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Observation of Intramolecular Excimer Emission of Benzyl Radical Pair Produced by Photolysis of [2.2]Paracyclophane

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Photochemistry of [2.2]paracyclophane in glassy solvents at 77 K was studied. With irradiation, a species in which two benzyl radicals are linked together with an ethylene bridge was produced. From the ESR study, the radicals were found to form the benzyl radical pair in harder solvents. The emission spectrum and the emission lifetime of the radical species showed remarkable dependence on the solvent viscosity. In harder solvents, a new broad emission was observed on the longer wavelength side of the structured emission of the benzyl radical. From the studies of the excitation spectrum and the emission lifetime, this broad band was concluded to be the intramolecular excimer fluorescence of the radical pair. The photo-reaction of [2.2]paracyclophane was found to be biphotonic, occurring from a higher triplet state excited *via* the lowest triplet state.

[2.2]Paracyclophane (PC) is a typical molecule for studying the transannular interaction, and its electronic structure was studied by several authors both experimentally and theoretically.1) Photochemistry of PC is also interesting in connection with its electronic structure. The biradical and the zwitter ion *etc.* were assumed by Helgeson and Cram as photochemical intermediates in the photolysis of PC in solution at room temperature.2)

We studied the photochemistry of PC in glassy solvent at 77 K. Our main interest was laid on the confirmation of a photo-reaction intermediate, benzyl radical pair, and also on the transannular effect in the emissive state of this species.

Experimental

Materials. PC (the Aldrich Chemical Company) was purified by column chromatography and vacuum sublimation. 2-Methylpentane and 2-methyltetrahydrofuran (Tokyo Kasei) which were used as solvents, were distilled from lithium aluminium hydride. Isopentane (Tokyo Kasei) was used without further purification. The concentration of the sample was about 10^{-3} mol dm^{-3} throughout the experiment except the case of the absorption spectrum (10^{-4} mol dm^{-3}). Solutions were degassed by freeze-pump-thaw cycles. We used 2-methyltetrahydrofuran (MTHF), 2-methylpentane (2-MP), isopentane (IP), and mixed solvents of 2-MP and IP (10:0.3, 10:1, 4:1, 3:2, 1:1, and 3:7) as solvents. IP initially forms glass but gradually becomes snowy at 77 K, while other solvents form clear glass. The viscosities of these solvents at 77 K are greatly different from one another; 3.7×10^{20} cp at 77.5 K for MTHF,3) 2.4×10^{13} cp at 77.5 K for 2-MP,3) and $<8.9\times10^{5}$ cp at 77 K for IP.4)

Absorption Measurements. Ultraviolet and visible absorption spectra of photolysis products of PC were measured with a Cary 14 recording spectrophotometer. For the generation of *p*-methylbenzyl radical from *p*-xylene, a light of fourth harmonics (266 nm) of a YAG laser (Quanta Ray DCR-1) was used as an exciting source, and the absorption spectrum was measured.

ESR Measurements. The ESR spectra were recorded on a JEOL JES-FE-3AX spectrometer. The magnetic field was calibrated by measuring the resonance frequency of ^{1}H NMR.

Emission and Excitation Measurements. Emission spectra of the PC photoproduct were measured by using a 100 W super high-pressure mercury lamp and a Jarrell-Ash 1/4 M monochromator as an exciting system and a Spex 1700-111 monochromator and a Hamamatsu TV R636 photomultiplier as a detecting system. As an exciting source for the excitation spectrum measurement, a 500 W xenone lamp and the Spex monochromator were used.

Emission Lifetime Measurements. A nitrogen laser (Molectron UV24) pumped dye laser (DL-14) and the second harmonic generator (KDP (KH_2PO_4) crystal) were used for the emission lifetime measurement. The excitation wavelengths are 421 nm (*p*-bis(*o*-methylstyryl)benzene), 457 nm (7-diethylamino-4-methylcoumarin), and 322 nm (Rhodamin B and Cresyl Violet Perchlorate/KDP crystal). The duration of pulse is 4—8 ns and the line-width is about 0.01 nm. The emission was observed with a Nikon G-250 monochromator and a Hamamatsu TV R666S photomultiplier.

Results and Discussion

PC in glassy solvents was irradiated at 77 K with the use of 313 nm light of a super high-pressure mercury lamp. Initially green phosphorescence of PC with long lifetime was observed. By continuing irradiation, the yellowish emission with short lifetime was observed instead of the phosphorescence of PC. After irradiation, the glassy solution was colored yellow as observed previously by Bramwell and Gendell.5) The yellowish emission was also observed by using the longer wavelength light (365, 436 nm) for excitation. The absorption, ESR, emission, and excitation spectra of the species produced by photolysis of PC were measured and analyzed as follows.

Absorption Spectra of PC Photoproduct. By photolysis of PC in glassy solvent at 77 K, a new species was produced and existed stably in the solvent matrix. Absorption spectra of this new species produced at irradiation times of 2, 5, and 8 min in 2-MP were measured with the results shown in Fig. 1. There appear a few peaks in 260—270 nm, distinct peaks in 300—322 nm, and weak but distinct peaks near 450 nm. Kaupp *et al.* reported recently that a new species was produced by photolysis of PC in MTHF at 77 K, the absorption spectrum of which showed peaks near 320 and 450 nm.6) Their result is consistent with ours except for the wavelength region below 300 nm which was not measured by them.

The observed spectrum consisting of the three bands at 270, 320, and 450 nm is very similar to that of the

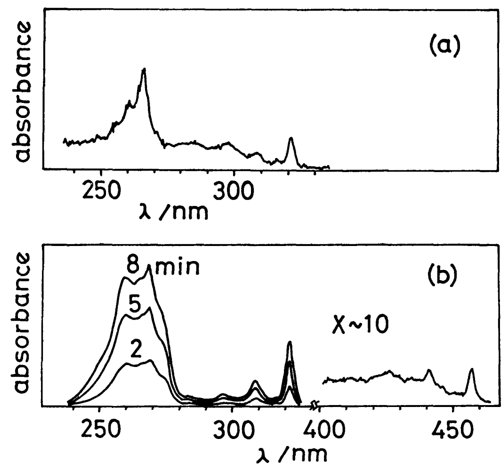
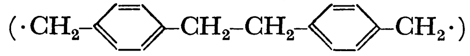
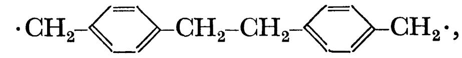


Fig. 1. Absorption spectra of (a) the *p*-methylbenzyl radical produced from *p*-xylene, (b) the PC photoproduct at respective irradiation times (2, 5, and 8 min) in 2-MP at 77 K.

benzyl radical produced from toluene or its methyl derivatives in glassy solvents at 77 K.[7] For the purpose of comparison, the observed absorption spectrum (240—340 nm) of the *p*-methylbenzyl radical produced from *p*-xylene is also shown in Fig. 1. It is evident that a species with the structure very similar to the *p*-methylbenzyl radical is produced by photolysis of PC.

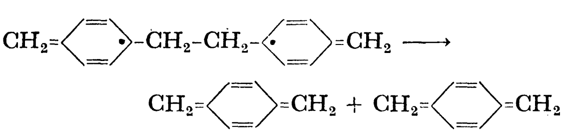
It is reasonable to consider that a C–C ethylene bridge of PC is dissociated at the primary reaction step and a biradical species in which two benzyl radicals are linked together by an ethylene bridge in the *p*-position  is produced. This biradical is expected to show the absorption spectrum similar to that of the *p*-methylbenzyl radical in agreement with the above-mentioned observation. This point has been investigated further with the aid of ESR spectroscopy.

ESR Spectra of PC Photoproduct. We measured the ESR spectra of PC photoproduct in glassy solvents at 77 K in order to certify the assignment to a biradical (two benzyl radicals linked with an ethylene bridge) and to elucidate its structure.

In MTHF, 2-MP, and the harder mixed solvents of 2-MP and IP (4:1, 3:2, and 1:1), two signals are observed in the $g \approx 4$ region. One is the signal of PC in the lowest triplet state, and this signal decreases its intensity with the increasing irradiation time (PC decreases by reaction) and decays slowly with the cut-off of exciting light. Its lifetime is the same as the phosphorescence lifetime. The other signal observed in the $g \approx 4$ region increases its intensity with the increasing irradiation time and does not decay with the cut-off of exciting light. The signal can be regarded as due to the $\Delta m=2$ transition of the radical pair in triplet. There are two possibilities for the radical pair. One is that of two benzyl radicals produced from PC, and the other is that of the benzyl radical with a solvent radical which is created by reaction of the radical with solvent. By the following considerations about the reactivity of the radical with solvlent, we confirm that the $\Delta m=2$ signal is due to the radical pair,  produced by photolysis of PC, and not owing to the interaction between the benzyl radical and the solvent radical.

The absorption spectrum in each solvent does not change compared with that of the *p*-methylbenzyl radical although small shifts are observed. Consequently, the production of the radical added to the solvent is unconceivable. A possible process of reaction with solvent is the abstraction of hydrogen atom. However, it is known that the benzyl radical produced from toluene does not abstract hydrogen atom from hydrocarbon, and not even from EPA.[8] The low reactivity of benzyl radical is due to the fact that benzyl radical is π-radical and the unpaired electron density at $-CH_2$ is decreased by resonance effect. (According to Hückel MO theory, unpaired electron densities are calculated to be 4/7 on the $-CH_2$ carbon and 1/7 on each of *o*- and *p*-carbons of the benzene ring.)

From the species where unpaired electron densities exist at each *p*-position of two benzyl radicals, the remaining C–C bridge can dissociate and two molecules of quinodimethane can be produced.



Kaupp reported that quinodimethane was produced by photolysis of PC in MTHF at 85 K.[9] The reported absorption spectrum of quinodimethane has many peaks below 300 nm[9] but the production of such species could not be detected in our experiment (photolysis at 77 K).

Therefore, the photoproduct of PC is expected to remain as the biradical at 77 K without the abstraction of hydrogen atom from the solvent used here nor the degradation to smaller fragments. It is considered that the biradical with an interaction between the two benzyl radicals was observed as a radical pair in the ESR spectrum. However, there is no strong interaction between the two benzyl radicals in the ground state, because the spectral shape of the absorption spectrum is the same as that of the *p*-methylbenzyl radical produced from *p*-xylene and the spectral shift is fairly small.

In contrast with the case in the $g \approx 4$ region of the ESR spectrum, a signal increases its intensity in the $g \approx 2$ region with the increasing irradiation in all solvents used. The spectra in various solvents are broad and the detailed analysis is difficult, but the following trends can be pointed out.

1. In MTHF, an intense and broad signal in which the splitting of fine structure is about 150 G ($1\ G=10^{-4}$ T) is observed together with weak but sharply structured signals. The structured signals are considered to be due to MTHF radical. The origin of the broad signal can be assigned to the radical pair in triplet because of its spectral shape.
2. In 2-MP, only a broad signal the origin of which

can be assigned to the radical pair is observed.

3. The spectral shapes in the 4:1 and the 3:2 mixed solvents of 2-MP and IP are similar to that in 2-MP. In the softer mixed solvent (1:1), a sharp signal overlaps the broad signal. In the 3:7 mixed solvent and in IP, the sharp signal has the rather complicated structure, but it may be partly due to the benzyl radical without the interaction with the other radical linked together. These results observed in the $g \approx 2$ region also support the scheme that a biradical produced by photolysis of PC is forming a benzyl radical pair.

The Structure of the Biradical as Revealed from ESR Spectra. The homolytic cleavage of one of the C–C bridges of PC at the benzyl radical pair formation increases freedom in the motions of the benzyl radicals. Consequently, in soft matrices, the biradical is expected to take an open structure in which the two benzene rings are not parallel but separate from each other. In the hard glassy solvents, however, the molecular motion of the rings is restricted and the biradical takes a structure in which a weak interaction between the two benzyl radicals is effective. From this view, we can expect that the zero-field splitting parameter, D^*, decreases with the increasing softness and the $g \approx 4$ signal disappears in some soft solvents. This expectation is fulfilled by the present observation. The $g \approx 4$ signal is observed in MTHF, 2-MP, and in harder mixed solvents of 2-MP and IP (4:1, 3:2, and 1:1), but cannot in the soft mixed solvent (3:7) and in IP. Furthermore, the D^* value has a tendency to be larger in harder solvents, as is seen in Table 1 in which the D^* values estimated from the positions of the $g \approx 4$ signals are tabulated.

TABLE 1. D^* AND CALCULATED r VALUES OF PC PHOTOPRODUCT

Solvent	D^*/cm^{-1} [a]	$r/\mathrm{Å}$ [b]
MTHF	0.015	5.6
2-MP	0.014	5.7
4 : 1[c]	0.012	6.0
3 : 2[c]	0.013	5.8
1 : 1[c]	0.010	6.4

a) The error is estimated as $\pm 0.001\ \mathrm{cm}^{-1}$. b) ± 0.2 Å. c) Mixed solvent of 2-MP and IP.

In a model in which two localized radicals are separated from one another in the distance of r, D^* and r are related by the following equation:

$$D^* = 3/2(g^2\beta^2/r^3).$$

On an assumption of g=2.0023, we calculated r from observed D^* with the aid of the equation. The result is shown in Table 1. With the use of the Hückel MO theory, the center of unpaired electron distribution is calculated to locate on the C–C bond connecting $-\mathrm{CH_2}$ and the benzene ring (see Fig. 2). r is considered to correspond approximately to the distance between the centers of unpaired electron distribution in the two benzyl radicals. As the result of cleavage of one of the C–C bridges the two benzene rings of PC gain motional freedom, facing obliquely and rotating about the remaining C–C bridge. In the non-twisted structure ((a) in Fig. 2), r is estimated to be about 4.6 Å. From the observed r, the two benzene rings are considered to take the twisted structure ((b) in Fig. 2). In harder solvents, the r value is smaller and this suggests that the twist angle is smaller compared with the case in softer solvents. In the 3:7 mixed solvent and in IP, the two benzyl radicals must be separated largely, so that the signal cannot be observed because of the scarce interaction.

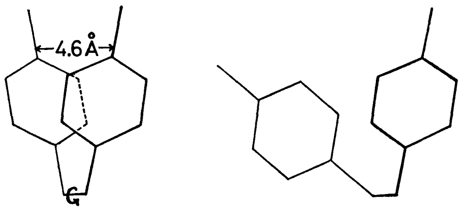


Fig. 2. Structure of the PC photoproduct in glassy solvents.
(a): Non-twisted, (b): twisted.

Hope *et al.* mentioned that the better fittings of crystal structure analysis was attained for PC by assuming a small twist of two benzene rings.[10] Andrews and Westrum suggested that from an anomaly in the heat capacity (C_p) near 50 K, the twisting motion became an active vibrational mode over 50 K.[11] These facts indicate that the two benzene rings may twist after cleavage of a C–C bridge.

Emission Spectra of PC Photoproduct. The benzyl radical produced from toluene or its methyl derivatives exhibits green emission and its spectrum is sharply structured. Kaupp *et al.* mentioned that the emission of PC photoproduct was similar to that of the *p*-methylbenzyl radical, and that the excimer-like emission was not observed.[6] However, in the present experiment new excimer emission of the benzyl radical pair produced from PC was observed in some solvents.

The emission spectra of PC photoproduct in MTHF, 2-MP, IP, and in mixed solvents of 2-MP and IP are shown in Fig. 3. The emission spectrum in IP is similar in the vibrational structure to that of the benzyl radical monomer produced from toluene. The excitation spectrum of the emission is the same as the absorption spectrum of benzyl radical, and this emission is caused by the excitation of either of the two benzyl radicals produced from one PC molecule.

In solvents harder than IP, a broad emission overlaps a monomer-like emission. Especially in 2-MP and MTHF, a clear peak appears in the longer wavelength region. Because of the appearance of the new band, the emission in 2-MP and in MTHF becomes yellow rather than green. The excitation spectrum measured by monitoring the sharp band is the same as the absorption spectrum, and that measured by monitoring only the broad band component (>600 nm) also exhibits the peaks around 320 nm and 450 nm, and is the same as the absorption spectrum. Therefore, the origin of the broad band is also the benzyl radical, and not the reaction product of PC with solvent. The new broad emission is considered to be caused by the interaction in the excited state between two benzyl radicals linked with the ethylene bridge.

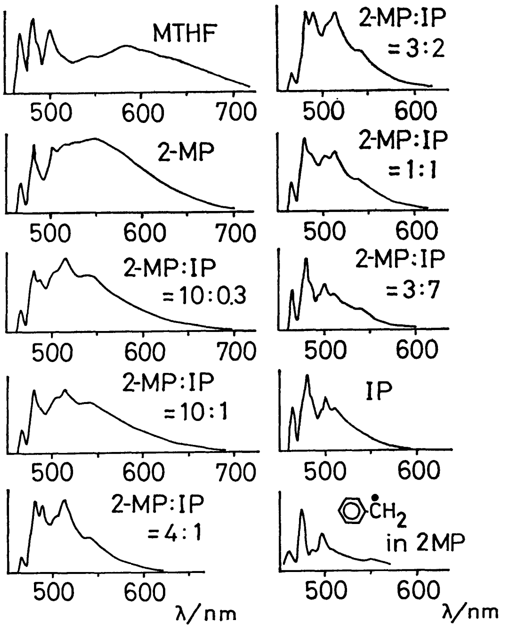


Fig. 3. Emission spectra of the benzyl radical in 2-MP and of the PC photoproduct in MTHF, 2-MP, IP, and mixed solvents of 2-MP and IP (10:0.3, 10:1, 4:1, 3:2, 1:1, and 3:7).

Table 2. Emission lifetime of PC photoproduct

Solvent	Lifetime/ns[a]
MTHF	55
2-MP	350
3 : 7[b]	560
IP	1100

a) The values cited are typical ones of several experiments. They are not always reproducible, depending on the condition of radical formation, *e.g.* irradiation time. b) Mixed solvent of 2-MP and IP.

Both the sharp band and the broad band show single exponential decay and their decay constants are equal to each other. Furthermore they are independent of excitation wavelengths. The rise time of the broad emission is too short to be observed within the exciting pulse duration, 4 ns. These kinetic results are consistent with the case of ordinary intramolecular excimer in solution where there exists rapid equilibrium between the excited monomer state and the excimer state. Therefore, it is reasonable to consider that the broad emission observed in 2-MP and MTHF is the intramolecular excimer fluorescence of the benzyl radical pair.

The peak of the excimer band is 580 nm in MTHF and 550 nm in 2-MP. In softer solvents, the excimer band moves toward the monomer band, although the peak wavelength of excimer band cannot be determined unambiguously. This may indicate that the stabilization energy of excimer is larger in harder solvents.

The emission lifetimes of PC photoproduct in several solvents are shown in Table 2 in the decreasing order of solvent viscosity. The emission lifetime in IP is about 1.1 μs, and the emission lifetime of the benzyl radical produced from toluene is reported to be 1.28 μs in EPA.[7d] In IP, the emitting species is the benzyl radical without the interaction with the other radical, and the lifetime in IP may become similar to that of monomer. The emission lifetimes in solvents harder than IP are shorter (see Table 2). A possible reason for this is that the recombination of the two benzyl radicals is enhanced in harder solvents. In harder solvents, the two radicals are located in the closer position (from the ESR study). The probability of the recombination process from the excited states of radical (monomer or excimer) may be larger in harder solvents, and the emission lifetime of radical may be more shortened.

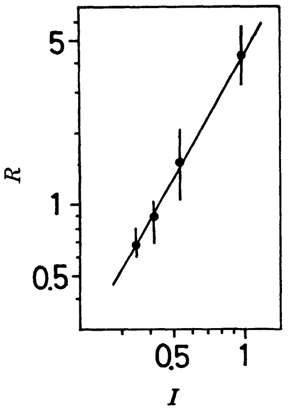


Fig. 4. Dependence of reaction rate, *R*, upon the intensity of exciting light, *I*.

Light Intensity Dependence of Reaction Rate. The absorbance at 322 nm of the PC photoproduct (biradical) increases at the initial stage linearly with irradiation time, and the initial reaction rate for the formation of the biradical can be determined. Figure 4 shows the dependence of this reaction rate, *R*, upon the exciting light intensity, *I*. The log-log plot of *R vs. I* shows a straight line, the slope of which is 1.8. This suggests the biphotonic mechanism for the formation of the biradical from PC. Therefore the photolysis of PC does not occur directly from the lowest excited state, S_1 or T_1, because of the energy deficiency. In the rigid media at low temperature, T_1 has a long lifetime (a few seconds). The higher triplet states which are populated by photon absorption of T_1 have sufficient energy for the photolysis of PC.

According to our previous paper on the $T_n \leftarrow T_1$ absorption spectrum of PC,[1b] we have a very weak band around 550 nm ($T_3 \leftarrow T_1$), an intense band around 380 nm ($T_4 \leftarrow T_1$), and a weak band around 340 nm ($T_5 \leftarrow T_1$). The 313 nm excitation corresponds to the $T_5 \leftarrow T_1$ transition the parentage of which is the local excitation corresponding to the $^3E_{1g}^- \leftarrow {}^3B_{1u}^+$ transition of the benzene ring. Therefore the locally excited T_5 state is considered to be the reactive state. Helgeson and Cram reported the wavelength-dependent photochemistry of PC in alcoholic solutions.[2] From the analysis of photoproducts at various exciting wavelengths, they proposed that the biradical composed of two benzyl radicals was produced only by the exciting light the wavelength of which is shorter than 230 nm, and that the zwitter ion (benzyl cation and anion) is produced by the excitation with 253.7 nm light. Their suggestion that the biradical is produced from higher excited states with sufficient energy is consistent with our conclusion.

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