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TRIPLET BENZENE-SENSITIZED CYCLOREVERSION OF ARYLCYCLOBUTANE

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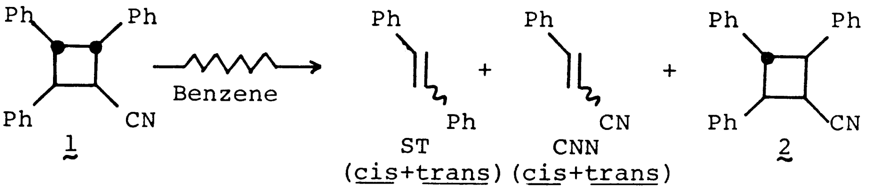
γ-Radiolysis of triphenylcyanocyclobutane(**1**) in benzene forms stilbene, cinnamonitrile and a stereo isomer of **1**. The effect of additives and the kinetic treatment show that the cycloreversion of **1** proceeds by benzene triplet sensitization. Spectroscopic measurement in pulse radiolysis suggests the existence of 1,4-biradical as an intermediate.

In recent years, cycloreversion reactions have been extensively studied. The cycloreversion proceeds by thermal or photochemical activations. Photochemical cycloreversion has become one of the most interesting fields.[1)] A clear account, however, is little given about the multiplicity of excited cyclobutane derivatives. In many cases, 1,4-biradicals were presumed as the intermediate in cycloreversion, although they were scarcely observed by spectroscopy.[1a)] Recently, a relatively long-lived triplet 1,4-biradical produced by Norrish type II reaction has been observed directly.[2)]

In this communication, we report the triplet sensitized cycloreversion of *r*-1,*t*-2,*t*-3-triphenyl-*c*-4-cyanocyclobutane(**1**) *via* the 1,4-biradical intermediate. Radiolysis of benzene(B) yields the triplet state of benzene in high efficiency (G=4.7).[3a)] Since the triplet state of benzene has relatively high energy(84.3 kcal/mol),[4)] γ-radiolysis of a benzene solution is a very useful method to produce the triplet state of the solute added in benzene.

γ-Radiolysis of **1**[5)] in benzene was carried out in Pyrex cells using a ^{60}Co source (4 kCi) at a dose rate of 6.19×10^{19} eV/g h at room temperature. The products were determined by GLC(OV-17). Stilbene(ST) and cinnamonitrile(CNN) isomers were obtained as main products and *r*-1,*t*-2,*c*-3-triphenyl-*c*-4-cyanocyclobutane(**2**),[6)] which is a stereo isomer of **1**, was produced as a minor product.



The effect of additives on the G values of ST and **2** is shown in Table 1. Addition of oxygen or naphthalene as a triplet quencher reduced the G values, while n-butyl chloride and methanol as ion scavengers scarcely affected. Thus, the main precursor of this reaction seems to be the triplet state of **1** produced by energy transfer

Table 1. Effect of Additives.[a)]

Additive	G(ST)[b)]	G(2)
None	1.8	0.5
Oxygen[c)]	1.4	0.4
Naphthalene	0.2	0.02
n-Butyl chloride	1.7	0.5
Methanol	1.6	0.5

a) [1]=0.02 mol dm^{-3}, [Additive]=0.2 mol dm^{-3}, Dose: 2.71×10^{19} eV.
b) Sum of cis and trans isomer.
c) Oxygen saturated.

Scheme 1.

$$B \xrightarrow{I} {}^3B^*$$
$${}^3B^* \xrightarrow{k_1} B$$
$${}^3B^* + 1 \xrightarrow{k_2} B + {}^3 1^*$$
$${}^3 1^* \xrightarrow{k_3} 1$$
$${}^3 1^* \xrightarrow{k_4} \text{Products}$$
$${}^3B^* + \text{Naph} \xrightarrow{k_5} B + {}^3\text{Naph}^*$$

from the triplet state of benzene.

We assume the mechanism (Scheme 1) for the radiolysis of 1 and the quenching of the triplet state of benzene by naphthalene (Naph). ${}^3B^*$ is the triplet state of benzene formed directly or indirectly from the ground state of a benzene molecule. A simple kinetic treatment gives Eq. (1) and (2):

$$\frac{1}{G^\circ} = \frac{1}{I}\left(1+\frac{k_3}{k_4}\right)\left(1+\frac{k_1}{k_2[1]}\right) \qquad (1)$$

$$\frac{G^\circ}{G} = 1+\frac{k_5[\text{Naph}]}{k_1+k_2[1]}\ , \qquad (2)$$

where G° and G are the sum of G values of ST and 2 in the absence and in the presence of naphthalene, respectively. A plot of 1/G° vs. 1/[1] gives a straight line, as shown in Figure 1. An extrapolated G value is calculated to be 3.6 from the intercept. This indicates that the cycloreversion proceeds in high efficiency (76 %) based on the G value of benzene triplet (G = 4.7).[3a)] From the slope and intercept of the

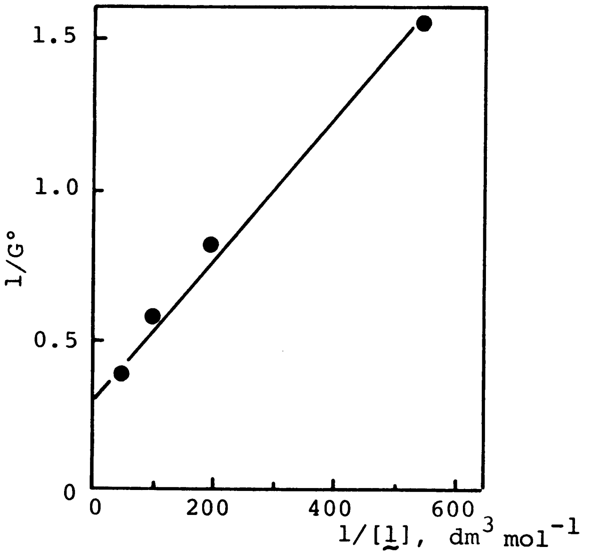


Figure 1. Dependence of G value on the concentration of 1. Dose: 2.71×10^{19} eV.

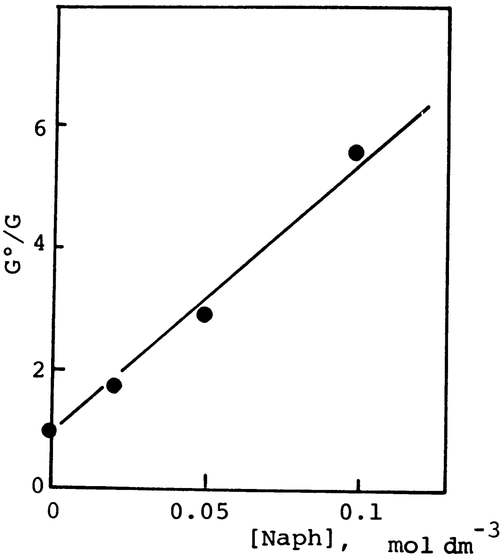


Figure 2. Dependence of G value on the concentration of naphthalene added in 1 solution. [1]= 0.02 mol dm^{-3}. Dose: 2.71×10^{19} eV.

straight line, k_1/k_2 is 9.2×10^{-3} mol dm^{-3}. Figure 2 shows a plot of G°/G vs. [Naph], from which it can be estimated that k_5/k_2 is 1.26. Assuming that k_5 is the diffusion-controlled rate constant ($k_5=1.0\times10^{10}$ dm^{3}mol^{-1}s^{-1}), we can calculate that $k_1=7.3\times10^7$ s^{-1} and $k_2=8.0\times10^9$ dm^{3}mol^{-1}s^{-1}. The lifetime of benzene triplet is estimated to be 14 ns from k_1 and almost agrees with a reported value.[7)]

Pulse radiolysis studies of benzene solution of **1** were carried out in Suprasil cells with 10 ns duration of 20 MeV electrons. The samples were free from oxygen either by several freeze-pump-thaw cycles or by bubbling with pure nitrogen for 15 min. Figure 3 shows optical absorption spectra of pure benzene and **1** solution measured at 200 ns and 700 ns after a pulse. In this wavelength range the optical density decreases with the time. This indicates the existence of transient species, although stilbene formed in this reaction has absorption around 300 nm.
The difference between the spectra at 200 ns and 700 ns is presented in Figure 4.

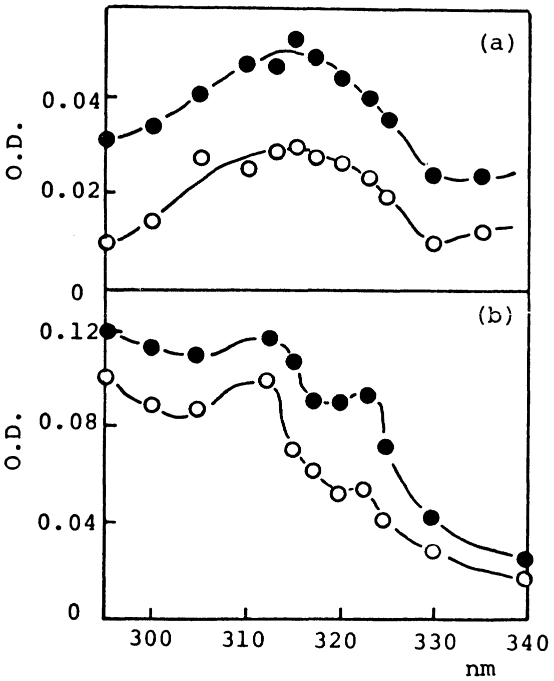


Figure 3. Optical absorption spectra at 200 ns (-●-) and 700 ns (-○-) after the irradiation of pure benzene(a) and **1** solution(b) with 10 ns pulse of 20 MeV electrons, 1.7 krad/pulse. [**1**]= 1.0×10^{-3} mol dm^{-3}.

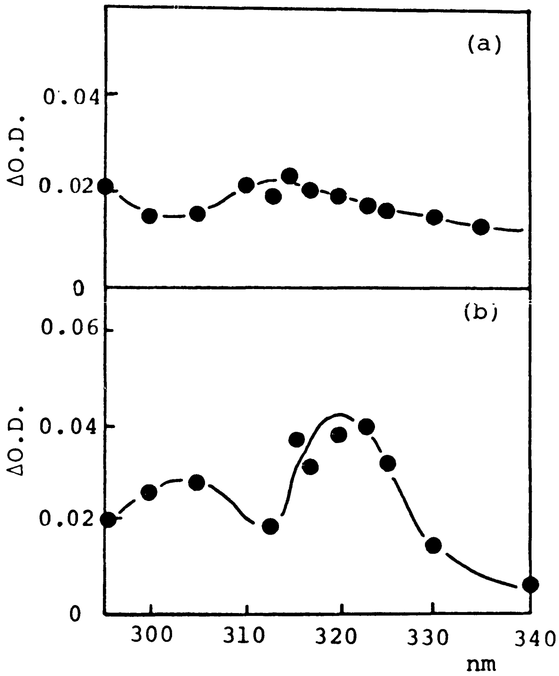


Figure 4. Difference between the spectra at 200 ns and 700 ns after a pulse. (a): benzene, (b): **1** solution.

The difference spectrum of benzene shows a broad and weak absorption, which is assigned to be a cyclohexadienyl radical.[8)] On the other hand, absorption maxima due to the transient species are observed at 305 nm and 320 nm in the case of **1**. This absorption spectrum is almost identical with that of the benzyl radical.[9)] Since the existence of the triplet 1,4-biradical intermediate is strongly supported by the formation of stilbene isomers and **2**, the transient absorption spectrum(Figure 4 (b)) seems to be that of a 1,4-biradical intermediate. The lifetime of the

1,4-biradical intermediate could not be determined owing to the overlap of the transient absorption and the permanent absorption.

A preliminary experiment showed that the transient species was quenched by oxygen. This result supports that a 1,4-biradical interacts with oxygen as reported by Small et al.10)

Furthermore, γ-radiolysis and pulse radiolysis studies were carried out about the r-1,t-2,t-3,c-4-tetraphenylcyclobutane. Similar results were obtained, although isomerization of the cyclobutane was not observed.

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5) **1** was prepared by UV irradiation of t-ST and t-CNN in acetonitrile and recrystallized three times from ethanol, mp. 136.5-137.5 °C. The structure assignment will be published elsewhere.
6) **2** was prepared by UV irradiation of t-ST and c-CNN in benzene.
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8) Cyclohexadienyl radical is produced by radiolysis of benzene,

$$C_6H_6 \rightsquigarrow \cdot C_6H_5 + H \qquad C_6H_6 + H \longrightarrow \cdot C_6H_7$$

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