Photocyclization of [2.2]Metacyclophane at 2537 Å[1)]

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The photochemical reaction of [2.2]metacyclophane at 2537 Å has been studied spectrophotometrically. Photocyclization took place to give 4,5,9,10-tetrahydropyrene not only in aerated but also in degassed solutions. The quantum yields for the reaction were independent of the irradiation time, concentration of starting material, light intensity, and addition of piperylene. However, the reaction quantum yields increased with temperature rise. The quantum yields in the aerated system were somewhat larger than those in the degassed system. Radiationless deactivation in $S_1(\pi\pi^*)$ was very efficient, whose quantum yield was assumed to be ~0.99, judging from the small reaction quantum yield (less than 0.01) and the lack of fluorescence and phosphorescence. It is proposed that the photocyclization of the molecule originates from $S_1(\pi\pi^*)$ to give intermediate M which is subsequently convreted into the product or the starting material. Activation energies in these processes were estimated.

The photochemical behavior of [2.2]metacyclophane (MCP) is of interest from the viewpoint of the interaction between the two benzene rings adjacent to each other.[3)] The transannular interaction would affect the photochemical and photophysical processes in MCP. In the case of [2.2]paracyclophane, the intramolecular excimer formation (the excimer fluorescence at 3350 Å)[4)] and the photochemical cleavage[5)] have been reported. The photochemical reactions of MCP in the presence of iodine have been carried out by Sato *et al.*[6,7)] and Hayashi and Sato[7)] who proposed that the photocyclization of MCP proceeds *via* the CT-complex formation between MCP and I_2. However, no photochemical reaction of MCP without oxidant has been reported.

The photocyclizations of compounds such as *cis*-stilbene[8,9)] and diphenylamines[10—14)] have been carried out. The bond formation between the proper atoms takes place *via* the lowest excited singlet state $S_1(\pi\pi^*)$ for the former[8,9)] and *via* the lowest triplet state $T_1(\pi\pi^*)$ for the latter,[11,13)] the intermediate with the central two hydrogen atoms having *trans*- and *cis*-form, respectively, being produced. The photocyclization of the former needs an oxidant such as oxygen. However, the reaction of the latter proceeds with and without oxygen.

This paper reports the photochemical reaction of MCP in degassed and aerated solutions in detail.

Experimental

[2.2]Metacyclophane (MCP) was supplied by Dr. T. Sato of Tokyo Metropolitan University. The starting material, after sublimation, was purified by column chromatography (Al_2O_3 and *n*-hexane) and by repeated recrystallizations. Cyclohexane and methylcyclohexane (G. R. grade, Tokyo Kasei Co., Ltd.) were purified by passing through silica gel column and by distillation. 4,5,9,10-Tetrahydropyrene (4HP) was prepared by the irradiation of MCP solution at 2537 Å and purified by column chromatography and repeated recrystallizations. 4HP was identified by means of NMR, IR, UV, mp and elemental analyses.

A low pressure mercury lamp with a Vycor glass filter was used as the 2537 Å radiation source. A xenon lamp, equipped with a diffraction grating, was used as the 2800 Å radiation source. Actinometry was carried out using a ferric oxalate solution.[15)] The quantum yields for the reaction were performed by spectrophotometry. No difference in quantum yield was observed at 20 °C for cyclohexane and methylcyclohexane. Thus methylcyclohexane was used in the temperature range 213—288 K. For the measurement of temperature effect on the quantum yield, a quartz Dewar flask designed for spectrometry was used as a reaction cell which controlled the temperature to within ±2 °C. In the measurements on degassed samples, the solutions were thoroughly degassed on a high-vacuum line by the freeze-pump-thaw-method. Emission spectra were measured with a Hitachi MPF-2 spectrofluorimeter. The conventional μ-s flash apparatus described previously[16)] was used.

Results

Figure 1(a) shows the spectral change of cyclohexane solution of [2.2]metacyclophane (MCP) during the course of photolysis at 2537 Å at 20 °C in the degassed system. This change indicates that the reaction product was 4,5,9,10-tetrahydropyrene (4HP). The photoproduct was identified by means of NMR, IR, UV, mp, and elemental analyses.[17)] The spectral change of the aerated solution of MCP was similar to that in the degassed system (Fig. 2). However, after long irradiation, a new absorption band appeared in the 320—335 nm range in the aerated system. The

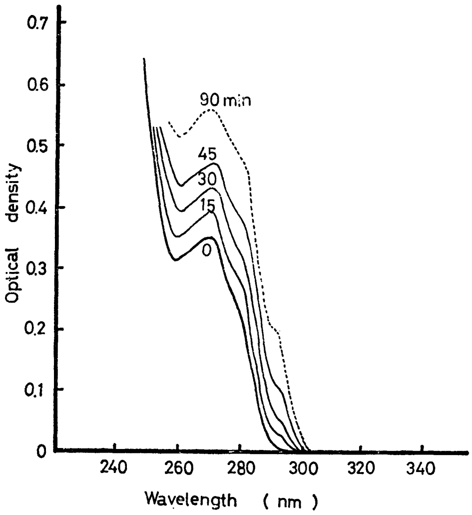

Fig. 1(a). Spectral change of MCP in degassed cyclohexane at 2537 Å and 20 °C. Numbers refer to time at measurement in minutes.

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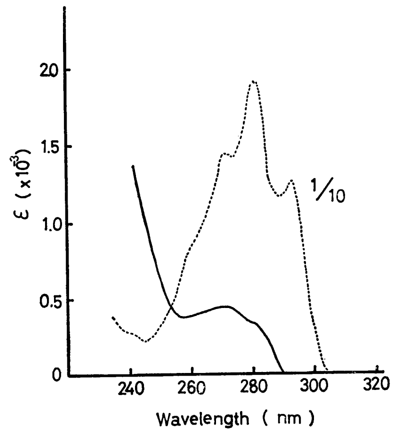


Fig. 1(b). UV absorption spectra of MCP and the photoproduct (4HP) in cyclohexane: line and broken line denote those in MCP and 4HP, respectively.

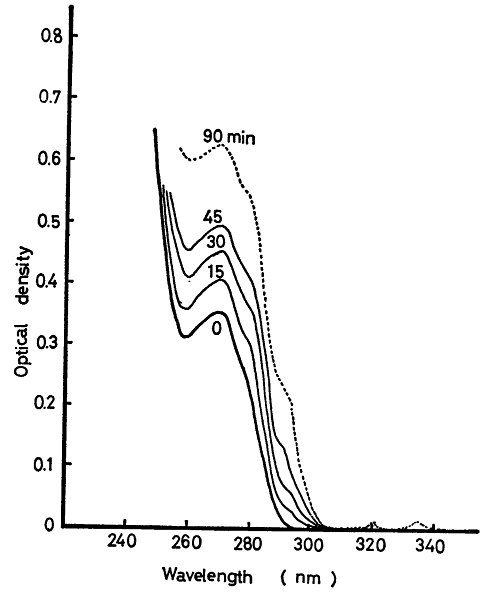


Fig. 2. Spectral change of MCP in aerated cyclohexane at 2537 Å and 20 °C.

band was assigned to that of pyrene, which was photochemically produced in the aerated solution.[17]

The molar extinction coefficients of MCP and 4HP in cyclohexane are given in Table 1. The quantum yields for the photocyclization of MCP were measured from the increase in the optical density at 293 nm, where there is a characteristic absorption band in the product. The quantum yields for the reaction were measured under various conditions at 20 °C. The results are shown in Fig. 3. The quantum yields for the product formation in cyclohexane at 2537 Å did not change with irradiation time (≤40 min), initial concentration of the starting material ($\leq 3\times10^{-2}$ M), light intensity (10^{14}—10^{15} photons s^{-1} ml^{-1}), and addition of piperylene as a triplet quencher ($\leq 7\times10^{-3}$ M). The quantum yields in degassed and aerated solutions at 2537 Å and 20 °C were $(1.7\pm0.2)\times10^{-3}$ and $(2.3\pm0.2)\times10^{-3}$, respectively. No wavelength effect on the reaction quantum yields at 2537 nad 2800 Å at 20 °C in cyclohexane was observed, but the temperature effect was significant, as shown in Fig. 4. The quantum yields in degassed and aerated conditions increased with temperature rise. A similar tendency to the temperature effect on the yields was observed both in

TABLE 1. MOLAR EXTINCTION COEFFICIENTS OF MCP AND 4HP IN CYCLOHEXANE AT 20 °C

Compound	λ_{max} (nm)	ε ($M^{-1}\,cm^{-1}$)
MCP	272	4.4×10^2
4HP	271	1.46×10^4
	281	1.80×10^4
	293	1.30×10^4

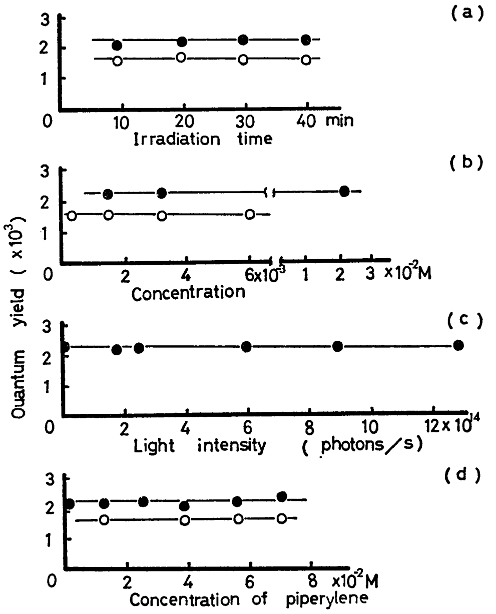


Fig. 3. Dependence of quantum yield for the product formation in cyclohexane at 2537 Å and 20 °C.
(a) On irradiation time with initial concentration of 3.2×10^{-3} M. (b) On concentration of MCP. (c) On light intensity. (d) On addition of piperylene.
○: in degassed cyclohexane. ●: in aerated cyclohexane.

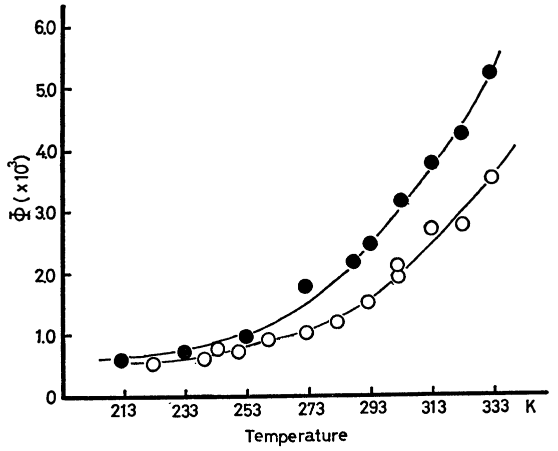


Fig. 4. Dependence of the reaction quantum yield on temperature.
○: in degassed condition, ●: in aerated condition.

degassed and aerated solutions. Although the quantum yields for product formation were very small ($\leq 10^{-2}$) as shown in Fig. 4, neither fluorescence in cyclohexane at 20 °C nor phosphorescence in a MP matrix at 77 K was observed. The long-lived intermediate could not be observed by means of conventional μs flash photolysis.

Discussion

The photocyclization of MCP in the degassed system is an intramolecular reaction, since no concentration effect of the starting matrial was observed on the quantum yields (Fig. 3b). The possibility for the charge transfer formation between MCP and dissolved oxygen in the ground state is unlikely, judging from their UV spectra and the concentration effect on the quantum yields. It seems that the photocyclization originates from the lowest excited singlet state $S_1(\pi\pi^*)$, since the addition of piperylene as a triplet quencher ($E_T=2.48$ eV) did not affect the quantum yields in the concentration range $10^{-4}-7\times10^{-3}$ M (Fig. 3d), dissolved oxygen (2.3×10^{-3} M)[14] increased the quantum yields for the reaction compared with those in the absence of oxygen (Figs. 3 and 4), and no excitation wavelength was observed on the yields.

The experimental results can be accounted for the following scheme, which is simplified in the processes of internal conversion and intersystem crossing.

$$S_0 + h\nu \longrightarrow S_1 \tag{0}$$

$$S_1 \longrightarrow S_0 \tag{1}$$

$$S_1 + O_2 \longrightarrow S_0 + O_2 \tag{1q}$$

$$S_1 \longrightarrow M \tag{2}$$

$$M \longrightarrow P + (H_2) \tag{3}$$

$$M \longrightarrow S_0 \tag{4}$$

$$M + O_2 \longrightarrow P + (HO_2,\ H_2O_2) \tag{5}$$

where S_0 and S_1 are the ground and the lowest excited singlet states of MCP, respectively, M is the intermediate and P is the photoproduct (4HP). The quantum yields for the product formation Φ_0 and Φ in degassed and aerated conditions, respectively, can be expressed by the following equations, using the steady-state approximation.

$$\Phi_0 = \frac{k_2}{k_1+k_2}\cdot\frac{k_3}{k_3+k_4} \tag{6}$$

and

$$\Phi = \frac{k_2}{k_1+k_{1q}[O_2]+k_2}\cdot\frac{k_3+k_5[O_2]}{k_3+k_4+k_5[O_2]} \tag{7}$$

where $k_1 \gg k_2+k_{1q}[O_2]$, because of very small quantum yields for the reaction ($<10^{-2}$) and the lack of fluorescence and phosphorescence. From Eqs. (6) and (7), we obtain

$$\frac{\Phi}{\Phi_0} = \left(1+\frac{k_4}{k_3}\right)\left(\frac{k_3+k_5[O_2]}{k_3+k_4+k_5[O_2]}\right) \tag{8}$$

If $k_3+k_5[O_2] \gg k_4$, we have

$$\frac{\Phi-\Phi_0}{\Phi_0} = \frac{k_4}{k_3} \tag{9}$$

If the rate constants k_3 and k_4 have activation energies E_3 and E_4 and frequency factors A_3 and A_4 respectively, we get the following equation from (9).

$$\log\left(\frac{\Phi-\Phi_0}{\Phi_0}\right) = \log\left(\frac{A_4}{A_3}\right) - \frac{E_4-E_3}{2.3RT} \tag{10}$$

We have no exact data of the E_3 value. However, the value of the activation energy E_3 in the molecular dehydrogenation process is assumed to be smaller than that of E_4, considering a similar process in diphenylamines.[14] Figure 5 shows the plot of $\log\{(\Phi-\Phi_0)/\Phi_0\}$ as a function of T^{-1}. The reason why the plot is bent at about 285 K (Fig. 5) is due to the fact that the relation $k_3+k_5[O_2] \gg k_4$ does not hold at temperatures higher than 285 K where the value of k_4 becomes appreciable in comparison with that of k_3 and $k_5[O_2]$. From the slope of the plot ($T \leq 285$ K) in Fig. 5, we obtain $E_4=E_3+4$ kcal/mol.

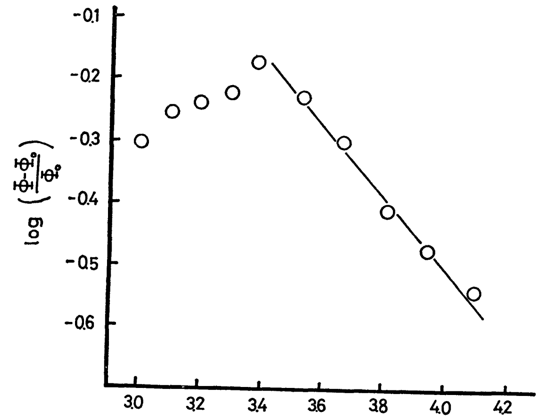


Fig. 5. Plot of $\log\{(\Phi-\Phi_0)/\Phi_0\}$ *vs.* T^{-1}

In the low temperature range ($213 \leq T \leq 285$ K), Eq. (7) is simplified as

$$\Phi = \frac{k_2}{k_1} \tag{7'}$$

If the rate constant k_2 has an activation energy E_2 and frequency factor A_2, and the value of k_1 is almost constant in the temperatures ($213 \leq T \leq 285$ K), we obtain the following equation from Eq. 7′.

$$\log \Phi = \log\left(\frac{A_2}{k_1}\right) - \frac{E_2}{2.3RT} \tag{11}$$

Figure 6 shows the plots of $\log \Phi$ *vs.* T^{-1} and of $\log \Phi_0$ *vs.* T^{-1}.

From the slope of the plots, the value of E_2 can be estimated to be about 2 kcal mol^{-1} both in aerated and degassed solutions. This indicates that $k_3 \gg k_4$ in Eq. (6) at low temperatures, and the values of the quantum yields Φ in the aerated system become close to those in the degassed system with the fall of temperature (Fig. 4). Activation energy E_2 in the ring clousre process from S_1 to M is almost the same as that of *cis*-stilbene (2.6 kcal mol^{-1}).[9] MCP undergoes photocyclization to give the cyclized product even in the degassed system. However, in the case of *cis*-stilbene, dissolved oxidant is necessary to yield to corresponding photoproduct. The difference in their reactivities might be due to the intermediate structure: whether the *cis*-form or the *trans*-form of the two central hydrogen atoms in the intermediate would control the mole-

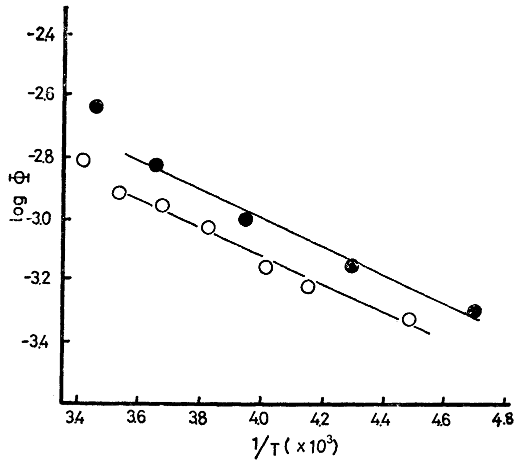
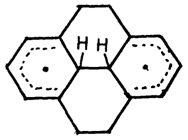


Fig. 6. Plot of $\log \Phi$ (or $\log \Phi_0$) *vs.* T^{-1}
○: $\log \Phi_0$, ●: $\log \Phi$.

cular dehydrogenation process (Eq. (3)). If the intermediate has a *cis*-form, it will thermally split into a cyclized product plus a hydrogen molecule. The photocyclization of MCP corresponds to this case, although we could not observe any transient by means of the conventional μs flash photolysis. It seems that the following structure is probable for the intermediate M.



M

Radiationless deactivation (Eq. 1) is the main process in the excited singlet state of MCP, whose quantum yield is assumed to be ~0.99, on the basis of very low quantum yields for the product formation (>0.01) and the lack of fluorescence and phosphorescence. A small π-electronic interaction between the two benzene rings in the ground state is known, since the lowest transition in the molecule (λ_{max} 272 nm, $\varepsilon=4.4\times10^2$) corresponds to the $^1B_{2u}\leftarrow{}^1A_{1g}$ transition in benzene (λ_{max} 256 nm, $\varepsilon=2.2\times10^2$). It is obvious that the transannular interaction due to the proximity of two benzene rings in MCP causes the large radiationless deactivation and the very small ring-closure in the $S_1(\pi\pi^*)$ state. One explanation for the large deactivation is that the molecular structure of MCP probably promotes the internal conversion in Eq. (1), due to the vibronic coupling between S_1 and S_0 states. Another possibility is that a chemical energy wasting process such as reversible isomerization might be involved in Eq. 1, and responsible for the radiationless deactivation in S_1. The lifetime of S_1 is very short judging from the present results. A similar large radiationless deactivation is known in the case of biphenylene. Lack of photoluminescence of biphenylene has been observed,[18] the first singlet excited state being responsible for the main nonradiative channel on the basis of its lifetime (~10 ps).[19]

The abnormal shifts in the UV spectrum of [2.2] paracyclophane shows a large π-electronic interaction between the parallel planes of two benzene rings in the molecule.[20] An excimer fluorescence in [2.2]paracyclophane at 3550 Å indicates the charge transfer interaction in the emitting state.[4] The photochemical ring-opening reactions of [2.2]paracyclophane take place, which depend upon the excitation wavelengths.[5] The electronic and steric features in these isomers would cause the difference in photochemical and photophysical processes.

The proposed mechanism of the photocyclization of MCP in degassed and aerated cyclohexane is shown in Eqs. 0—5.

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