Photooxygenation of Diphenanthro[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene

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The photooxygenation of diphenanthro[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene (DPP) due to visible-light irradiation was investigated by measuring the absorption spectra and applying semi-empirical molecular orbital methods. It was shown theoretically that molecular oxygen attaches to the central benzene ring of DPP to give an endo-peroxide. The oxygen gradually detaches from the endo-peroxide at room temperature, reproducing DPP. The activation energies for both the reactions of oxygen attachment and detachment were determined based on the temperature dependences of the reaction rates in benzene; 10.0±5.5 kJ mol^{-1} for the attachment reaction and 83.8±2.5 kJ mol^{-1} for the detachment reaction.

Diphenanthro[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene (DPP) is an undecacyclic condensed aromatic hydrocarbon which has an approximate two-fold symmetry axis along the direction perpendicular to the molecular plane (Fig. 1a). An ethanol or benzene solution of DPP is yellowish green, but turns colorless upon visible-light irradiation. This phenomenon can be interpreted as a being photooxygenation reaction;[1] DPP reacts with singlet molecular oxygen O_2 ($^1\Delta_g$) to form its endo-peroxide (ODPP). Such an endo-peroxide, in which some larger distortions are apparent, is attracting increasing attention in the filed of cancer research; the distortions may affect the formation of the diol epoxides from the parent molecule in the carcinogenic process.[2,3]

So far, studies of the photooxygenation of polycyclic aromatic hydrocarbons (PAHs) have concentrated on relatively small molecules, such as anthracene and its derivatives;[4] only a few studies have been performed for larger PAHs, because of difficulty in synthesis and purification.[5] We have synthesized several large PAHs and have examined their photooxygenation reactions; for example, dibenzo[*a,j*]perylene (DBP) and DPP were reactive, but tetrabenzo[*a,cd,j,lm*]perylene, dinaphtho[3,2,1-*cd*: 3′,2′,1′-*lm*]perylene, dibenzo[*a,rst*]naphto[8,1,2-*cde*]pentaphene were unreactive. The photooxygenation of DBP was investigated previously;[5] though the structure of the endo-peroxide and the rate of O_2 detachment were determined, the rate of O_2 attachment could not be measured quantitatively because of rapidness of the reaction. DPP underwent substantially slower photooxygenation than did DBP. Accordingly, it is adequate to carry out a detailed study on the kinetics involving O_2 attachment. This paper mainly describes the experimental results concerning the photooxygenation reaction of DPP. The geometry of ODPP, which has not yet been determined experimentally, was calculated by semi-empirical molecular orbital methods.[6]

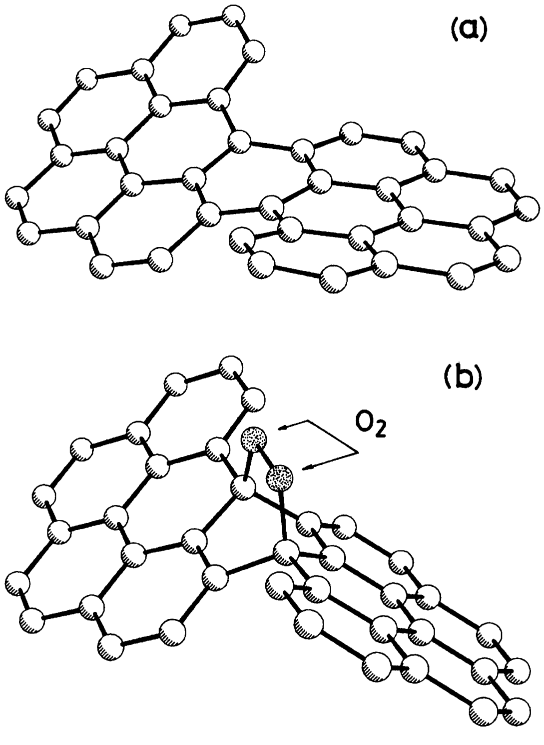

Fig. 1. Perspective drawings of (a) DPP and (b) its endo-peroxide (ODPP) without hydrogen atoms.

Experimental

DPP was prepared by a previously reported method.[7] Briefly, naphthanthrone was condensed with copper powder, zinc chloride, and sodium chloride. The crude product was dissolved in toluene and passed through a column of alumina. The thus-obtained DPP was further purified by high-vacuum sublimation.

A benzene solution of DPP (1×10^{-5} M; 1 M=1 mol cm^{-3}) in a 1 cm rectangular silica cell was irradiated by a Nihon Bunko CRM-FA light source equipped with a 2 kW Xe-lamp and diffraction grating monochromator. The energy of light emitted from the light source was measured with a thermocouple; it was 17.3×10^4 erg cm^{-2} s^{-1} for 510 nm light. The spectral change induced by the irradiation was observed with a Hitachi U-3210 spectrophotometer. For a comparison, the same measurements were carried out for a solution which had been degassed.

The rates of O_2-attachment to DPP due to light irradiation and thermal O_2-detachment from ODPP were observed by the same spectrophotometer; the temperature of the solution was controlled at several points by a thermostat.

It was also confirmed that singlet molecular oxygen reacts with DPP in its ground state to cause the same phenomenon as that arising from photooxygenation. The singlet molecular oxygen was produced by adding NaOCl (ca. 5% commercial antiseptic solution PURELOX) onto H_2O_2 (35%, Koso Chemical Ltd.), and was immediately introduced into a benzene solution of DPP.[5)]

Results and Discussion

Spectral Change. Figure 2a (broken curve) shows the absorption spectrum of DPP in a benzene solution before light irradiation; the band due to the first π–π^* transition appears in the wavelength region of 400—550 nm and its maximum is at 510 nm. When the solution was irradiated by 510 nm light, the intensity of the band began to decrease; after 30 min of irradiation, it was significantly reduced and a new absorption band appeared in the region of about 320—380 nm (Fig. 2a, solid curve). For a sample solution that had been degassed, no changes were observed in the spectrum by irradiation. From this it was confirmed that the spectral change arises from oxygen attachment to DPP and a resulting division of its large π-electron system into small ones.

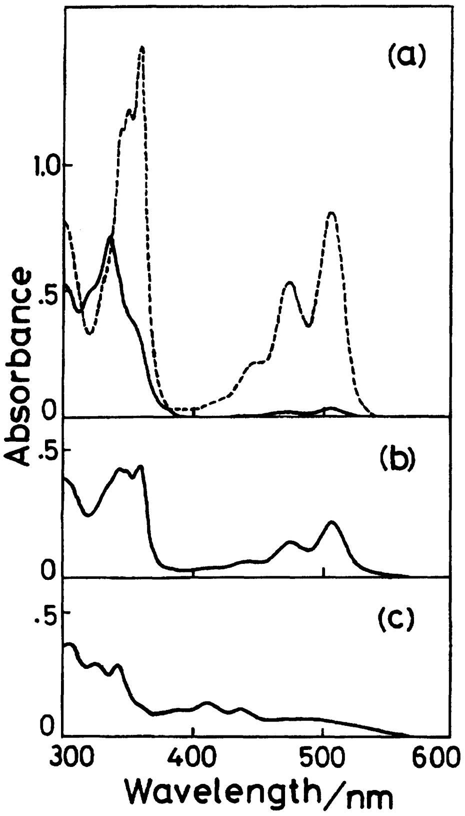

Fig. 2. Excitation wavelength (λ) dependence of the absorption spectrum of DPP in benzene after 30 min irradiation: λ=(a) 510 nm (solid curve); broken curve represents the spectrum before irradiation, (b) 400 nm, and (c) 360 nm.

The photobleached solution regained its original color when it was left in the dark at room temperature; almost 100% intensity could be recovered after the solution had stood for 48 h. Namely, ODPP gradually releases the attached oxygen, reproducing DPP.

The spectral change after irradiation for a definite time depended on the irradiation wavelength (λ). For $\lambda \geq 400$ nm, the decrease in the absorption intensity was proportional to the absorbance of DPP at λ, whereas the spectral shape was preserved; the decrease was the largest for $\lambda=510$ nm and the smallest for $\lambda=400$ nm (Fig. 2b). The spectra after irradiation returned to the original, as described in the preceding paragraph. Contrary, for $\lambda<400$ nm, the spectra changed in a quite different manner; in addition to a decrease in the absorption intensity, the shape also greatly deviated from the original one, as shown in Fig. 2c. Since these changes were irreversible, they can be ascribed to photofragmentation of DPP.

Such a photooxygenation reaction is considered to arise from the following mechanism:[5)]

$$\mathrm{D(Ground)} + h\nu \rightarrow \mathrm{D^*(Singlet)}$$

$$\mathrm{D^*(S)} \rightarrow \mathrm{D^*(Triplet)}$$

$$\mathrm{D^*(T)} + \mathrm{O_2} \rightarrow \mathrm{D(G)} + \mathrm{O_2^*}$$

$$\mathrm{D(G)} + \mathrm{O_2^*} \rightarrow \mathrm{DO_2}$$

where D and D* represent the ground and excited states of DPP respectively, and O_2^* represents singlet molecular oxygen, O_2 ($^1\Delta_g$). It is noted that the light energy absorbed by a DPP molecule is utilized not for oxygen attachment directly, but for the production of O_2^*. In fact, a similar spectral change was observed when the benzene solution of DPP was treated with singlet molecular oxygen, as described in the experimental section.

Geometry of ODPP. The molecular geometry of DPP has been determined by Oonishi et al.,[7)] whereas that of ODPP has not yet been reported. Accordingly, we performed semi-empirical molecular orbital calculations to obtain the optimized geometry of ODPP. Since the details concerning the calculations were reported previously,[6)] only the geometry is shown in Fig. 1b. An O_2 molecule attaches to a pair of carbon atoms which has the largest π-electron density of the highest occupied molecular orbital; it divides the large π system of DPP into two equivalent small π systems. Moreover, the O_2-attachment causes a change in the hybrid of the carbon atoms from sp^2 to sp^3, which leads to a large bend in the molecular plane. This geometry of ODPP is the most energetically stable, and its calculated excitation energies are in good agreement with the experimental results.[6)] These show the reliability of the calculation, though the geometry should be confirmed by experiments.

Reaction Rate. The rate of O_2 attachment was measured by monitoring the decreasing band at 510 nm of DPP with an increase in irradiation time (t); the temperature (T) of the solution was kept constant at several points. The variations of the band intensity with t are shown in Fig. 3, where the intensity is normalized to its initial value. At $T=283$ K, the reaction proceeds very rapidly until $t=30$ min, then becomes slower by degrees, and finally attains an equilibrium state. The time dependence of the reaction is almost identical at higher T, though the rate becomes slower with increasing T. This indicates that the reverse reaction, i.e., the O_2-detachment, advances appreciably with T. Therefore, the O_2-detachment reaction, which is thought to be first order, should be investigated before analyzing the data of the O_2-attachment reaction.

The rate of O_2-detachment was also measured by monitoring the band at 510 nm. The band intensity increased with time, obeying the first-order reaction scheme, as was expected (Fig. 4a). The rate depended strongly on the temperature (T); it increased about 10-times faster as T was increased from 283 to 303 K (Fig. 4b). This T-dependence of the rate can be explained in terms of the Arrhenius formula,

$$k_\mathrm{d} = A_\mathrm{d} \exp(-E_\mathrm{d}/RT), \tag{1}$$

where k_d, A_d, and E_d represent the rate constant, frequency factor, and activation energy for the O_2-detachment reaction, respectively. Figure 5 shows a T^{-1}–$\ln k_\mathrm{d}$ plot; all data lie on a straight line. From the intercept and slope of the line, A_d and E_d were calculated to be 1.7×10^{10} s^{-1} and 83.8±2.5 kJ mol^{-1}, respectively. These values can be compared with the A_d and E_d values for DBP in benzene, 1.9×10^{11} s^{-1} and 89.5±2.1 kJ mol^{-1}, respectively.[5] The frequency factor for DPP is about one order smaller than that for DBP. This is probably due to the difference in the molecular size. In general, thermolysis of the endo-peroxides is considered to occur when excess energy provided by surrounding molecules gets into the C–O vibration of endo-peroxides. Then the probability that such an energy flow occurs is smaller in DPP having eleven benzene rings, than in DBP having seven benzene rings, because in DPP the energy can more easily be spread among more numerous vibrational modes, so that the C–O vibration is less frequently excited. On the other hand, the difference in the activation energy is rather small; the E_d for DPP is by 5.7 kJ mol^{-1} lower than that for DBP. This indicates that the endo-peroxide of DPP is less stable than that of DBP. In fact, the endo-peroxide of 9,10-diphenylanthracene is fairly stable and its activation energy for O_2-detachment is 116.2±0.8 kJ mol^{-1},[8] which is much larger than the E_d values for DBP and DPP.

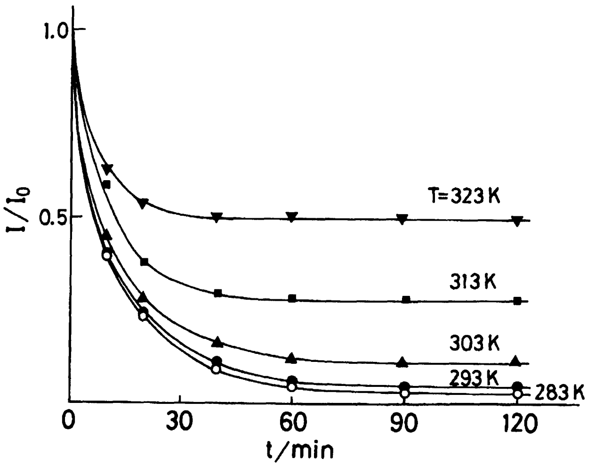

Fig. 3. Variations of the 510 nm-band intensity with the irradiation time; the intensity is normalized to each initial value.

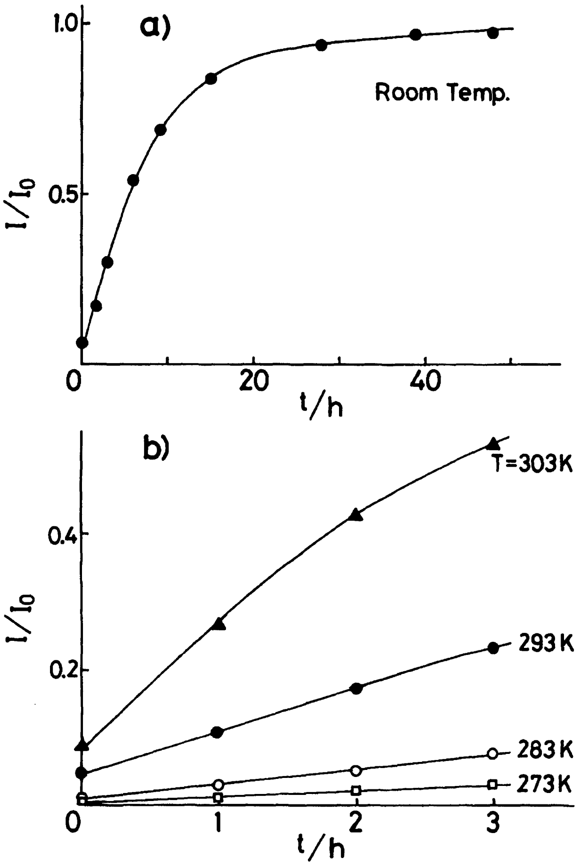

Fig. 4. Variations of the 510 nm-band intensity with time after 2 h irradiation; the intensity is normalized to the value before light irradiation; (a) at room temperature (about 300 K); (b) at several temperatures controlled.

By using the E_d value, the activation energy for the O_2-attachment reaction can also be evaluated as follows. At the equilibrium state,

$$k_\mathrm{a}[\mathrm{D}][\mathrm{O}_2^*] = k_\mathrm{d}[\mathrm{DO}_2], \tag{2}$$

where k_a is the rate constant for the O_2-attachment reaction and [D], $[\mathrm{O}_2^*]$, and $[\mathrm{DO}_2]$ are the concentrations of DPP, singlet molecular oxygen, and ODPP, respectively. It is likely that the concentration of oxygen

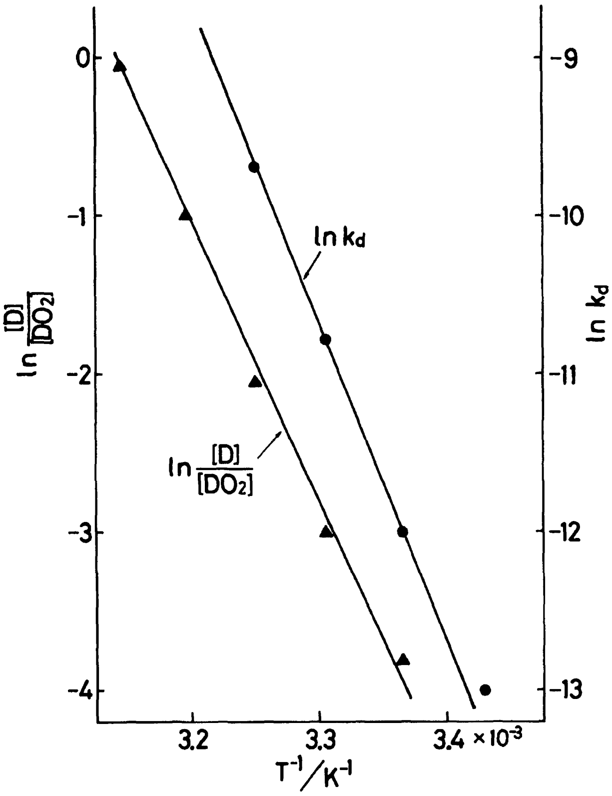

Fig. 5. Arrhenius plots of the rate constant for the O_2 detachment reaction, k_d, and the ratio of the concentration of DPP to that of ODPP, [DPP]/[ODPP].

which dissolves in benzene, $[O_2]$, remains unchanged during the reaction, because the decrease of O_2 due to formation of DO_2 is constantly supplied from the atmosphere. In addition, $[O_2]$ is relatively large, estimated to be about 10^{-3} M at ordinary atmospheric pressure, and oxygen diffuses considerably fast in the solution.[9] Accordingly, O_2^* is generated efficiently by a sensitized energy transfer. Furthermore, O_2^* survives sufficiently longer than the excited states of DPP; the lifetime of O_2^* is 24 μs in benzene.[10] If these are taken into account, $[O_2^*]$ is assumed to be constant. Substituting

$$k'_a = k_a[O_2^*] \tag{3}$$

and rearranging, we have

$$k_d/k'_a = [D]/[DO_2], \tag{4}$$

where the right side shows a measurable quantity. k_a can also be represented by the following Arrhenium formula with the frequency factor (A_a) and activation energy (E_a),

$$k_a = A_a \exp(-E_a/RT). \tag{5}$$

Substituting Eqs. 1, 3, and 5 into Eq. 4, and carrying out some elementary calculations, we find that

$$[D]/[DO_2] = (A_d/A'_a)\exp\{-(E_d - E_a)/RT\}, \tag{6}$$

where $A'_a = A_a[O_2^*]$. Taking the logarithm of the both sides,

$$\ln([D]/[DO_2]) = \ln(A_d/A'_a) - (E_d - E_a)/RT, \tag{7}$$

that is, $\ln([D]/[DO_2])$ should be a linear function of T^{-1}. The results are shown in Fig. 5. As was expected, a straight line can be drawn; this supports the validity of the assumption that $[O_2^*]$ is constant. The slope of the straight line gives $E_d - E_a = 73.8 \pm 3.0$ kJ mol^{-1}. Therefore, $E_a = 10.0 \pm 5.5$ kJ mol^{-1}. It is noted that A'_a is determined to be 2.2×10^{-2} s^{-1} from the intercept. However, $[O_2^*]$ is necessary to obtain the frequency factor for k_a. The E_a value is compatible with one of the general findings concerning the O_2 attachment to PAHs, that O_2^* undergoes 1,4-cycloaddition to PAHs with low activation energy (say about 20 kJ mol^{-1}) because a ground state PAH and O_2^* correlate directly to the endo-peroxide (see Fig. 6).[10]

State Correlation Diagram. The relative energy of the ground state of ODPP is determined from

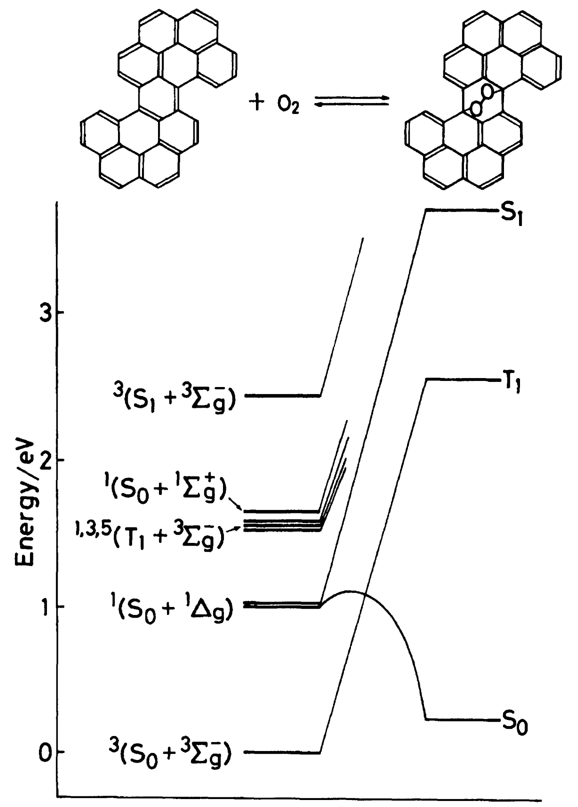

Fig. 6. State correlation diagram depicting the photooxygenation of DPP and thermal deoxygenation of the photooxygenation product (ODPP). The relative energies of the states were estimated from a complete neglect of differential overlap (CNDO/S) and configuration interaction (CI) calculation and the activation energies for both the reactions of O_2 attachment and detachment. S_i and T_i denote the singlet and triplet energy levels of DPP or ODPP, and the notation of $^1(S_0 + ^1\Delta_g)$ means a singlet state of a complex of DPP(S_0) and $O_2(^1\Delta_g)$.

the activation energies. Since the activation energy for the reaction of DPP and O_2^* is 10 kJ mol^{-1} and O_2^* lies 98 kJ mol^{-1} higher than O_2,$^{11)}$ we can locate the transition state for the reaction at 108 kJ mol^{-1} above DPP+O_2. The activation energy for ODPP→DPP+O_2 is 84 kJ mol^{-1}. If the O_2 attachment and detachment reactions are related by microscopic reversibility, like in the case of 9,10-diphenylanthracene,$^{8)}$ they share a common transition state. Therefore, the energy of ODPP is 24 kJ mol^{-1} higher than that of DPP+O_2 (see Fig. 6).

If the transition state is assumed to have C_2 symmetry, the state correlation diagram, which illustrates that photooxygenation of DPP and thermal deoxygenation of ODPP, is obtained, as shown in Fig. 6.$^{10)}$ From the diagram, the DPP+O_2 state is found to correlate with the lowest triplet state of ODPP, and the DPP+O_2^* state correlates directly with the ODPP ground state, indicating that the reaction DPP+O_2^*→ODPP is spin allowed.

Quantum Yield. We measured the overall quantum yield of the present photooxygenation upon irradiation of a benzene solution (1×10^{-5} M) by 510 nm light under atmospheric pressure. For 30 min of irradiation the solution absorbed 2.18×10^{19} photons and 1.57×10^{16} molecules of DPP were photooxygenated. Therefore, the quantum yield was 7.2×10^{-4}. This value is about 50-times smaller than that for DBP, 3.3×10^{-2} for 7.2×10^{-6} M.$^{5)}$ The quantum yield of photooxygenation might be affected by the efficiency of O_2^* production by a sensitized energy transfer and the activation energy for O_2 attachment. To account for the large difference in the quantum yield between DPP and DBP, we are now calculating the excited states of both molecules and the transition states in their photooxygenation reaction using molecular-orbital methods.

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