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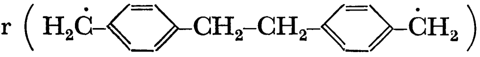
# Photodissociation Reaction from Higher Excited Triplet States of [2.2]Paracyclophane

Shun-ichi Ishikawa, Junko Nakamura,[†] and Saburo Nagakura*
*The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106*
[†] *The Institute of Physical and Chemical Research, Wako, Saitama 351*

(Received September 3, 1980)

The mechanism of photodissociation of [2.2]paracyclophane in glassy solvent at 77 K was studied. It is concluded that the dissociation of the $CH_2$–$CH_2$ bridge occurs from higher triplet states ($T_n$) *via* the lowest triplet state as an intermediate. The efficiency of the reaction depends on the characters of $T_n$ states; high from the locally excited state, and low from the charge-transfer state.

The electronic structure of [2.2]paracyclophane (PC) has been studied both experimentally and theoretically.[1)] The most predominant character of the molecule is the transannular interaction. In PC, there exist two different kinds of excited states, the locally excited (LE) state within the constituent moieties, the benzene rings of PC, and the charge-transfer (CT) state. The LE and CT bands were observed in the $S_n \leftarrow S_0$ and $T_n \leftarrow T_1$ absorption spectra.[1)] When PC is excited to different kinds of electronic states, photoreactions characteristic of respective states are expected to occur.

Helgeson and Cram studied photochemistry of PC in the alcoholic solution at room temperature.[2)] From the analysis of photoproducts at various exciting wavelengths, they proposed an interpretation that the excitation to different singlet electronic states of PC produces different reaction intermediates.[2)] In a previous paper,[3)] we found that photodissociation occurred on the $CH_2$–$CH_2$ bridge of PC in glassy solvents at 77 K, and that a species with two benzyl radicals linked together  was produced. The reaction rate was found to be proportional to the square of the exciting light intensity.

In this paper, the relation between the reactivity and the nature of excited states of PC was investigated.

## Experimental

PC and the solvents, 2-methylpentane (2-MP) and 2-methyltetrahydrofuran (MTHF), were purified by the same methods as described previously.[3)] The samples with the concentration of $10^{-3}$ mol dm$^{-3}$ in each solvent were degassed by freeze-pump-thaw cycles.

For photolysis of PC, the following exciting sources were used; a 1 kW super high-pressure mercury lamp (Pyrex and $NiSO_4$ solution filters for 313 nm light, and Toshiba UV-D33 S and UV 35 filters for 365 nm), a 500 W super high-pressure mercury lamp with a Jarrell-Ash 1/4 m monochromator, and a nitrogen laser (Molectron UV 24) pumped dye laser (DL 14). Dyes used are 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (365—380 nm), 4,4‴-bis(2-butyloctyloxy)-*p*-quarterphenyl (380—395 nm), 2-(4-biphenylyl)-6-phenylbenzoxazole (395—405 nm), 4,4′-diphenylstilbene (405—415 nm), 1,4-bis(2-methylstyryl)benzene (415—425 nm), coumarin 120 (425—445 nm), and 7-diethylamino-4-methylcoumarin (445—450 nm). The intensity of the dye laser was monitored by the use of a power meter (Laser Precision RKP 312).

The optical alignment used for pursuing radical production from PC is of the parallel beam type[1b)] (Fig. 1). An exciting light (1 kW mercury lamp or dye laser) and a monitoring light were set to pass the same part of a sample. The wavelength of the monitoring light is 322 nm which corresponds to the absorption peak of the radical produced from PC.[3)]

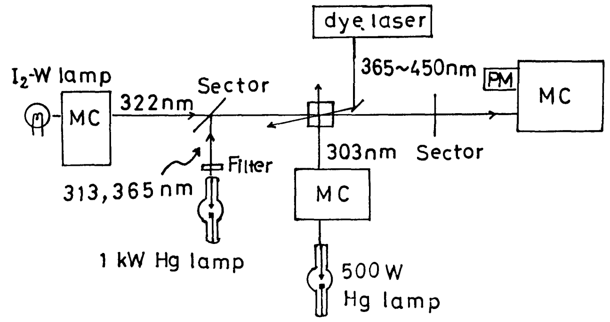
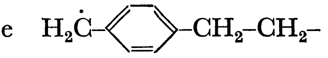
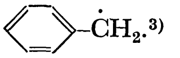


Fig. 1. Optical alignment used for the measurement of the reaction rate of PC.

## Results and Discussion

In the present study, experiments were made by using two different exciting light beams; a weak monochromatic light beam at 303 nm from a 500 W mercury lamp (first beam) and a strong light beam at 365 nm from a 1 kW mercury lamp (second beam). The second beam alone caused no reaction because PC has no absorption at 365 nm. With the use of the first beam only, the reaction occurs very slowly. With the simultaneous use of both beams, the reaction proceeds faster by an order of magnitude than with the use of the first beam alone. The reaction product is known to be  [3)] Since the produced radical is stable at 77 K, the relative reaction rate, $R$, can be defined by the absorbance change, $\Delta A$, at an appropriate wavelength. Actually we measured $\Delta A$ at 322 nm corresponding to one of the peak wavelengths of the product. The reaction rate is proportional to the intensity of the second beam. This experimental result confirms that the reaction proceeds through an intermediate state.

In rigid media at 77 K, the most appropriate state for this intermediate is the lowest triplet state, $T_1$, which has a sufficiently long lifetime (a few seconds).

This is supported by the facts that the reaction occurs by the irradiations of the first and second beams with intervals of several seconds as well as by their

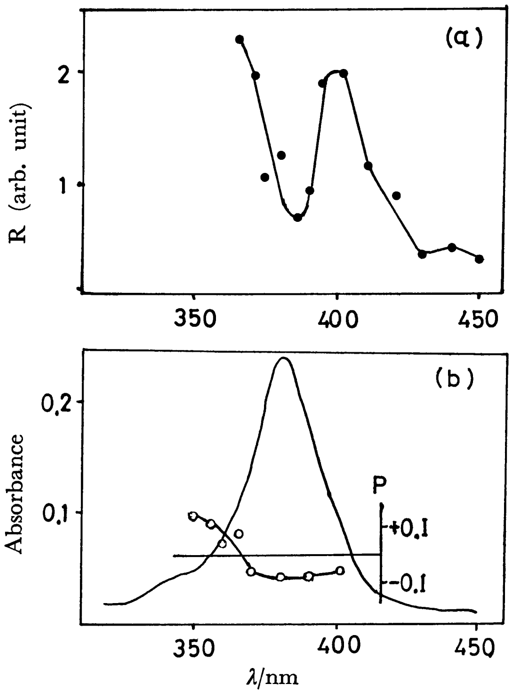


Fig. 2. (a) Dependence of reaction rate, *R* ($\Delta A$ (322 nm) $s^{-1}$), upon the wavelength of second exciting light. (b) $T_n \leftarrow T_1$ absorption spectrum of PC along with its polarization, *P*.

simultaneous irradiations and also that the reaction does not occur at room temperature at which the lifetime of $T_1$ is very short. From this veiw, the higher triplet states which are populated by $T_n \leftarrow T_1$ absorption are considered to be the reactive state of PC.

Several reactions show the biphotonic nature in the rigid media at low temperature; photoionization,[4] decomposition of solvent sensitized by solute,[4b] photoisomerization,[5] $\beta$-bond fission of substituted aromatics[6] and hydrogen abstraction from solvent.[7] The intermediate states of these reactions were found to be $T_1$.

In the next experiment, a weak 313 nm light (first beam) by which the reaction occurs to a negligibly small extent and a dye laser (second beam) were used for excitation. The dye laser beam is suitable for the present experiment since it is highly monochromatic (line-width is less than 0.01 nm) and the intensity per unit wavelength is high. Figure 2(a) shows the relative reaction rate (normalized to the second beam intensity) with 365—450 nm light as the second beam. The $T_n \leftarrow T_1$ absorption spectrum of PC and its polarization are also shown in Fig. 2(b).

In the present case where the first beam is weak, the concentration of the molecules populated in the $T_1$ state is small. Under these conditions, the reaction rate, *R*, is proportional to the second beam intensity, $I(\lambda)$, the molar extinction coefficient of $T_n \leftarrow T_1$ absorption, $\varepsilon(\lambda)$, and the reaction efficiency of the $T_n$ state, $\phi_n(\lambda)$. Here $\lambda$ is the wavelength of the second beam.

$$R \propto I(\lambda)\varepsilon(\lambda)\phi_n(\lambda).^{8)}$$

A plot of *R versus* $\lambda$ in Fig. 2(a) shows the $\lambda$ dependence of $\varepsilon(\lambda)\phi_n(\lambda)$, since the *R* values are normalized to the second beam intensity. We can see from this figure that the rate of radical production around 380 nm which corresponds to the maximum of the $T_n \leftarrow T_1$ absorption is smaller compared with the rate at the shorter and longer wavelengths. This means that $\phi$ is much smaller for the upper triplet state of the 380 nm band than for the neighboring triplet states.

The $T_n \leftarrow T_1$ absorption spectrum of PC was analyzed previously.[1b] According to the analysis, the upper state of the 380 nm band is the CT state and the LE states exist at the higher and lower energy sides. Therefore, it is reasonable to consider that the radical production occurs effectively from the LE state but ineffectively from the CT state. This indicates that the photoreactivity is sensitive to the electronic structure of the excited state from which the reaction occurs.

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