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Photolyses of Tetraphenylcyclobutanes at 254 nm

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Photolyses of 1,2,3,4-tetraphenylcyclobutanes (TPCB) at 254 nm in hydrocarbon solvents have been studied by means of fluorometry, nanosecond time-resolved spectroscopy, and measurements of the reaction quantum yields. The photolysis of TPCB originates from the $S_1(\pi,\pi^*)$ state to give *trans*-stilbene nearly concertedly at higher temperatures (>200 K). Significant temperature and cis-effects were observed. The radiationless rate constants for the dissociation (k_r) and the other radiationless (k_n) processes decreased with lowering temperature. The value of k_r for γ-1,*t*-2,*t*-3,*c*-4-TPCB at 300 K, for example, was 4.7 times greater than that for γ-1,*t*-2,*c*-3,*t*-4-TPCB. The Arrhenius parameters of the relaxation processes were also determined. No intramolecular excimer emission was observed.

The photochemistry of four-membered rings has been extensively studied.1) Cyclobutane photochemistry involving selectivities in cleavage orientations upon irradiation is one of the most interesting fields among them. A number of studies on photolyses of cyclobutanes have been reported.2—10) Kaupp3) has shown that there is a clear preference for photochemical fission of the cyclobutane bond bearing the chromophore and the substituent which sterically interacts most effectively with the chromophore (cis-effect) and that the photolysis proceeds *via* short-lived 1,4-biradicals. As for tetraphenylcyclobutanes, they undergo photochemical cycloreversion to yield *trans*-stilbene.2,3) However no quantitative work on photolyses of tetraphenylcyclobutanes has been performed.

In the course of our studies of photochemistry of benzene derivatives,11—13) the title compounds (see below) were chosen in the present work from the following interests:

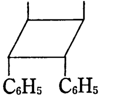
(1) How about the reactive state and the dissociation rate?

(2) How about the relaxation processes of the excited state of tetraphenylcyclobutanes?

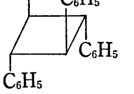
(3) Is there cis-effect2,3) on photochemical and photophysical processes of the molecules?

and (4) How about intramolecular excimer formation? In a previous work,13) an weak intramolecular excimer emission of [2.2]metacyclophane is observed, which is an exception of the $n=3$ rule.14) A large internal conversion of [2.2]metacyclophane occurs due to a conformational change in the excited state.

This paper reports the relaxation processes of excited tetraphenylcyclobutanes (**1** and **2**) studied by means of fluorometry, nanosecond time-resolved spectroscopy, and measurements of the reaction quantum yields under various temperatures.



γ-1,*t*-2,*t*-3,*c*-4-tetraphenylcyclobutane
1



γ-1,*t*-2,*c*-3,*t*-4-tetraphenylcyclobutane
2

Experimental

Starting materials (1,2,3,4-tetraphenylcyclobutanes (**1** and **2**)) were prepared by the photodimerization of transstilbene in benzene,15) and purified by silica-gel column chromatography using a mixture of benzene and cyclohexane (1:3) as the eluent. Methylcyclohexane, cyclohexane and isopentane (G.R.-grade products from Tokyo Kasei) were purified by passing them through a silica-gel column and then distillations. In the measurements of degassed samples, the solutions were thoroughly degassed by the freeze-pump-thaw-cycles.

A low-pressure mercury lamp (20 W) with a Vycor glass filter was used as the 254-nm radiation source. Acitnometry was carried out using a ferric oxalate solution (0.006 M).16) The quantum yields for the product formation were measured by spectrophotometry. For the measurements of temperature effects upon the reaction quantum yields and fluorescence lifetimes, a quartz Dewar flask designed for spectrometry was used, the temperature being controlled to within ±2 °C. Measurements of absorption and fluorescence spectra were the same as reported previously.17) The fluorescence quantum yields were measured by comparison with that of toluene in cyclohexane ($\phi_F=0.14$).18) The fluorescence decay was recorded with a Hitachi nanosecond time-resolved spectrophotometer (pulse width 11 ns), and the lifetime was determined by the convolution method when it was shorter than 20 ns.19)

Results

The spectrum of a 3.4×10^{-4} M cyclohexane solution of γ-1,*t*-2,*t*-3,*c*-4-tetraphenylcyclobutane (**1**) changed markedly upon irradiation with the 254-nm light at 300 K as shown in Fig. 1. A new band with maximum at 295 nm (ε: 2.74×10^4 M^{-1} cm^{-1}) appeared. The spectral change shows the formation of *trans*-stilbene as a sole photoproduct, as reported by Kaupp.2,3) The geometric isomer (**2**) was scarcely observed by the TLC method. The quantum yields for the product formation in cyclohexane at 300 K was 0.84±0.04. The quantum yields at 300 K did not change with variation in irradiation time (1—10 min), concentration of the starting material (10^{-4}—10^{-2} M), addition of 1,3-pentadiene ($<2\times10^{-2}$ M), and light intensity (10^{14}—10^{16} quanta ml^{-1} s^{-1}). Dissolved oxygen had no effect on the reaction quantum yields. The quantum yield Φ_r in MP (methylcyclohexane: isopentane=3:1 in volume) was the same as that in cyclohexane. Similar results were obtained in the

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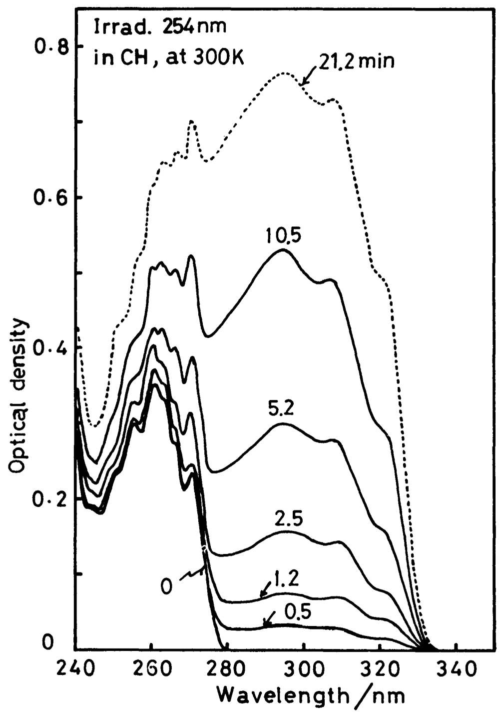


Fig. 1. The spectral change of a 3.4×10^{-4}M cyclohexane solution of No. 1 with lapse of time at 254 nm. Numbers refer to time of measurement in minutes.

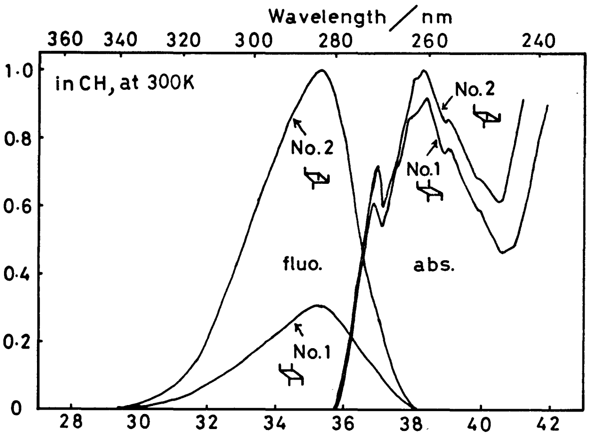


Fig. 2. Absorption and fluorescence spectra of tetraphenylcyclobutanes (No. 1 and 2) in cyclohexane.

case of γ-1,*t*-2,*c*-3,*t*-4-tetraphenylcyclobutane (**2**).

Figure 2 shows the absorption (**1**: $\lambda_{max}=261$ nm, $\varepsilon=1.03\pm0.02$ M^{-1} cm^{-1}; **2**: $\lambda_{max}=261$ nm, $\varepsilon=1.15\pm0.02$ M^{-1} cm^{-1}) and fluorescence ($\lambda_{max}=284$ nm for **1** and **2**) spectra of the starting materials in cyclohexane, which are very similar to those of toluene. No intramolecular excimer emission could be detected. No phosphorescence could be observed in MP at 77 K, as reported by Kaupp.[2)]

The reaction quantum yields Φ_r, fluorescence quantum yields Φ_f, fluorescence lifetimes τ_f and radiative rate constants k_f in MP at 300 K are listed in Table 1. The significant temperature effects upon Φ_r and τ_f in MP were observed as shown in Figs. 3 and 4, respectively. The Φ_r values decreased with lowering temperature. In contrast, the values of τ_f increased with lowering temperature, and they were 48±3 ns (**1**) and 46±3 ns (**2**) at 77 K. The photolyses of the samples took place even at 77 K in MP rigid matrices, although the Φ_r values were very small. The Φ_r values of **1** were greater than those of **2** at various temperatures as shown in Table 1 and Fig. 3.

TABLE 1. EXPERIMENTAL DATA OF Φ_f,$^{a)}$ τ_f, k_f, AND Φ_r OF TETRAPHENYLCYCLOBUTANES IN MP AT 300 K

Samples	$\Phi_f/10^{-2}$	τ_f/ns	$k_f/10^6$ s^{-1}	Φ_r
1	0.5±0.1	0.8±0.5	6.3	0.84±0.04
2	1.7±0.2	2.5±0.4	6.8	0.62±0.03

a) Determined by comparison with the fluorescence quantum yield of toluene ($\Phi_F=0.14$), see the Ref. 18.

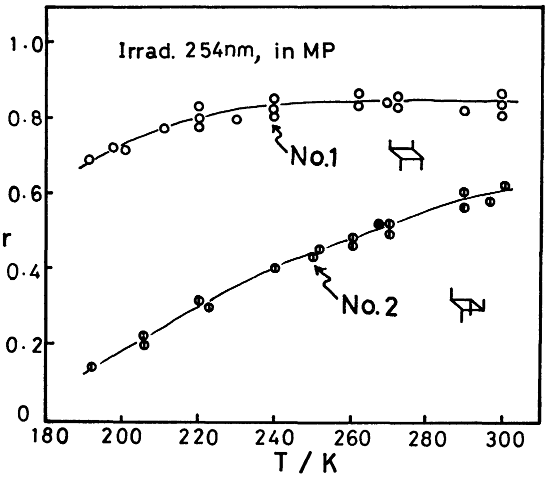


Fig. 3. The temperature dependence of the reaction quantum yields Φ_r in MP.

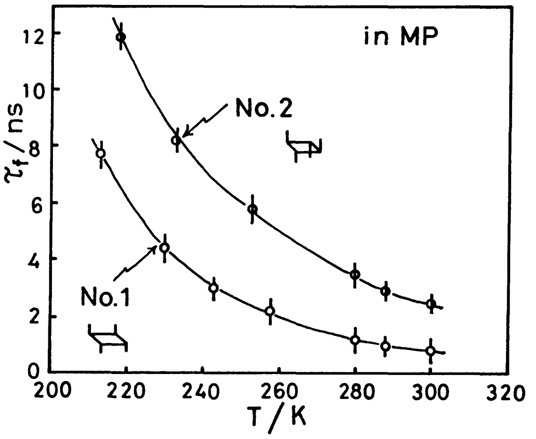


Fig. 4. The temperature dependence of the fluorescence lifetimes τ_f in MP.

Discussion

Kinetic Analyses. The presence of triplet quenchers ([1,3-pentadiene]$<2\times10^{-2}$ M and [dissolved oxygen]$\approx2\times10^{-3}$ M)[20)] do not affect the Φ_r values. The results indicate that the photolyses of 1,2,3,4-tetraphenylcyclobutanes (**1** and **2**) proceed *via* the

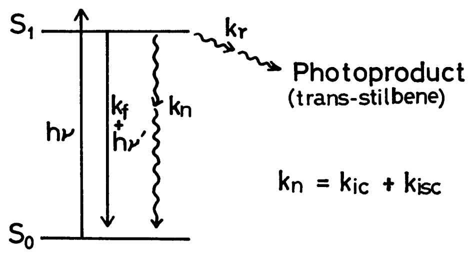


Fig. 5. A schematic energy state diagram for the photolyses of tetraphenylcyclobutanes.

excited singlet state and/or very short-lived triplet state. The fact that no phosphorescence of tetraphenylcyclobutanes could be observed suggests the existence of a relatively fast radiationless channel (probably cleavage) in the lowest triplet state. There may be two pathways of photochemical cleavage of the starting materials via the excited singlet and triplet states. However, the radiationless processes (cleavage and internal conversion) other than intersystem crossing are very predominant in the S_1 state at higher temperatures (>200 K), as will be discussed later. Accordingly, the reaction quantum yield *via* the triplet state must be small in comparison with that *via* the excited singlet state at higher temperatures (>200 K). That is, the reactive state at higher temperatures (>200 K) should be the lowest excited singlet state $S_1(\pi,\pi^*)$.

The experimental results at higher temperatures (>200 K) can be accounted for by the scheme shown in Fig. 5, where S_0 and S_1 are the ground and the lowest excited singlet states of the starting materials respectively, k_f radiative rate constant, k_r dissociation rate constant, and k_n radiationless rate constant of internal conversion k_{ic} plus intersystem crossing k_{isc}. From the usual steady-state approximation, the reaction quantum yield Φ_r is given by

$$\Phi_r = \frac{2k_r}{k_f+k_n+k_r} = 2k_r\tau_f \qquad (1)$$

The dissociation rate k_r may be expressed by Eq. 2,

$$k_r = k_r^0 + A_r\exp\left(\frac{-\Delta E_r}{RT}\right) \qquad (2)$$

where k_r^0 is the dissociation rate constant independent of temperature, A_r frequency factor of dissociation, and ΔE_r potential barrier in the dissociation process. At higher temperatures (>200 K), the value of k_r^0 is negligible compared with that of the second terms in Eq. 2, since the Φ_r values is very small at 77 K. Equation 3 is derived from Eqs. 1 and 2.

$$\log\left(\frac{\Phi_r}{2\tau_f}\right) = \log A_r - \frac{\Delta E_r}{2.303RT} \qquad (3)$$

The plot of $\log\{\Phi_r(2\tau_f)^{-1}\}$ *vs.* T^{-1} obtained experimentally, which agrees with Eq. 3, is shown in Fig. 6a. The values of A_r and ΔE_r obtained from the linear plot in Fig. 6a are listed in Table 2.

Similarly, the rate constant k_n may be written as the following equation:

$$k_n = k_n^0 + A_n\exp\left(\frac{-\Delta E_n}{RT}\right) \qquad (4)$$

where k_n^0 is the rate constant for the radiationless processes of k_{ic} plus k_{isc} independent of temperature, A_n frequency factor and ΔE_n potential barrier in the radiationless processes. The k_n^0 values for **1** and **2** are estimated to be about $1.5\times10^7\ s^{-1}$ from the data of τ_f at 77 K and k_f. Therefore, one can derive Eq. 5.

$$\log(k_n - k_n^0) = \log A_n - \frac{\Delta E_n}{2.303RT} \qquad (5)$$

where the values of k_n can be evaluated experimentally by the following equation: $k_n = \tau_f^{-1} - (k_r + k_f)$. The plot of $\log(k_n - k_n^0)$ *vs.* T^{-1} is shown in Fig. 6b, which agrees with Eq. 5. The values of A_n and ΔE_n are also summarized in Table 2.

Dissociation Process. Let us consider the dissociation process k_r in the S_1 state. It is well-known that benzene derivatives undergo the β-bond fission upon irradiation[21] and the predissociation proceeds *via* the lowest excited singlet state $S_1(\pi,\pi^*)\ {}^1B_2$ to give

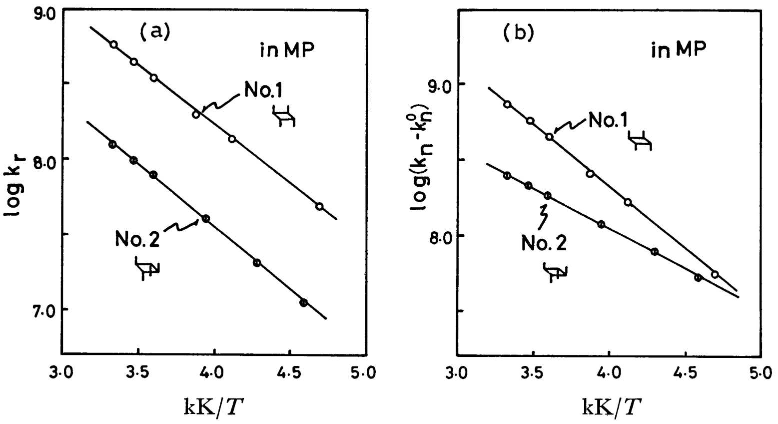
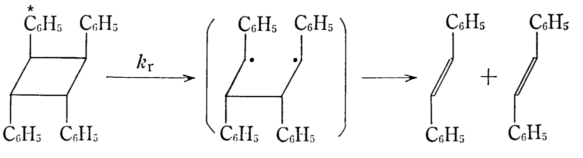


Fig. 6. (a) Plots of $\log k_r$ *vs.* T^{-1} and (b) plots of $\log(k_n - k_n^0)$ *vs.* T^{-1}.

Table 2. Frequency factors A_r and A_n and potential barriers ΔE_r and ΔE_n for k_r and k_n, respectively

Samples	$A_r/10^{11}\ s^{-1}$	ΔE_r/kcal mol^{-1}	$A_n/10^{11}\ s^{-1}$	ΔE_n/kcal mol^{-1}
1	2.0 (±0.3)	3.5 (±0.2)	4.2 (±0.5)	3.7_5 (±0.3)
2	0.79 (±0.07)	3.8_3 (±0.2)	0.13_8 (±0.03)	2.3_8 (±0.3)

the geminate radicals.[11,12] It seems that the photochemical cleavage of tetraphenylcyclobutanes has analogy to those of benzene derivatives. Kaupp[2,3] suggests that the photochemical reaction of tetraphenylcyclobutanes proceeds *via* a short-lived 1,4-biradical. Thus, the β-bond fission *via* the $S_1(\pi,\pi^*)$ of γ-1,*t*-2,*t*-3, *c*-4-tetraphenylcyclobutane (**1**), for example, can be expressed by Eq. 6. Of course, the β-bond fission of the starting molecule to produce the 1,4-biradical occurs from the vibrationally relaxed S_1 state judging from the values of τ_f. It is known that the vibrational relaxation times in condensed media are of the order of 10^{-12} s.[22] If the biradical had a lifetime enough to yield the starting material *via* the back reaction, the geometrical isomer (**2**) of the starting molecule besides *trans*-stilbene would be yielded as a photoproduct resulting from rotational diffusion and subsequent recombination of the biradical. However, such photochemical isomerization was scarcely observed during the photolysis of **1**. Similar result was obtained in the case of **2**. Thus, it is reasonable to consider that the biradical is very unstable and is instantaneously broken to yield two molecules of *trans*-stilbene as shown in Eq. 6. The dissociation quantum yields are, therefore, nearly equal to $\Phi_r/2$. It can be said that the β-bond fission of tetraphenylcyclobutanes proceeds nearly concertedly to give two molecules of *trans*-stilbene. This mechanism supports the assertion that there may be a significant concerted component to the cycloreversion reaction in the excited singlet state of *cis*-1,2-diphenylcyclobutane as reported by Jones and Chow.[23]



(6)

1 1,4-biradical *trans*-stilbene

The experimental results show quantitatively cis-effect in that **1** undergoes dissociation only to *trans*-stilbene and the values of k_r for **1** are greater than those for **2** (Fig. 6a). For instance, the dissociation rates k_r for **1** and **2** at 300 K can be estimated to be $5.5\times10^8\ s^{-1}$ and $1.2\times10^8\ s^{-1}$, respectively. The frequency factor A_r for **1** is greater than that for **2**, and the potential barrier ΔE_r is small in comparison with that for **2** as shown in Table 2. The cis-effect may be caused by a steric strain between adjacent benzene rings of **1**. The crossing probability from the S_1 state to the repulsive state of the β-bond between proper carbon atoms in cis-form may be larger than that in trans-form.

Radiationless Processes. The rate constant k_n is comprised of k_{ic} (internal conversion $S_1\rightarrow S_0$) plus k_{isc} (intersystem crossing $S_1\rightarrow T_1$). The k_n values increase considerably with elevating temperature according to Eq. 4. At higher temperatures (>200 K), the temperature dependent rate $(k_n-k_n^0)$ becomes very much greater than that of k_n^0 and the values of $(k_n-k_n^0)$ for **1** are large compared with those for **2**, as can be seen in Fig. 6b. The values of k_n for **1** and **2** at 300 K, for example, are evaluated to be $7.8\ (\pm0.7)\times10^8\ s^{-1}$ and $2.5\ (\pm0.3)\times10^8\ s^{-1}$, respectively. These facts indicate that steric effect is responsible for k_n as well as k_r at higher temperatures (>200 K).

The internal conversion rate constant k_{ic} is markedly enhanced due to a conformational change in the excited state.[13,24] In a similar manner, the k_n value may increase according to the enhancement of internal conversion. A conformational change among the substituted benzene rings of tetraphenylcyclobutanes in the S_1 state would be expected. However, the fact that no intramolecular excimer emission could be observed suggests the existence of large steric hindrance among the benzene rings in the S_1 state. Other possible mechanism for the large value of k_n at higher temperatures is explained by the "channel 3" decay where energy levels of isomers are incorporated as intermediate states of $S_1\rightarrow S_0$ internal conversion.[25]

The lifetimes τ_f (0.8±0.5 ns for **1** and 2.5±0.4 for **2**) are very shorter than that of toluene (34±2 ns in MP) at 300 K.

Finally, one can understand that such short lifetimes of the starting materials result from the large values of k_r and k_n (probably k_{ic}) at room temperature.

Conclusion

The photolyses of 1,2,3,4-tetraphenylcyclobutanes at higher temperatures (>200 K) proceed *via* the $S_1(\pi,\pi^*)$ state to give *trans*-stilbene nearly concertedly. The relaxation processes of the excited molecules are mainly comprised of the dissociation k_r and the other radiationless processes k_n, which are markedly dependent upon temperature. Significant cis-effect was also observed in photochemical and photophysical processes of the sample molecules.

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