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Intermediates and Mechanism of Photo-Oxygenation Reaction of Triethylamine

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The electronic absorption spectrum caused by the charge transfer interaction between oxygen and triethylamine was studied quantitatively. It is concluded that there is no particular stabilization between them due to the charge transfer interactions. The intermediate radicals produced by the excitation of triethylamine-O_2 in the region of the charge transfer band were studied by the ESR method at various temperatures from 77 to 300 K. The chemical analysis of the irradiation products of the same system was also carried out. The radicals observed are methyl, ethyl, and possibly, $(C_2H_5)_2N\dot{C}HCH_3$, $\dot{O}OH$ and $(C_2H_5)_2NO\cdot$. The products identified are acetaldehyde and diethylamine. Based on these results, the various reactions taking place in the overall photochemical process were speculated.

It is well known that oxygen gives rise to charge transfer(CT) absorption spectra with various organic substances.[1] The upper states for the absorption processes are theoretically predicted to be almost pure ionic pairs, $D^{+}\cdots O_2^{-}$, where D is an electron donor. In the case of aniline derivatives, we have found that an ion-pair formation occurs from this excited CT state followed by electron recombination leading mostly to the ground state of aniline.[2] In the case of aliphatic compounds, on the other hand, oxidation reactions seem to ensue generally.

Systematic studies of the photo-chemical reactions of such oxygen CT complexes seem to be very important, because, by doing so, we might be able to get a general information on the chemical driving forces for the CT complexes which are related with such biological processes as photosynthesis. The photo-oxygenation process is also very important as one taking part in the auto-oxidation. In spite of these importances, there seems to have been rather scanty work on direct photo-oxygenation reactions so far, aside from numerous works concerning photo-sensitized oxygenation reactions.[3] In the case of ethyl ether, Stenberg *et al.*[4]

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[1] H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960), and earlier papers cited there.

[2] M. Hori, H. Itoi, and H. Tsubomura, This Bulletin, **43**, 3765 (1970).

[3] For instance, C. S. Foote, *Science*, **162**, 963 (1968).

[4] V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967).

found that the excitation of the O_2-ether system in the region of its CT absorption leads mainly to the formation of ethyl acetate. For aliphatic amines, Stratford[5] studied the direct photo-oxidation of trialkylamines in detail. He found that, in the case of tri-*n*-butylamine, dibutylamine, butyric acid and tributylamine *N*-oxide are among the products.

Experimental

Materials. Reagent grade triethylamine was dried overnight with potassium hydroxide, and fractionally distilled with a Widmer column. *n*-Heptane and most other hydrocarbons were treated with concentrated sulfuric acid, washed, dried with calcium chloride and then with sodium wire, and fractionally distilled. Acetonitrile was dried with calcium chloride and refluxed with phosphorus pentoxide and fractionally distilled. Commercially available pure oxygen was dried by liquefaction with liquid nitrogen.

Measurements of the CT Absorption Spectra. Pure triethylamine (TEA) or the *n*-heptane solution of TEA was placed in an ampoule with a magnetic rotor inside and a side arm connected to a quartz cell for the spectral measurements. The ampoule was connected through a ground glass joint to a vacuum line, and the TEA or the solution was degassed by means of the freeze-pump-thaw technique. After the absorption spectrum was measured at room temperature, oxygen was introduced into the line at *ca.* 1 atm pressure, the line being closed and the pressure being read quickly with a mercury manometer. Then, the liquid was vigorously stirred by the magnetic stirrer for a few minutes and the pressure drop was read. By this procedure, the concentration of the oxygen in the solution could be determined. The solution was transferred to the quartz cell and its ultraviolet absorption spectrum was measured by use of a Cary 15 spectrophotometer.

ESR Measurements. The ESR measurements were made using a JES-3BX or a JES-ME-2X spectrometer of Japan Electron-Optics Laboratory Co. at the X band. The magnetic field was measured by use of the proton magnetic resonance signal. The *g*-values of short-life species were determined by inclusion of a Mn^{2+} reference sample.

The solution containing TEA was put into a pyrex ampoule connected to a quartz ESR capillary cell. After dried oxygen gas was bubbled in, the solution was transferred into the ESR cell, which was then placed into a Dewar vessel and cooled with liquid nitrogen. The cell was irradiated with a Ushio 500 W high pressure mercury lamp through a Toshiba UV-D2 glass filter which transmits the light in the region of the CT band (300—400 nm).

The Analysis of the Photo-Oxygenation Products. TEA in a reaction vessel (a cylinder, 24 mm in diameter) made of sodium glass, transparent beyond 310 nm, was irradiated with the 500 W high pressure mercury lamp 25 cm apart from the reaction vessel with oxygen bubbling in through a glass capillary tube. The reaction products were analyzed by the gas chromatographic, chemical and IR techniques.

Results

UV Absorption Spectra. In Fig. 1, the absorption spectra of *n*-heptane solutions of TEA dissolving oxygen are shown, the absorption of the deoxygenated solution being subtracted for each curve. From the absorbances and the amount of dissolved oxygen determined by the manometric method, the Benesi-Hildebrand plot[6] was made, which leads to molar extinction coefficients of 640 at 310 nm, 970 at 300 nm, and 1550 at 290 nm. The equilibrium constants obtained ranged from 0.05 to 0.08, showing that the binding between oxygen and TEA is very weak or practically nil. In Fig. 2, the Benesi-Hildebrand plot for λ=290 nm is shown as an example.

ESR Studies. The excitations of TEA in *n*-heptane in the range of the CT band at 77 K for about 10 min gave an ESR spectrum as shown by curve A in Fig. 3. The spectrum is symmetric with respect to the magnetic field, the *g* value being 2.0025. The intensity increased with irradiation till about 2 hr, after which it began to be saturated. At 77 K, the

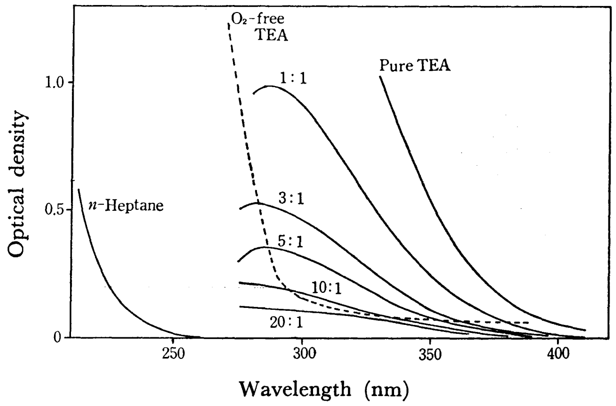

Fig. 1. The ultraviolet absorption spectra caused by oxygen dissolved in *n*-heptane, triethylamine, and their *n* : 1 mixtures (The absorption of the degassed solution is subtracted for each curve.).

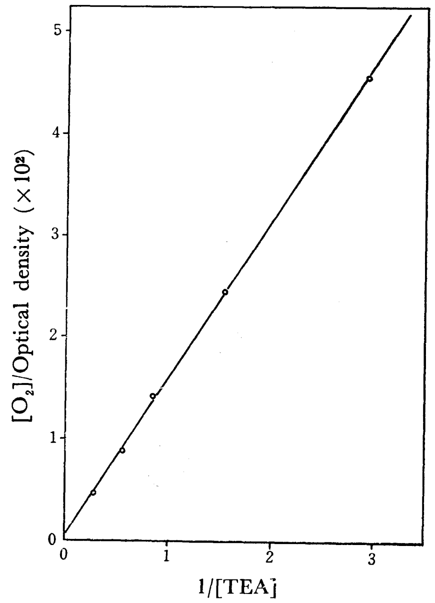

Fig. 2. The Benesi-Hildebrand plot of the absorption caused by oxygen dissolved in *n*-heptane solutions of triethylamine at 290 nm.

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5) M. J. W. Stratford, U. S. Dept. Com., Office Tech. Serv., P. B. Report, 144250, p. 46 (1959).

6) For instance, L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).

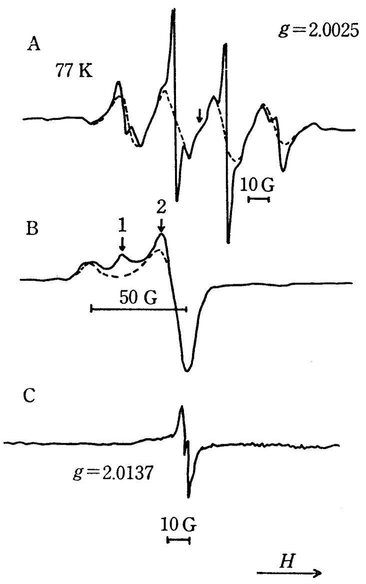

Fig. 3. The ESR spectra of the species produced by the UV-irradiation of triethylamine(1) : n-heptane(5)-O_2 at 77 K (A), followed by warming in the dark (B and C).

Fig. 4. The ESR spectrum of UV-irradiated triethylamine(1): decalin(1)-O_2 at 77 K.

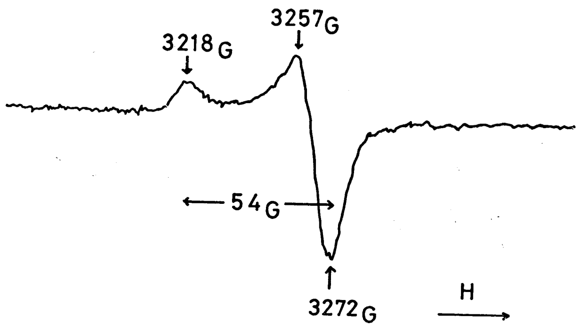

Fig. 5. The ESR spectrm of UV-irradiated triethylamine(1): isopentane(5)-O_2 at 77 K.

spectrum stayed unchanged after the light was turned off. The intensity was proportional to the concentration of oxygen. It was confirmed that n-heptane and methylcyclohexane dissolving oxygen did not show any ESR signal when irradiated.

The spectrum has a prominent quartet, with an intensity ratio of approximately 1 : 3 : 3 : 1 and a hyperfine coupling constant of 26 G. These features show that methyl radical is present in the solution. It has been confirmed that similar spectra were obtained when TEA in acetonitrile or a 1 : 1 mixture of n-propyl and isopropyl alcohols was UV-irradiated at 77 K.

When the component of the spectrum due to the methyl radical is subtracted from the spectrum of Fig. 3A, the curve shown by the broken line is obtained. This appears to be a symmetric quartet, but might more probably be a sextet which is due to a five proton system (see later sections). From the present situation, the species most relevant to this spectrum is the ethyl radical.

In the case of the decalin solution, an ESR spectrum was obtained as shown in Fig. 4. A similar spectrum was obtained for the methylcyclohexane solution. Here, the structure due to the methyl radical is much weaker, and the sextet is prominent. This result can be understood by assuming that the methyl radical is more mobile in these solvents at 77 K than in the other solvents and is unable to survive at 77 K, while the larger radical relevant to the sextet is less mobile and more stable at the same temperature.

Table 1. The g-factors of peroxy radicals

	g_1	g_2	g_3
In isopentane matrix at 77 K	2.0034	2.0034	2.0369
In n-heptane matrix at elevated temp	2.0029	2.0029	2.0353
OOH[7]	2.0044	2.0044	2.0393

For the case of the isopentane solution, a spectrum was obtained showing large anisotropic g-factors (Fig. 5 and Table 1). The g-factors are a little different from those of OOH and the species for the spectrum may be assigned to an organic peroxy radical. It is often recognized that the isopentane matrix at 77 K is softer than other matrices, so that oxygen can move through the matrix at 77 K, making encounter with a radical and reacting with it even at that temperature.

When the liquid nitrogen in the Dewar vessel was removed and the irradiated solution of TEA was allowed to warm up, the ESR spectrum changed as shown in Fig. 3 for the case of n-heptane solution. The analysis of curve B as assigned to a peroxy radical reveals that the peak indicated by an arrow (1) is no doubt due to a different species and the peak indicated by an arrow (2) shows that a small amount of methyl radical still survives in that spectrum. What remains is very much similar to the spectrum of the isopentane solution (Fig. 5 and Table 1) and undoubtedly represents that the same species are present in the two cases. At intermediate temperatures between those for curve A and B, the methyl quartet gets weaker while at the same time the peroxy signal gets stronger. These results indicate that as the matrix begins to soften, the methyl and ethyl radicals transform into diamagnetic species and the oxygen molecules begin to move through the matrix and react with a carbon radical to form the peroxide.

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7) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **47**, 5441 (1967).

At the still higher temperature, the ESR signal almost disappears once, and then reappears taking the form shown by curve C in Fig. 3. This is a slightly split singlet with the g-value of 2.016, which is not accurate because of the fast scanning. The spectrum fades out quickly at higher temperature. The average g-value for the peroxy spectrum of curve B is 2.0137, fairly close to the above-mentioned value and therefore the spectrum C is attributable to the same peroxy radical as that for curve B rapidly rotating in the warm matrix. The disappearance of the signal at the intermediate temperature then indicates a dimerization reaction as shown below,

$$\mathrm{RO\dot{O}} + \mathrm{RO\dot{O}} \longrightarrow \mathrm{ROOOOR},$$

taking place when the radicals gets fairly mobile. The dimer then dissociates into the monomer radicals at higher temperature, giving spectrum C. Such a dimerization-redissociation phenomenon was observed before.[8]

By irradiating continuously a n-heptane solution of TEA at room temperature, an ESR spectrum was obtained as shown in Fig. 6. The spectrum was very weak and the intensity was proportional to the oxygen pressure. It disappeared immediately when the light is extinguished. The spectrum shows the characteristics of the nitrogen hyperfine structure, with $g=2.0036$ and the nitrogen coupling constant $a_N=15$ G. From the stability of this species, it is most probably an N-oxyl radical. The a_N value of diethylamine-N-oxyl radical observed is 16.7 G.[9] Also, g and a_N of di-t-butylamine-N-oxyl are 2.00595 and 15.36 G, respectively.[10] These values nearly agree with those obtained for the observed spectrum, and from the present situation, it seems most probable that the species obtained is diethylamine-N-oxyl (Et_2NO).

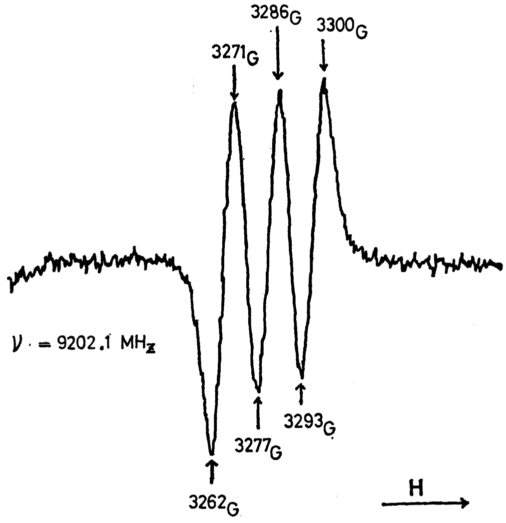

Fig. 6. The ESR spectrum of a species formed by continuous UV-irradiation of triethylamine (1): n-heptane(5)-O_2 at room temperature.

The Analyses of the Photo-Oxygenation Reaction Products. When TEA bubbled with oxygen was irradiated at room temperature in the region of the CT band for a few minutes as described in Experimental section, the amine became turbid, and then began to color yellow. By further irradiation, the yellow color deepened and brown viscous liquid gradually accumulated at the bottom. These processes took about one hour. In the case where the oxygen gas, together with some volatile reaction products, was passed into a cold trap, containing a dilute sulfuric acid solution of 2,4-dinitrophenylhydrazine, a yellow precipitate was immediately formed. The precipitate was purified by recrystallization and identified as the phenylhydrazone of acetaldehyde by elementary analysis and by comparison of its IR spectrum with that of the authentic sample. The yellow-colored sample was also found to contain diethylamine, by treating the sample with p-toluenesulfonyl chloride under Hinsberg's method.

The gas-chromatographic analyses of the amine solutions were carried out also at various stages of the irradiation. At the stage where the amine became first turbid, a peak whose retention time agreed with that of acetaldehyde appeared, together with an unidentified one and the large peak of TEA. By further irradiation, another peak was found. Then, from a sample taken at the stage of yellow coloration, a peak was obtained which is assigned to diethylamine by its retention time, together with at least two small peaks at the longer retention time. The last one agreed in the retention time with that of a product obtained from a reaction mixture of acetaldehyde and diethylamine. The amounts of acetaldehyde and diethylamine obtained are estimated to be about 1 mol% of TEA. The gas-chromatogram of the brown, viscous, bottom layer was very broad and no component was clearly identified.

The infrared spectra of the irradiated sample at various stages were measured as shown in Fig. 7. By the irradiation, absorptions appear at the regions

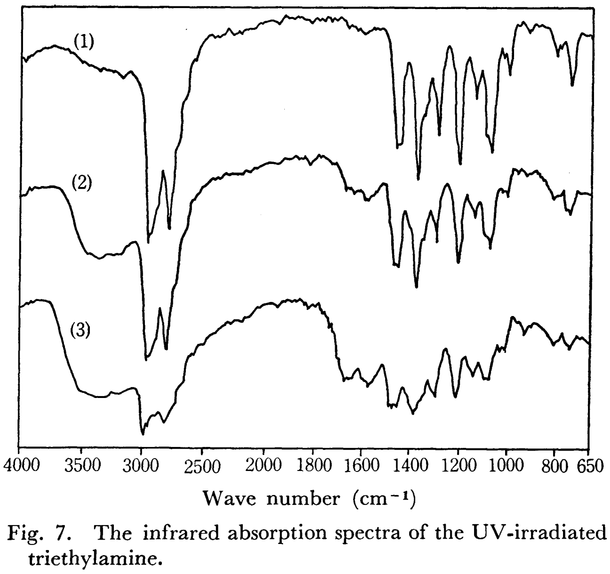

Fig. 7. The infrared absorption spectra of the UV-irradiated triethylamine.

(1) Before irradiation.
(2) The upper layer of the yellow-colored sample.
(3) The lower layer of the same sample.

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[8] N. Yamamoto, H. Tsubomura, and F. Sakiyama, An unpublished result.

[9] A. Hudson and A. Hussain, *J. Chem. Soc., Ser. B*, **1967**, 1299.

[10] R. J. Faber, F. W. Markley, and J. A. Weil, *J. Chem. Phys.*, **46**, 1652 (1967).

of 3300 and 1600 cm^{-1}, which suggest the appearance of an amino group or a hydrogen-bonded OH species and carbonyl groups, respectively.

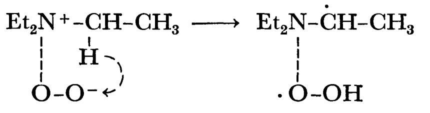
Discussion

Under the present experimental conditions, it is obvious that the first step of the photo-oxygenation reaction of TEA is the formation of the charge transfer state.

$$\mathrm{Et_3N\cdots O_2} \xrightarrow{h\nu} \mathrm{Et_3N^+\cdots O_2^-} \qquad (1)$$

At 77 K, the following two processes can be considered.

1. The proton transfer process from the charge transfer state.



$$\begin{array}{l}\mathrm{Et_2N^+\text{-}CH\text{-}CH_3}\\ \ \ |\quad \mathrm{H}\\ \mathrm{O\text{-}O^-}\end{array} \longrightarrow \begin{array}{l}\mathrm{Et_2N\text{-}\dot{C}H\text{-}CH_3}\\ \qquad\quad |\\ \qquad \mathrm{\cdot O\text{-}OH}\end{array} \qquad (2)$$

(named R· hereafter)

The calculation of the enthalpy change for this process by use of known thermochemical data leads to the conclusion that the above process is almost isothermal or slightly endothermic.

2. Re-excitation from the charge transfer singlet state. Though there is no data for the lifetime of the CT state, it might be possible that the CT triplet state which is first attained by photo-excitation degrades to a more stable CT singlet state having a spin different from that of the ground state or to the amine's triplet state, then reabsorbs another photon, and is excited to a higher state. From such higher states, the dissociation of the C–H, C–C, or C–N bond might be probable.

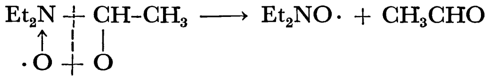
$$\mathrm{^3[Et_3N^+\cdots O_2^-]} \longrightarrow \underbrace{\mathrm{^1[Et_3N^+\cdots O_2^-]\ or\ ^3[Et_3N]\cdots O_2}}_{\Big\downarrow h\nu'} \qquad (3)$$
$$\mathrm{\dot{C}H_3\ \dot{C}_2H_5,\ Et_2\dot{N},\ R\cdot,}\ etc.$$

This second process probably accounts for the methyl and ethyl signals of our ESR measurements at 77 K. It might be possible also that the radical produced by the first process(designated by R·) and the HOO· radical form a pair with $S=0$, or 1. This might be the reason why the signals for R· and HOO· were too weak to be observed in our experiments.

By warming up the matrix, our results tell that the signals for the methyl and ethyl radicals become weaker, and simultaneously, the signal for the peroxy radical increases. These changes can easily be attributed to the softening of the matrix, making the alkyl radicals unstable and the oxygen molecules to diffuse through the matrix till they encounter and react with the larger radicals, for instance, R·, to form the peroxy radical ROO·.

$$\mathrm{R\cdot + O_2 \longrightarrow ROO\cdot}$$

The peroxy signal observed, with a slight splitting by a proton, seems to support its assignment to the above-mentioned species, ROO·. The presence of *N*-oxyl radical found from the ESR measurements by continued irradiation at room temperature and that of acetaldehyde from chemical analysis suggest the following process from this ROO·.



$$\begin{array}{l}\mathrm{Et_2N \nmid CH\text{-}CH_3}\\ \quad\ \uparrow\quad |\quad |\\ \quad \mathrm{\cdot O \nmid O}\end{array} \longrightarrow \mathrm{Et_2NO\cdot + CH_3CHO}$$

(ROO·)

The origin of the diethylamine isolated from the photolysis product is not clear, but at least part of the material might have been formed from diethylamino radical obtained in process 2.

The overall processes leading to the yellow viscous material seem to be extremely complex. One possible route is the condensation reaction between acetaldehyde and diethylamine *via* the formation of an enamine.

$$\mathrm{CH_3CHO + Et_2NH \longrightarrow CH_2{=}CH\text{-}NEt_2 + H_2O}$$
$$\Big\downarrow$$

More condensation reactions

The *N*-oxyl radical, some peroxides and other radicals formed photo-chemically may take part in the further reactions.

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