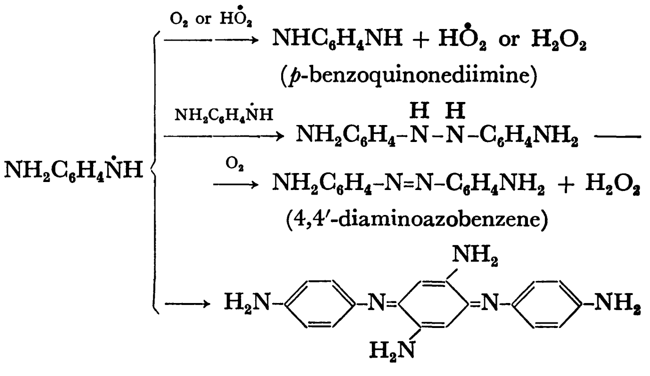
It might be worthwhile to note that no photodissociation of ether took place when deaerated ether was irradiated in the region of the CT absorption. Of course, reabsorption processes for the various radicals and other intermediates formed undoubtedly take place, which make the overall mechanism more complicated and harder to interpret.

The p-*Phenylenediamine–O_2 System.* The ESR signal detected in the irradiated cyclohexane solution at room temperature is attributable to the peroxy radical, but whether it is the hydroperoxy radical or alkylperoxy radical has not yet been proved. In view of the reaction products, it is more likely to assign it to the hydroperoxy radical. The ESR signal observed by irradiation at 77 K is most likely due to *p*-aminoanilino radical, in view of the *g*-value and the reaction products.

From the result described above, the reaction path might be as follows:



$$\mathrm{PPD} \xrightarrow{h\nu} \mathrm{{}^1PPD^*} \xrightarrow{O_2} \mathrm{H_2NC_6H_4\overset{+}{N}H_2} \cdots \mathrm{O_2^-} \longrightarrow \mathrm{NH_2C_6H_4\dot{N}H} + \mathrm{H\dot{O}_2}$$



$$\mathrm{NH_2C_6H_4\dot{N}H} \xrightarrow{O_2 \text{ or } H\dot{O}_2} \mathrm{NHC_6H_4NH} + \mathrm{H\dot{O}_2} \text{ or } \mathrm{H_2O_2}$$

(*p*-benzoquinonediimine)

$$\mathrm{NH_2C_6H_4\dot{N}H} \xrightarrow{NH_2C_6H_4\dot{N}H} \mathrm{NH_2C_6H_4{-}\overset{H}{N}{-}\overset{H}{N}{-}C_6H_4NH_2} \xrightarrow{O_2} \mathrm{NH_2C_6H_4{-}N{=}N{-}C_6H_4NH_2} + \mathrm{H_2O_2}$$

(4,4′-diaminoazobenzene)

(Bandrowski's base)

The reaction path to lead to Bandrowski's base has not been clarified. But the studies of the dark reactions made in our laboratory between PPD and electron acceptors, *e.g. p*-benzoquinone, and the reactions between $\mathrm{PPD^+}$ cations and other amines or PPD itself, indicated the formation of indamine-type compounds ($\mathrm{H_2N{-}C_6H_4{-}N{=}C_6H_4{=}NH_2^+}$), Bandrowski's base, and, in certain cases, diazocompounds, $\mathrm{NH_2{-}C_6H_4{-}N{=}N{-}C_6H_4NH_2}$.[6] Therefore, it seems very probable that both such thermal reactions and the photo-oxygenation reactions described in this paper pass through the $\mathrm{PPD^+}$ cation, which, by subsequent proton transfer, forms the radical of the type $\mathrm{H_2N{-}C_6H_4{-}\dot{N}H}$.

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