

cis-trans Isomerization of 1,2-Bis(4-methoxyphenyl)-
cyclopropanes via a Cationic Chain Mechanism

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Radiation-induced cis-trans isomerization of 1,2-bis(4-methoxyphenyl)cyclopropanes(CP) has been investigated in benzonitrile solution. The isomerization from cis-CP to trans-CP proceeded efficiently ($G = 80$) via a cationic chain mechanism. Three types of transient species were spectroscopically detected by pulse radiolysis and γ -irradiated low-temperature matrix studies. The reaction mechanisms are discussed on the basis of these direct observations.

It has been well-known that diarylcyclopropanes isomerize via excited states, radicals, and radical ions.¹⁾ However, the mechanistic details for the isomerizations via the radical cation remain obscure. It has been reported that the photo-induced isomerization of 1,2-diphenylcyclopropane in the presence of an electron acceptor proceeds via an electron transfer mechanism.^{2,3)} In this case, back electron-transfer occurs within the radical ion pair involving the ring-opened radical cation which leads to the formation of a 1,3-biradical intermediate. By the rapid ring-closure of the biradical, the isomerization reaction comes to completion. On the other hand, Mizuno et al. reported that cis-1,2-bis(4-methoxyphenyl)cyclopropane (cis-CP) isomerizes by a cationic chain process.⁴⁾ Recently, it has been reported that the isomerization of a methoxyphenyl derivative of cyclopropane is induced by a one-electron chemical oxidation even at -90°C .⁵⁾ In the present paper we would like to report the chemical reactivity of free radical cation of CP on the basis of the direct observation of the transient intermediates.

Aerated or deaerated benzonitrile solutions of cis-CP were irradiated by ^{60}Co γ -ray. The 100 eV yields (G value) of trans-CP increased up to 22.6 (at 36 mmol dm^{-3} of cis-CP) with increasing the concentration of cis-CP.⁶⁾ The double reciprocal plots of $G(\text{trans-CP})$ against the concentrations of cis-CP are shown in Fig. 1. The limiting G value which is obtained by the extrapolation of G values to an

infinite concentration was about 80. The reaction was completely retarded by the addition of a small amount of triethylamine (3 mmol dm^{-3}). Since a G-value of radical cation formation in neat benzonitrile is less than one,⁷⁾ the present isomerization is concluded to proceed by a cationic chain mechanism. Enhancement of the isomerization by added oxygen might be caused by an increased yield of radical cation and the increased lifetime due to the trapping of solvated electrons by oxygen.⁸⁾ The isomerization from trans-CP to cis-CP was very inefficient; $G(\text{cis-CP})$ was 2.3 at 25 mmol dm^{-3} of trans-CP in an aerated benzonitrile solution.

The absorption spectra of a γ -irradiated butyl chloride solution of CP at low temperature are shown in Fig.

2.⁹⁾ The spectrum observed for cis-CP at 77 K exhibited absorption bands with λ_{max} at 490 and 560 nm besides a very broad band around 800 nm. Upon warming up to 100 K the absorption band at 490 nm decreased gradually and a new sharp absorption with λ_{max} at 580 nm appeared. On the other hand, the spectrum for trans-CP at 77 K with λ_{max} at 400 and a broad band around 800 nm was different from that of cis-CP and the formation of the new band at 580 nm was also weakly observed.

The transient absorption spectra recorded at various times after an 8-ns pulse irradiation¹⁰⁾ to 1,2-dichloroethane solutions of CP at room temperature are shown in Fig. 3. The absorption spectra observed for cis-CP were somewhat

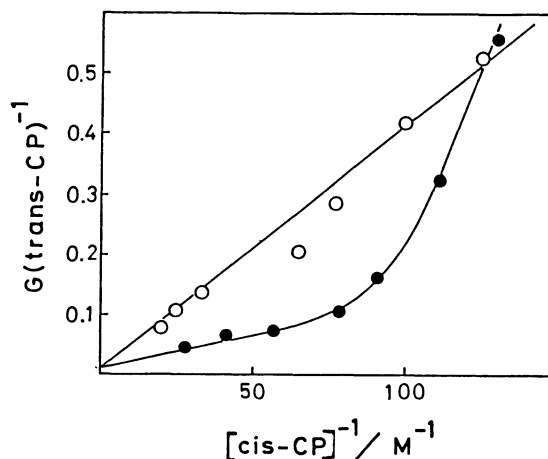


Fig. 1. γ -Radiolysis of benzonitrile solution of cis-CP.

—○— : deaerated solution.
—●— : aerated solution.
Dose : 430 Gy/h.

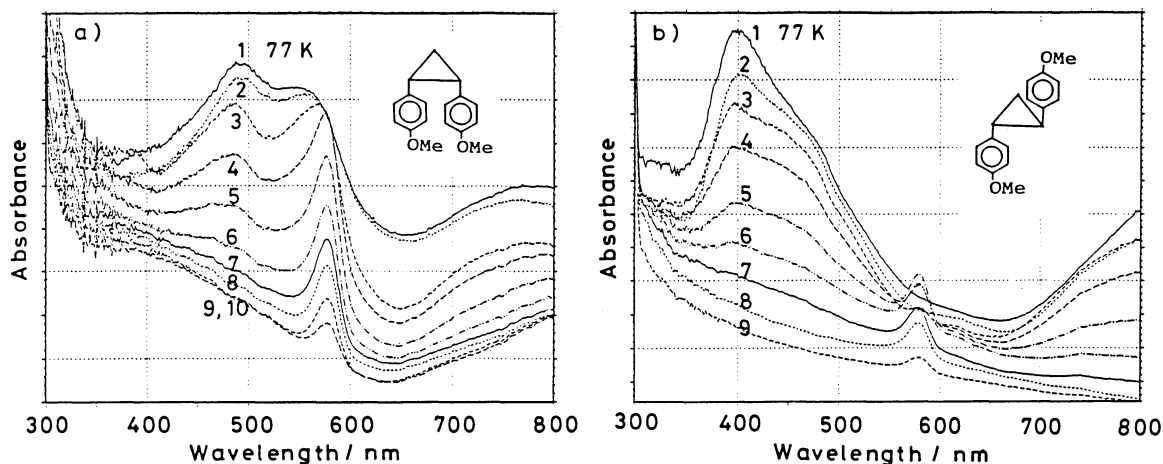


Fig. 2. Absorption spectra of γ -irradiated BuCl solution of CP (20 mmol dm^{-3}) at 77 K and on warming up to about 100 K. a) cis-CP b) trans-CP
1: 77 K 2-9 or 2-10: during the warming.

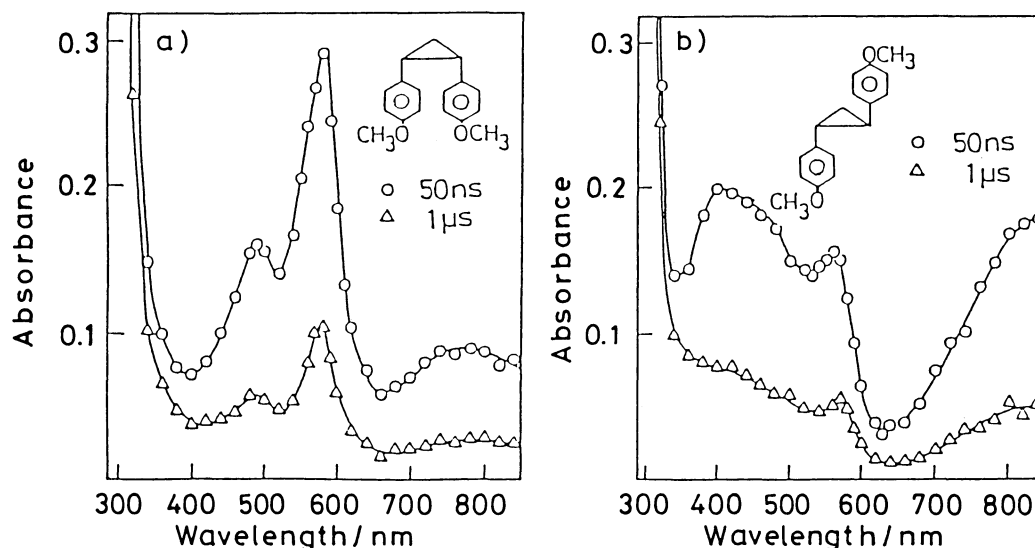
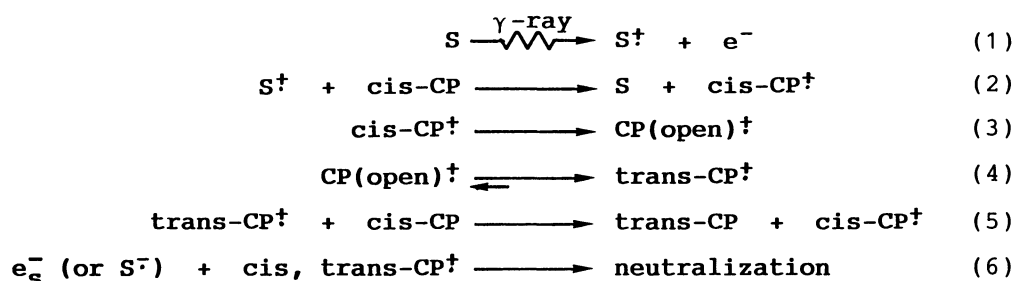


Fig. 3. Pulse radiolysis of 1,2-dichloroethane solutions of CP (5 mmol dm^{-3}) at room temperature. a) cis-CP b) trans-CP.

different from that at 77 K and characterized by a very strong 580-nm band. On the other hand, the absorption spectra of trans-CP were rather similar to that at 77 K and the 580-nm band was very weakly detected. Since these transient species can be quenched by the addition of triethylamine (25 mmol dm^{-3}), it is clear that these are cationic species.

Let us consider the structure of these transient species. The transient absorption bands with λ_{max} at 490 nm and 400 nm observed at 77 K may be assigned to the cis- and trans-CP radical cation, respectively. On the other hand, the 580-nm band commonly observed in both systems but in a different extent may be assigned to a ring-opened radical cation, whose formation was predominant for cis-CP in consistent with the high efficiency of the isomerization from cis-CP to trans-CP.

On the basis of the spectroscopic behavior of the intermediates and the oxidation potentials of cis-CP and trans-CP, the following radical-cation chain mechanism (Reactions 1-6) is consistent with the present isomerization from cis-CP to trans-CP.



Initial ionization of solvent molecules (s) by γ -ray is followed by an inter-molecular charge transfer to the solute molecule, cis-CP (Reaction 2) since the ionization potential of cis-CP is sufficiently lower than that of the present solvent (benzonitrile or butyl chloride).¹¹⁾ Chemical reactivities of cis-CP[†]

thus formed (Reactions 3 and 4) are compatible with the present spectroscopic observation. The key step for the chain mechanism is charge transfer from trans-CP⁺ to cis-CP (Reaction 5). This step is endothermic by ca. 10 kJmol⁻¹ on the basis of oxidation potentials of cis- and trans-CP.¹²⁾ However, the energy will be sufficiently provided by thermal energy or compensated by a nonvertical charge transfer. The final step (Reaction 6) is neutralization of cationic species derived from the solute by solvated electron or more probably by anionic species derived from solvent (S⁻ or Cl⁻). The mechanistic details for the inefficient isomerization from trans-CP to cis-CP are not clear at present.

Finally, we would like to emphasize that the cis-trans isomerization of CP proceeds through a free cationic mechanism. Thus, the efficiency becomes very high under these reaction conditions. Such an efficient isomerization could not be observed in the case of 1,2-diphenylcyclopropane and 1,2-bis(4-methylphenyl)cyclopropane.

The authors wish to thank the members of the Material Analysis Center of ISIR for the spectral measurement by a Multichannel Photodetector.

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- 8) The similar enhancement by oxygen was also observed in the photo-reaction; see Ref. 4.
- 9) The spectra were measured by a Multichannel Photodetector (MCPD-100, Otsuka Electronics Co.).
- 10) Experimental details of pulse radiolysis were reported elsewhere [H. Nishino, S. Toki, and S. Takamuku, *J. Am. Chem. Soc.*, **108**, 5030 (1986)].
- 11) On the basis of ionization potentials of butyl chloride (10.67 eV), benzonitrile (9.71 eV), and anisole (8.21 eV), the exothermic charge transfer is readily estimated. Although the ionization potentials of CP's are not available, they seem to be lower than that of anisole.
- 12) The oxidation potentials of cis- and trans-CP were measured as 0.65 and 0.55 V versus Ag/Ag⁺ in acetonitrile, respectively.

(Received December 1, 1987)