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Steady-Light Irradiation and Flash Photolysis Studies of [2.2]Metacyclophane-Iodine Systems. Mechanistic Implications of Transannular Dehydrogenation Reaction

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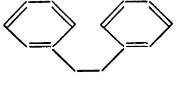
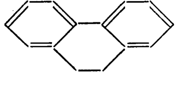
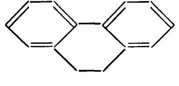
Irradiation of cyclohexane solutions of [2.2]metacyclophane in the presence of iodine is shown to yield 4,5,-9,10-tetrahydropyrene as the initial product. In order to clarify the mechanism of the cyclodehydrogenation reaction, steady-light irradiation, and flash photolysis experiments have been carried out. The rate of formation of 4,5,9,10-tetrahydropyrene is followed by UV spectra measurements using a characteristic band maximum at 292 nm. The rate of appearance of 4,5,9,10-tetrahydropyrene is found to be proportional to the absorption of light. The reaction is a one photon process. The reaction rate is almost constant when the concentration of iodine is less than 7×10^{-4} mol/*l*, but decreases gradually with higher concentrations. A long-lived species, whether radical or excited triplet, can not be detected by flash techniques. It is most likely that the first step involves the excited singlet. Involvement of CT-complex is proposed.

Due to the proximity of two benzene rings, [2.2]-metacyclophane (MCP) shows transannular interaction which causes spectral anomalies and results in transannular reactions to give pyrene derivatives.[2] Spectral studies of the charge transfer complexes involving TCNE and other electron acceptors were reported.[3]

Sato *et al.* reported on a photochemical transannular reaction of MCP induced by iodine.[4] Examination of the photoreaction using a high-pressure mercury lamp gave the following results:[5] a) Irradiation of degassed MCP-I_2-cyclohexane solutions results in a spectral change indicative of the formation of 4,5,9,10-tetrahydropyrene (4HP), which can be isolated in a fair yield. b) When photolysis is continued, further dehydrogenation occurs to give 4,5-dihydropyrene (2HP) and pyrene. c) No appreciable reaction occurs when the solution is photolyzed in air in the absence of iodine. d) Besides an oxidant, iodine appears to play a special role in the photoreaction. e) A light source with 253.7 nm line is the most effective one.


MCP


4HP


2HP

A mechanistic study of the transannular reaction is especially attractive in comparison with the related photocyclization reactions such as the formation of phenanthrene from *cis*-stilbene,[6] photolytic cleavage of [2.2]paracyclophane,[7] and photoequilibrium in certain metacyclophane compounds.[8]

In order to reveal the initial stage of the reaction, to account for acceleration of the reaction with iodine and to provide mechanistic implications, this paper records spectral studies under steady-light conditions and flash photolysis experiments.

Experimental

Materials and Procedures. [2.2]Metacyclophane (MCP)[9,10] was purified by combining recrystallization and column chromatography. 4,5,9,10-Tetrahydropyrene (4HP) and 4,5-dihydropyrene (2HP) were recrystallized three times from ethanol and sublimed. Cyclohexane (Wako Junyaku G.R. grade) was purified by the ordinary method. Purity was confirmed by UV spectrum and gas chromatography. Apparatus similar to that reported[11] was used for the steady-light illumination. The light source is a Ushio U12-1E low pressure mercury lamp operating at 100 V, supplied through a voltage stabilizer. The reaction temperature was 30°C. The sample solutions were degassed 7—8 times by the freeze-pump-thaw method ***in vacuo*** (the degassed solution). Aerated solutions were also used. At various time intervals, the sample cell was taken out and the absorption spectra were measured with a Hitachi EPU-2A spectrophotometer or a Shimadzu RM autorecording spectrophotometer. The effect of wavelength on the quantum yields was studied by choosing monochromatic light selected from a Toshiba SHL-100UV mercury lamp with a suitable

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[1] Photochemistry of [2.2]Metacyclophanes, Part II, for Part I see Ref. 3. Photo-Aryl Coupling and Related Reactions. X: Part IX, T. Sato, K. Nishiyama, S. Shimada, and K. Hata, This Bulletin, **44**, 2858 (1971).

[2] Reviews: R. W. Griffin, Jr., *Chem. Rev.*, **63**, 45 (1963); T. Sato, *Kagaku no Ryoiki*, **23**, 672, 765 (1969); T. Sato, *Nippon Kagaku Zasshi*, **92**, 277 (1971).

[3] S. Hayashi, and T. Sato, *Nippon Kagaku Zasshi*, **91**, 950 (1970).

[4] T. Sato, E. Yamada, Y. Okamura, T. Amada, and K. Hata, This Bulletin, **38**, 1049 (1965).

[5] T. Sato, M. Wakabayashi, S. Hayashi, and K. Hata, *ibid.*, **42**, 773 (1969).

[6] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **84**, 4361 (1962); *ibid.*, **85**, 828 (1963); *ibid.*, **86**, 3094 (1964). N. J. Turro, "Molecular Photochemistry," W. A. Benjamin. Inc., New York (1965), p. 234; F. R. Stermitz in O. L. Chapman ed., "Organic Photochemistry," Vol. 1, Mercel Dekker Inc., New York (1967), p. 249.

[7] R. C. Helgeson and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 509 (1966).

[8] H. R-Blattman, D. Menche, E. Heilbronner, R. J. Molyneus, and V. Boekelheide, *ibid.*, **87**, 130 (1965).

[9] M. Fujimoto, T. Sato, and K. Hata, This Bulletin, **40**, 600 (1967).

[10] S. Akabori, T. Sato, and K. Hata, *J. Org. Chem.*, **33**, 3277 (1968); T. Sato, S. Akabori, S. Muto, and K. Hata, *Tetrahedron*, **24**, 5557 (1968).

[11] M. Koizumi, H. Obata, and S. Hayashi, This Bulletin, **37**, 108 (1964).

combination of Hoya or Toshiba glass filters, an aqueous solution of nickel sulfate (100 g/300 m*l*, 1 cm) and an interference filter. The quantity of light absorption was measured by a potassium ferrioxalate actinometer,[12] or a calibrated Kipp & Zonen thermopile and a Shimadzu K-2 potentiometer.

Main xenon flash lamp (96J, duration time of 15 μsec) of the flash photolysis apparatus was followed by a second flash after 50 μsec and the transmitted light, after being passed through a Nalumi RM spectrography/monochromator, was led to a dry-plate. Alternatively, transmitted light was received by a Hamamatu photomultiplier and observed with the aid of an Iwasaki oscilloscope.

Results and Discussion

Steady Light Experiments. *General Features of the Photooxidation*: A spectral change occurs when a degassed MCP-I_2-cyclohexane solution is irradiated using 253.7 nm light as shown in Fig. 2. When irradiation is continued new maxima appear at 260, 268, 280, 292, 320, and 334 nm, which are ascribed to 4HP (see Fig. 1). The structure of 4HP was confirmed by IR and NMR spectra, and by direct comparison with the authentic material. The formation of 4HP is almost quantitative.

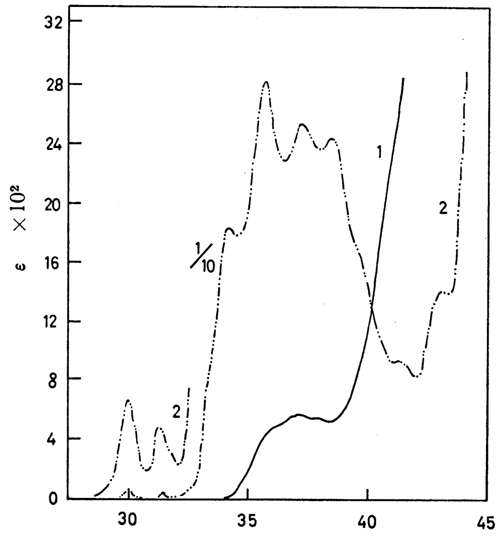

Fig. 1. Absorption spectra in cyclohexane.
(1): [2.2]Metacyclophane,
(2): 4, 5, 9, 10-Tetrahydropyrene.

On further irradiation, 4HP is converted in to 2HP and eventually to pyrene.[5] The reaction occurs successively. The secondary dehydrogenation steps are, however, much slower than the formation of 4HP from MCP and can be neglected. No thermal reactions occur with dilute solution. The transannular bonding is possible only under photolytic conditions.

An absorption maximum due to iodine, occurring at 525 nm diminished during the course of irradiation (Fig. 2). Conversion of iodine to hydrogen iodine could be inferred, but attempts to characterize it failed.

Quantum yields of the reaction are summarized in Table 1. The results indicate that the most efficient

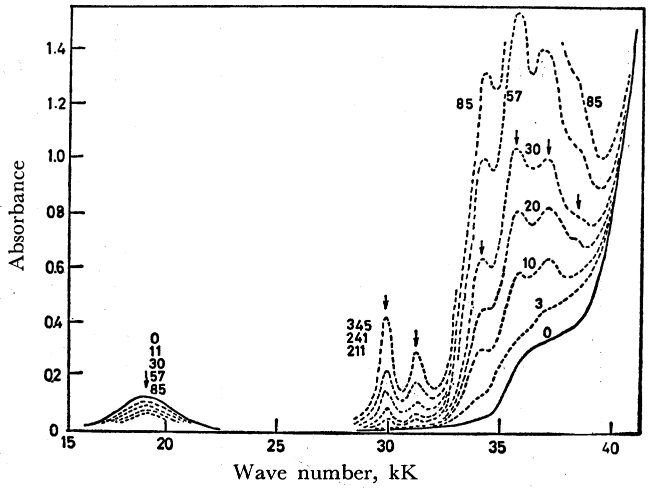

Fig. 2. Change of absorption spectra of the mixed solution of [2.2]metacyclophane and iodine by UV-irradiation (degassed cyclohexane solution).
[MCP]: 5.1×10^{-4}mol/*l*, [I_2]: 1.44×10^{-4}mol/*l*
Numbers denote the time of illumination (min).

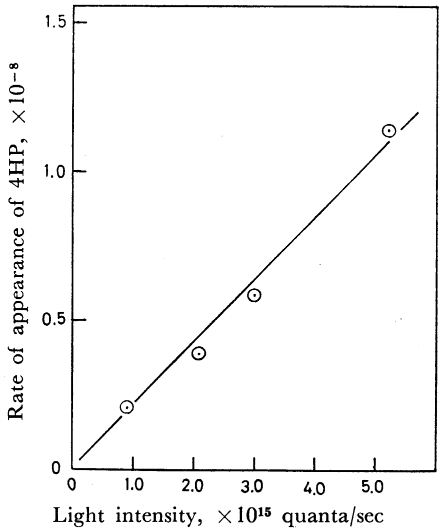

Fig. 3. Effect of the incident light intensity on the rate of appearance of 4HP.

Table 1. The quantum yield
[MCP]: 5.5×10^{-4} M; [I_2]: 1.6×10^{-4} M

Exciting light, nm	Quantum yield
253.7	6.2×10^{-3}
296.7, 280.2	
302.2—302.8	5.3×10^{-3}
312.6—313.2	
546.1	
577.0—579.0	0
No Filter	5.5×10^{-3}

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[12] C. A. Parker, *Proc. Roy. Soc.* (London), **220A**, 104 (1953).

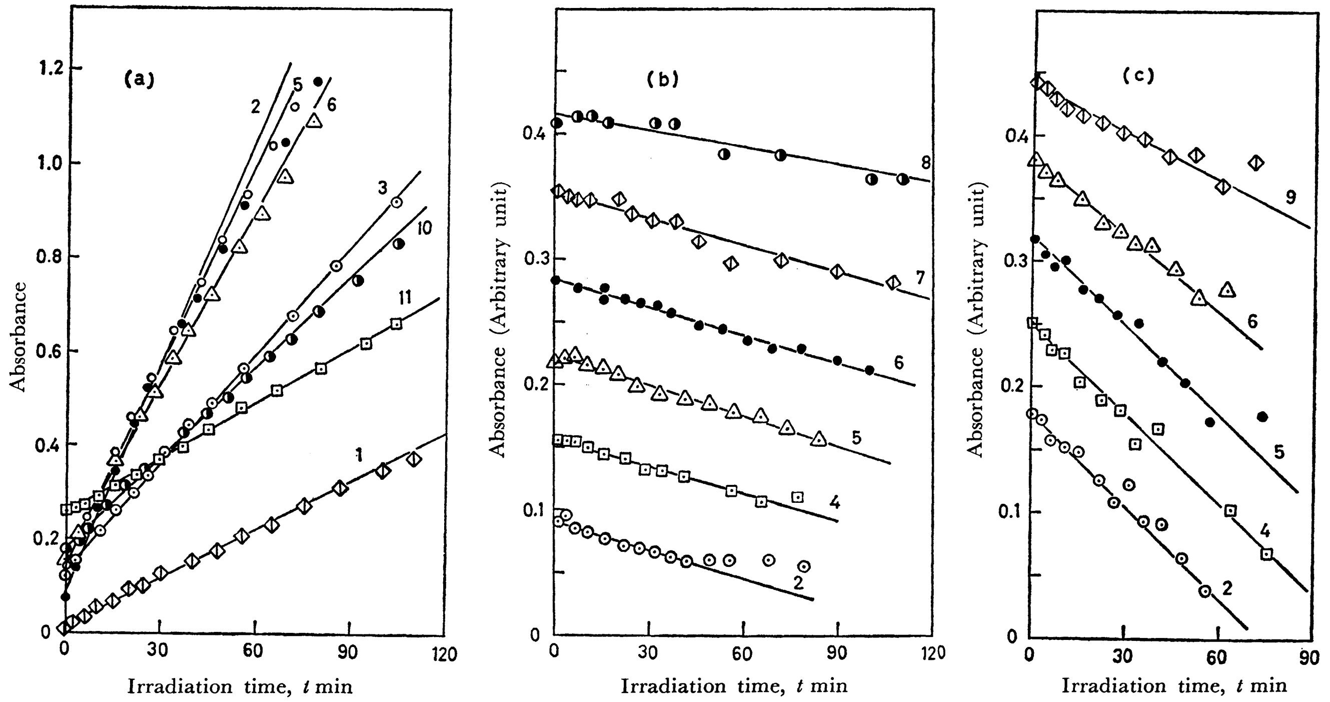

Fig. 4. Effect of iodine initial concentration.
a): Absorbance at 292 nm *vs.* t plot. b): Absorbance at 520 nm *vs.* t plot. c): Absorbance at 272 nm *vs.* t plot.
[MCP]: 5.1×10^{-4} mol/l
[I$_2$]: 1) 0 4) 3.26 7) 10.5 10) 17.6
2) 0.99×10^{-4} mol/l 5) 4.31 8) 11.5 11) 25.0
3) 1.05 6) 6.46 9) 13.5

light is 253.7 nm line. Excitation of iodine absorption in the visible region using a 500 W tungsten lamp was not effective. The experiments described hereafter were carried out with a low pressure lamp. The reaction rate was determined by UV spectra following absorbance changes at 292 nm with appropriate time intervals.[13]

Effect of Light Intensity: A satisfactory linear correlation was obtained from plots absorbance *vs.* t at the initial stage. We see from Fig. 3 that the rate of appearance of 4HP (evaluated from the initial slope of the run for reaction) is proportional to light intensity. The main reaction is a one photon process.

Effect of Initial Iodine Concentration on the Rate: Since absorbing species at 253.7 nm are MCP, 4HP, and iodine, the light absorption can be expressed as follows.

$$\begin{aligned} I_{\rm abs} &= (I_0/d)(1-\exp(-2.303dD_t)) \times 10^3 \\ D_t &= \varepsilon_{\rm MCP}C_{\rm MCP} + \varepsilon_{\rm I}C_{\rm I} + \varepsilon_{\rm 4HP}C_{\rm 4HP} \end{aligned} \qquad (1)$$

In the present studies, however, the conversion of MCP does not exceed 15%. For treatment of the initial stage of the reactions the term due to 4HP can be neglected.

$$\begin{aligned} I_{\rm abs} &= (I_0/d)(1-\exp(-2.303d(\varepsilon_{\rm MCP}C_{\rm MCP}+\varepsilon_{\rm I}C_{\rm I}))) \times 10^3 \\ &= 2.303I_0(\varepsilon_{\rm MCP}C_{\rm MCP}+\varepsilon_{\rm I}C_{\rm I}) \times 10^3 \qquad (2) \end{aligned}$$

where $C_{\rm MCP}$, $C_{\rm I}$, $C_{\rm 4HP}$, $\varepsilon_{\rm MCP}$, $\varepsilon_{\rm I}$, and $\varepsilon_{\rm 4HP}$ represent concentration and molar absorptivity of MCP, iodine, and 4HP, I_0 and d are light intensity and sample path length, respectively. Molar absorptivity of 4HP is more than ten times that of MCP and iodine, and would cause inner filter effects but only at a later stage. Assuming that only MCP takes part in reaction and that the rate of disappearance is proportional to light absorption, the following formula is obtained.

$$\begin{aligned} -\frac{{\rm d}C_{\rm MCP}}{{\rm d}t} &= \frac{{\rm d}C_{\rm 4HP}}{{\rm d}t} = kI_{\rm abs}\frac{\varepsilon_{\rm MCP}C_{\rm MCP}}{\varepsilon_{\rm MCP}C_{\rm MCP}+\varepsilon_{\rm I}C_{\rm I}} \\ C_{\rm 4HP} &= 2303kI_0\varepsilon_{\rm MCP}C_{\rm MCP}t = k_{\rm 4HP}t \qquad (3) \end{aligned}$$

Eq. (3) indicates that the formation of 4HP is proportional to the reaction time. This was satisfied experimentally (Fig. 4-a).

The reaction rate changes with iodine concentration[5]. For the sake of quantitative study, reaction mixtures with various iodine concentration were subjected to photolytic reaction. A good linear relationship was observed between $C_{\rm 4HP}$ and reaction time (t) for several sets of mixtures (Fig. 4-a), although at very low iodine concentration some discrepancies were found except for the initial stage of the reaction. The rate of formation of 4HP($k_{\rm 4HP}$) can be calculated from the slope.

At 253.7 nm iodine behaves also as an absorbing species and its decay being observed. Cleavage of iodine to radicals $I_2 \rightarrow 2I\cdot$ occurs, making it an attacking species. The relation between iodine concentration and rate of 4HP formation is shown in Fig. 5. When iodine concentration exceeds 7×10^{-4} mol/l, the reaction rate decreases gradually, possibly due to an innerfilter

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[13] At 292 nm, $\varepsilon_3 \gg \varepsilon_1$, ε_2, $\varepsilon_1+\varepsilon_2$, where ε_1, ε_2, and ε_3 are molar absorptivities for MCP, I$_2$, and 4HP, respectively. Therefore, absorbance increase in this region is assumed to be due to 4HP.

effect of iodine. This indicates that the following scheme is not the sole path.

$$\left.\begin{array}{l} I_2 \xrightarrow{h\nu} I_2^* \rightarrow 2I\cdot \\ MCP + 2I\cdot \rightarrow 4HP + 2HI \end{array}\right\} \qquad (4)$$

The fact that the dehydrogenation reaction proceeds with a significant rate even at very low iodine concentration ($<7\times10^{-4}$ mol/l) suggests two possibilities involving either a CT-complex between MCP and iodine or a rather long-lived intermediate subjected to iodine attack. For the latter case MCP can be excited to a triplet state, which may undergo electron and proton transfer reactions

$$\left.\begin{array}{l} MCP^* + I_2 \rightarrow MCP^+ + I_2^- \\ MCP^+ + I_2^- \rightarrow 4HP + 2HI \end{array}\right\} \qquad (5)$$

From flash photolysis experiments, however, such species could not be detected.

The rate of disappearance of iodine (k_I) determined at 525 nm also depends on the initial iodine concentration, as for k_{4HP}. Decrease of MCP leads to 4HP formation. The rate is in a complimentary relation (Fig. 4-b, Fig. 5).

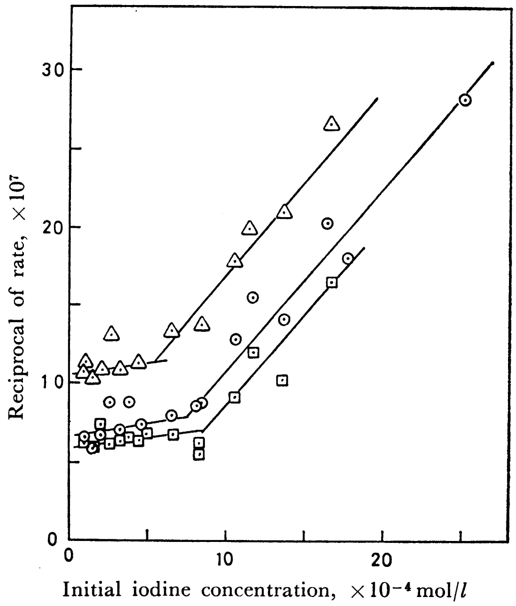

Fig. 5. Reaction rates (k_{4HP}, k_{MCP}, k_I) *vs.* initial iodine concentration plot.
⊙: 4HP, △: MCP, ⊡: Iodine

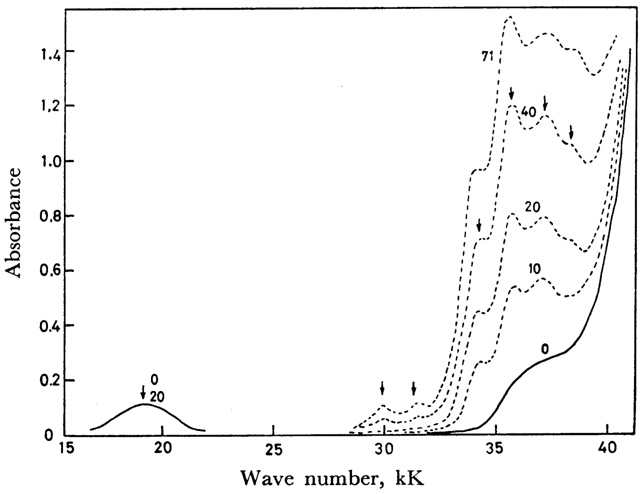

Fig. 6. Spectral change when the MCP containing iodine in the aerated solution was irradiated by 253.7 nm.
[MCP]: 5.1×10^{-4} mol/l, [I_2]: 1.4×10^{-4} mol/l
Numbers denote the time of illumination (min).

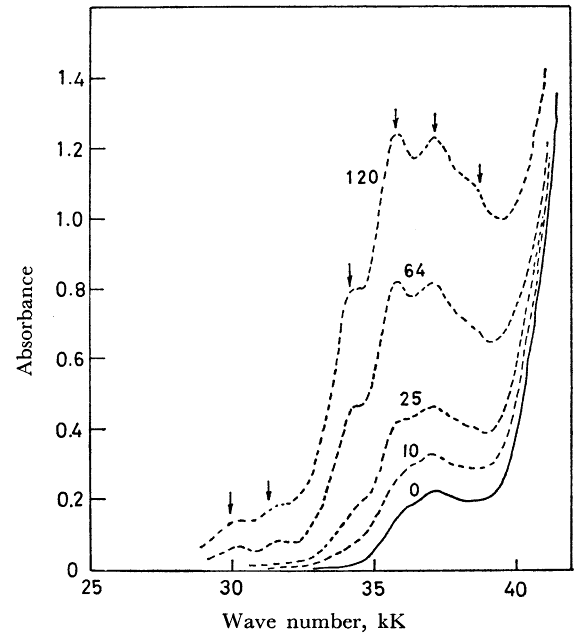

Fig. 7. Change of absorption spectra of MCP by UV-Irradiation (aerated cyclohexane solution).
[MCP]: 5.0×10^{-4} mol/l
Numbers denote the time of illumination (min).

Spectral changes observed by illuminating an aerated MCP-I_2-cyclohexane system are shown in Fig. 6. Recently, Sorimachi, Shizuka, and Morita[14] reported that the photolytic reaction of MCP to 4HP occurred in the absence of iodine. Photodehydrogenation with oxygen is, however, much slower than with iodine. Even slower rate of reaction was observable with degassed cyclohexane solutions (Fig. 7). Although the ability of hydrogen abstraction in *cis*-stilbene-phenanthrene reactions is considered to be in the order $I\cdot > O_2 > I_2$,[6] it does not hold in the present case. This suggests that an essentially different mechanism is involved in the photolytic reaction of MCP. Irradiation of *cis*-stilbene gives 4*a*,4*b*-dihydrophenanthrene in a reversible process, which in the dark reaction is oxidized by an added oxidant. On the other hand MCP is subjected to irreversible oxidation on irradiation. Even with the lack of unsaturation connecting two aromatic moieties, MCP undergoes photodehydrogenation by virtue of favorable molecular geometry, proximity of coupling positions and great strain energy.

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[14] H. Shizuka, K. Sorimachi, and T. Morita, Abstracts of Papers, the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

Apparent activation energy of the reaction is 5.5 kcal/mol which can be compared with 5.0 kcal/mol found for stilbene.

The Effect of MCP Initial Concentration. Experiments carried out with MCP concentrations show that the rate of 4HP formation is proportional to MCP concentration. The relation between MCP concentration and k_0 which can be calculated from k_{4HP} assuming $k_{4HP}/C_{MCP}=k_0$, is shown in Fig. 8. The values represent approximate quantum yields. For $[MCP] \geqq 5 \times 10^{-4}$ mol/l, k_0 is almost constant. No such linear correlation exists with more dilute solutions.

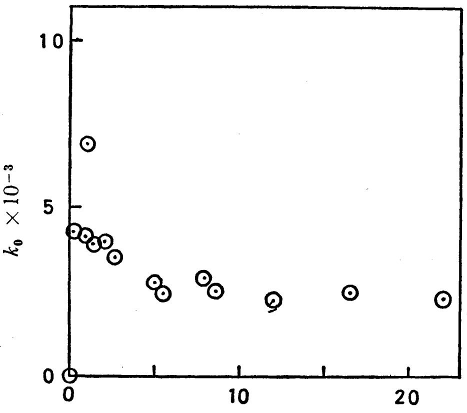

Fig. 8. k_0 *vs.* MCP concentration plot.
$[I_2]$: 3.3×10^{-4}mol/l

Flash Technique Experiments. Although the overall process of the I_2-induced dehydrogenation of MCP can be written as $MCP+I_2 \xrightarrow{h\nu} 4HP+2HI$, it is necessary to know whether it is such a simple reaction or a multistep reaction going through some intermediates. Muszkat and Fisher[15] presented a free radical mechanism involving radical species such as PH·, formed by hydrogen abstraction from dihydrophenanthrene PH_2, and HO_2· in the *cis*-stilbene-phenanthrene reaction. In order to solve the problems flash photolysis experiments were carried out for degassed cyclohexane solutions of MCP-I_2, MCP and I_2.

No absorption spectra suggesting the presence of an intermediate was observed. If an intermediate with a lifetime longer than 5×10^{-5} sec had been involved, the corresponding absorption could have been observed. For several wavelength regions, the diminishing absorption after main flash was followed by oscilloscope observation. Although absorption due to the product was observed, no diminishing absorption characteristic of an intermediate was detected.

Formation of Molecular Complex. The results of flash photolysis eliminate the possibility that the reaction proceed through a long-lived intermediate such as triplet species. As an alternative, we can postulate an intermediacy of the CT complex between MCP and iodine. The UV spectrum of a mixture of MCP (~10^{-2} mol/l) and iodine (~10^{-3} mol/l) in cyclohexane showed the presence of a band maximum at 334 nm which was absent in the individual spectra (Fig. 9). The band position is in agreement with the expected maximum[16] 336 nm, calculated from the ionization potential of MCP, 8.41 eV.[3]

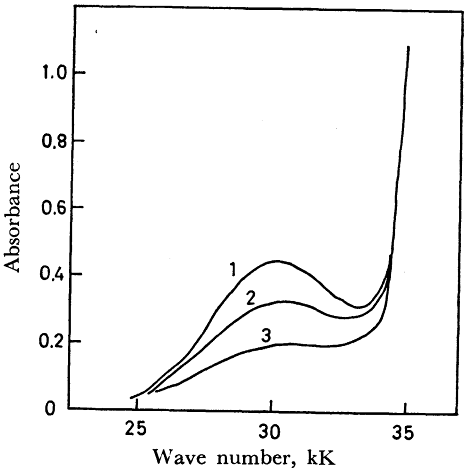

Fig. 9. Absorption spectra of the molecular complex between MCP and iodine in cyclohexane solution.
$[I_2]$: 2.21×10^{-3}mol/l, [MCP]: 1) 1.44×10^{-2}mol/l, 2) 0.931, 3) 0.508

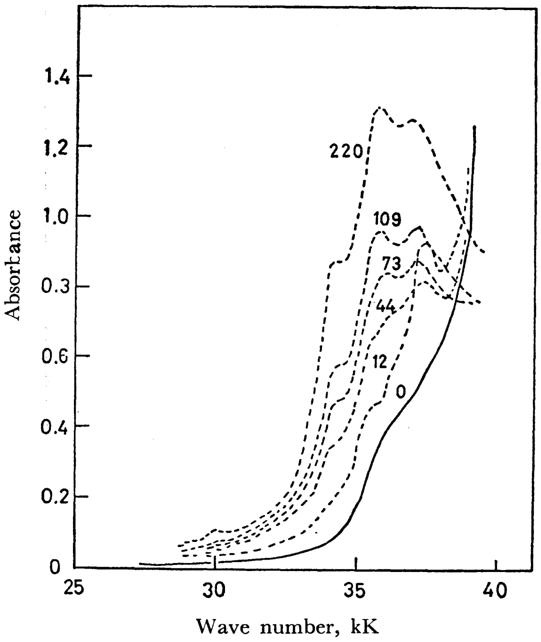

Fig. 10. Change of the absorption spectra of the solution containing MCP and *p*-benzoquinone by UV-irradiation.
[MCP]: 5.0×10^{-4}mol/l
[BQ]: 5.0×10^{-4}mol/l
Numbers denote the time of illumination (min).

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[15] K. A. Muszkat and E. Fisher, *J. Chem. Soc.*, *B*, **1967**, 662.

[16] Briegleb[18] presents the relation between the ionization potential (I_D) of the electron donor and the transition energy($h\nu_{CT}$) of CT-band as follows.

$$h\nu_{CT} = I_D - C_1 + \frac{C_2}{I_D - C_1}$$

Since $C_1=5.20$ eV, $C_2=1.5$ eV in iodine, calculation gives $h\nu_{CT}$ using $I_D=8.41$ eV.

TABLE 2. PHYSICAL PROPERTIES FOR THE MCP-I_2 COMPLEX (20.2°C)

Hydrocarbon	$\lambda_{\text{CT. max.}}$ nm	$\varepsilon_{\max}$	K l/mol	$-\Delta H$ kcal/mol	$-\Delta S$ cal/mol/deg	$-\Delta G$ kcal/mol
MCP	334	1050	16.7	1.83	3.9	0.69
m-Xylene[18]	318	12500	—	—	—	—

The equilibrium constant K and the molar absorptivity ε of the complex calculated from the Rose-Drago equation[17] are in agreement with experimental values. This suggests the possibility that the photocyclodehydrogenation of MCP proceed by complexing with iodine.

As compared with the *m*-xylene-I_2 complex, the MCP complex absorbs at a longer wavelength region with intensity of about one-tenth. The difference is caused by a transannular electronic interaction which delocalize electron density in a charged structure, and also by bent benzene structure.[2] The equilibrium constant is larger than that of *m*-xylene, which is about 3 l/mol, but smaller than that of the MCP-TCNE complex.

Experiments with p-*Benzoquinone and Others.* *p*-Benzoquinone (BQ) and benzophenone (BP)[19] were also found to be effective as an oxidant.

The spectral change indicating the formation of 4HP upon irradiation with MCP–BQ–cyclohexane solutions is shown in Fig. 10. The reaction is rather complex since both MCP and BQ absorb at 253.7 nm. The formation of 4HP appears to be slower compared with iodine.

With BP as an oxidant, 4HP was formed when both MCP and BP were excited although no reaction occurred when BP alone was excited.[19] Abstraction of aryl hydrogens with BP and BQ is interesting when we consider the fact that they are usually photo-reduced only with good hydrogen donors.

On the other hand, irradiation of MCP-TCNE complex gave no indication of 4HP formation. Electon affinity[20] increases in the order O_2(0.7—0.9 eV) < iodine(1.7—1.8 eV) < BQ(2.0 eV) < TCNE-(2.89 eV). A stronger complex can be formed in this order. No relation exists between reactivity and this order.

General Discussion

Photolysis reaction of MCP differs in many ways with respect to the cyclization reaction of *cis*-stilbene, in which oxidation of the dihydrophenenthrene intermediate is accomplished both with oxygen and iodine in the dark reaction. It also differs from the photolysis reaction of [2.2]paracyclophane case since no ring cleavage product could be obtained. In the presence of iodine the rate of formation of 4HP is rapid as compared with other oxidants. This suggests that iodine plays a special role in the photocyclization. Mechanistic considerations, however, reveal that the action of iodine is not simple and appears to involve complicated processes.

From the results of flash photolysis study and the fact that photodehydrogenation was not scavenged by oxygen, one could eliminate the possibility of involvement of MCP triplet (Eq. (5)).

If the reaction comprises uncomplexed MCP in the excited singlet state as given by

$$\left.\begin{array}{l} \text{MCP} \xrightarrow{h\nu} \text{MCP}^* \\ \text{MCP}^* + \text{I}_2 \rightarrow \text{4HP} + \text{2HI} \end{array}\right\} \tag{6}$$

one can expect the dependence of iodine concentration on the rate of formation of 4HP. The results given in Fig. 5, however, clearly indicate that the formation of 4HP is not affected by iodine concentration, if $[I_2] <$ *ca.* 7×10^{-4} mol/l. On the same basis, one can deny that iodine radical is involved in Eq. (4).

We propose the following scheme involving a molecular complex for the initial stage of the photolysis

$$\text{MCP} + \text{I}_2 \rightleftarrows (\text{MCP}\cdots\text{I}_2) \text{ (complex formation)} \tag{7}$$

$$(\text{MCP}\cdots\text{I}_2) \xrightarrow{h\nu} (\text{MCP}^*\cdots\text{I}_2) \tag{8}$$

$$(\text{MCP}^*\cdots\text{I}_2) \rightarrow (\text{MCP}\cdots\text{I}_2) \text{ or MCP} + \text{I}_2 \tag{9}$$

$$(\text{MCP}^*\cdots\text{I}_2) \rightarrow \text{4HP} + \text{2HI} \tag{10}$$

where MCP* denotes excited state of MCP. It is highly probable that the excited singlet MCP is reactive. This formulation fits nicely the experimental results.

No intermediate compound corresponding to 4*a*,4*b*-dihydrophenanthrene formulated in *cis*-stilbene cyclization can be postulated in the MCP case, since two benzene rings are not in conjugation. The fact that no long-lived species can be detected by flash photolysis and oxygen has little effect on the reaction suggests the absence of any free-radical intermediate such as the one lacking one hydrogen atom from MCP.

Whether step(10) is such a simple process or consists of multi-step reactions is not known. However, it might be attractive to assume electron transfer processes followed by dehydroiodination:

$$\left.\begin{array}{l} (\text{MCP}^*\cdots\text{I}_2) \rightarrow (\text{MCP}^+\cdot\text{I}_2^-) \\ (\text{MCP}^+\cdot\text{I}_2^-) \rightarrow \text{4HP} + \text{2HP} \end{array}\right\} \tag{11}$$

The importance of such electron transfer processes and charge-transfer resonance configuration (CT configuration) might be suggested as follows: a) Photolysis of [2.2]paracyclophane in methanol with

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[17] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138, 6141 (1959).

[18] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin-Göttingen-Heidelberg (1961).

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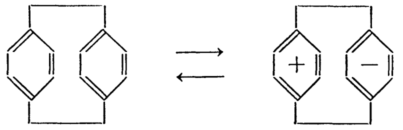
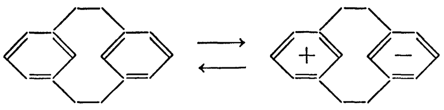
253.7 nm light can best be explained by assuming a CT configuration.7) b) With [2.2]paracyclophane, the contribution of CT configuration caused by transannular interaction can be seen even with molecules in the neutral ground state. With the anion radical the contribution can be assumed to be about 50%. Energy of the CT configuration was considered to be several eV.21) c) A similar interaction was observed with MCP and a delocalized configuration helps to form CT-complex. d) On contact with potassium film, MCP is shown to form 4HP anion radical instead of MCP anion radical. Martin and Gerson22) interpreted the result by assuming initial formation of MCP anion radical which undergoes transannular dehydragenation reaction. Kowata, Hoshino, and Koizumi,23) on the other hand, presented evidence that 4HP is formed first on the surface of the metal, and is then reduced to 4HP anion radical. Regardless of the mode of formation, hydrogen abstraction $C_{8,16}$ occurs very rapidly. The facile oxidation can be explained in terms of the large strain energy, calculated by Boyd *et al.*24) to be *ca.* 13 kcal/mol. The role of iodine is dual; it helps to increase delocalized configuration and acts as a hydrogen abstractor.



Ground configuration CT configuration
Neutral [2.2]Paracyclophane21)



Ground configuration CT configuration
Neutral MCP

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Appendix

The rate of disappearance of MCP is followed by calculating absorbance change of MCP, D^{272}_{MCP}, at 272 nm. After appropriate time intervals, the observed absorbance at 272 nm, D^{272}, can be expressed as follows.

$$D^{272} = D^{272}_{\mathrm{MCP}} + D^{272}_{\mathrm{I}} + D^{272}_{\mathrm{4HP}}$$

where D^{272}_{I} and D^{272}_{4HP} are the absorbances due to iodine alone, and 4HP at 272 nm, respectively. Thus D^{272}_{MCP} is calculated as follows.

$$D^{272}_{\mathrm{MCP}} = D^{272} - \frac{\varepsilon^{272}_{\mathrm{4HP}}}{\varepsilon^{292}_{\mathrm{4HP}}} D^{292}_{\mathrm{4HP}} - \frac{\varepsilon^{272}_{\mathrm{I}}}{\varepsilon^{520}_{\mathrm{I}}} D^{520}_{\mathrm{I}}$$

where D^{292}_{4HP} and D^{520}_{I} are the observed absorbances at 292 nm and 520 nm, respectively. The reaction rate of MCP, k_{MCP} is evaluated from the initial slopes (Fig. 4-c).

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