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**Conformational Peculiarity in the Photochemical Reaction of
10-(9*H*-Xanthenylidene)-9(10*H*)-anthracenone¹⁾**

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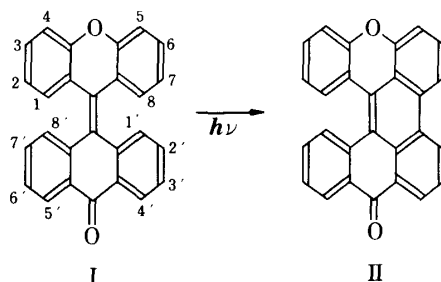
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Conformational peculiarity of 10-(9*H*-xanthenylidene)-9(10*H*)-anthracenone was studied in relation to the temperature effect in the photochemical cyclization and reduction reactions. On the basis of the experimental result that the temperature effect is negative for the former reaction but positive for the latter reaction, it was concluded that the population of the planar structure of the above molecule in solution decreases gradually at higher temperatures in favor of a twisted structure which contributes to the radical formation. This conclusion is consistent with the results of our previous polarographic and electron spin resonance studies of some thermochromic ethylenes. On the other hand, the planar structure of the molecule appears to be predominant over a wide range of temperature in the crystal state.

Keywords—absorption spectra; conformation; photochemical reaction; radical; thermochromic ethylene

10-(9*H*-Xanthenylidene)-9(10*H*)-anthracenone (I) is one of the thermochromic ethylenes whose conformational changes have recently become of interest.²⁾ We have already clarified by an electron spin resonance (ESR) study and by semi-empirical molecular orbital (MO) calculations that the anion radical generated by reduction of the neutral molecule I with potassium metal or with a platinum cathodic electrode has a perpendicularly twisted structure.³⁾ On the other hand, our polarographic study combined with HMO calculations has suggested that the neutral molecule I has an almost planar structure in solution.⁴⁾

In order to obtain detailed information about the conformational features of the neutral molecule I, we made use of the photochemical intramolecular cyclization from I to oxapenenone (II).⁵⁾ This is because the temperature effect in the above reaction is expected to reflect accurately the population of the planar structure of compound I. To investigate the effects of O₂ in the solvent on the photochemical reaction process, the temperature dependence of the photo-cyclization of I will be compared with that of the photo-induced radical formation.



Experimental

Compound I was synthesized and purified by a reported method.⁵⁾ Absorption spectra of the sample in solution were measured on a Shimadzu UV-360 spectrophotometer and the temperature was controlled by the use of a Shimadzu SPR-5 temperature controller. The crystal absorption spectra of I were measured for a circular transparent tablet prepared by the procedure commonly used in infrared spectral measurements.

For measurements of the photochemical reaction, compound I was dissolved in Wako spectrograde toluene. The solution, contained in an optical cell kept at various temperatures, was irradiated with a 500 W xenon lamp fitted with Toshiba V-CIA filter. The photochemical reaction was followed by measuring the absorbance changes at appropriate time intervals. The intensity of the exciting light was measured with a potassium ferri-oxalate actinometer and was found to be $1.1 \times 10^{-5} \text{ M s}^{-1} \text{ cm}^{-2}$.

ESR measurements of radical formation during similar irradiation were carried out on a JEOL 3BSX spectrometer. Compound I was dissolved in Merck spectrograde tetrahydrofuran dehydrated with Na-K alloy and outgassed under a vacuum. The reaction was followed by measuring the change of ESR signal intensity.

Results and Discussion

Figure 1 shows the changes of the solution absorption spectra of compound I during irradiation at *ca.* 380 nm (corresponding to the absorption peak in the spectrum of I). Irradiation was carried out on a $5.2 \times 10^{-5} \text{ mol dm}^{-3}$ toluene solution of I at various temperatures ranging from 0 to 80 °C, and the absorption spectrum was taken every 1 to 5 min. The cyclization reaction of I occurred effectively during the irradiation.

The temperature dependence of the increase of the absorption peak at 486 nm of the product compound II was measured. It was found that the rate of the intramolecular cyclization of I is remarkably affected by temperature in such a way that the reaction rate becomes slower at higher temperatures.

At the termination of the reaction, the product II was separated from the solution by evaporation of the solvent.

After several recrystallizations, the purity of the product was confirmed by elemental analysis and mass spectrometry.

Since the light-absorbing species remaining in solution is now restricted to compound I, we can apply the basic formula generally valid for the primary process of a photochemical reaction,⁶⁾ which indicates that the rate of the reaction is proportional to the light intensity, *i.e.*

$$\ln(\exp(\epsilon cd) - 1) - \ln(\exp(\epsilon c_0 d) - 1) = -1000\phi I_0 t,$$

where ϵ is the molar absorptivity of I, c is the concentration of I, c_0 is the initial concentration of I, d is the light path length, ϕ is the quantum yield, I_0 is the light intensity, and t is the reaction time. Figure 2 shows a plot of $\ln(\exp(\epsilon cd) - 1)$ against time, where the slope gives the

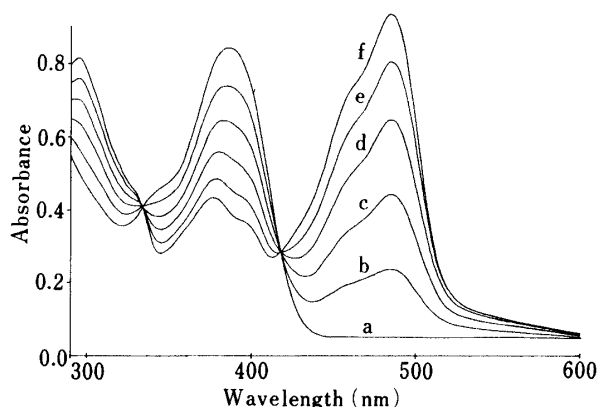


Fig. 1. Change of the Solution Absorption Spectrum Observed upon Irradiation

A $5.2 \times 10^{-5} \text{ mol dm}^{-3}$ toluene solution of I was irradiated at room temperature. Curve a indicates the initial absorption spectrum of I. Taking the course $a \rightarrow b \rightarrow c \dots$, it changed to curve f after the irradiation. The irradiation times were 2.5 min (b), 6 min (c), 10 min (d), 16 min (e) and 32 min (f).

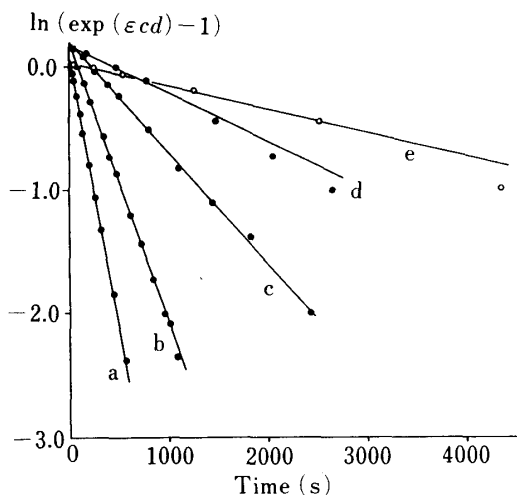


Fig. 2. The Rate of Photochemical Cyclization in Solution

Curve a indicates the rate at 2°C; b, at 20°C; c, at 39°C; d, at 59°C; e, at 77°C.

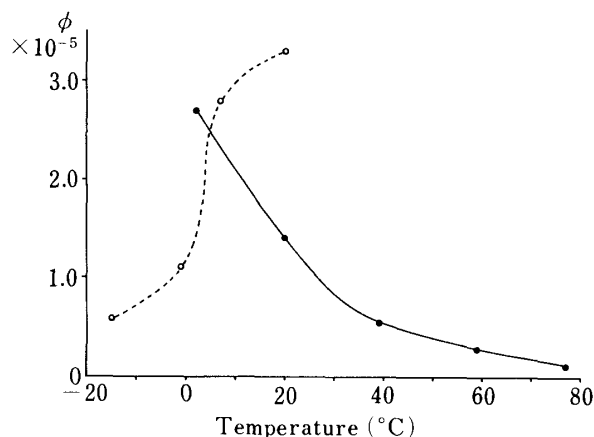


Fig. 3. The Temperature Dependence of Quantum Yields of Photocyclization and Radical Formation

The solid line indicates the photocyclization of I and the broken line indicates the radical formation. The scale on the vertical axis is for the solid line. The quantum yield is shown as relative values for the radical formation because the radical concentration was not determined.

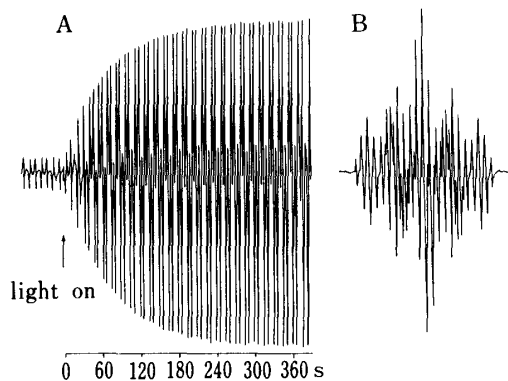


Fig. 4. The Time Course of Radical Generation

A: The change of intensity of the maximum signal at room temperature on irradiation with light.

B: The ESR spectrum generated by irradiation with light.

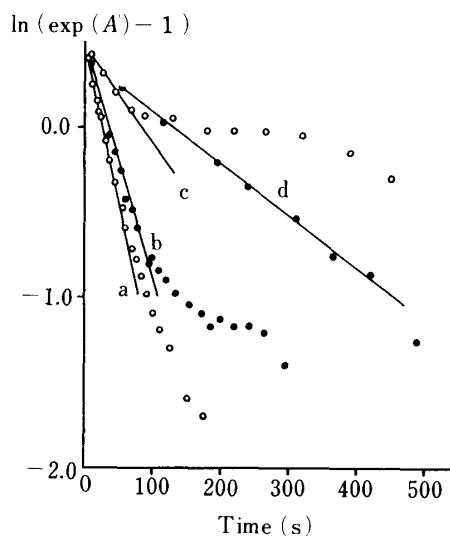


Fig. 5. The Rate of Radical Generation from I

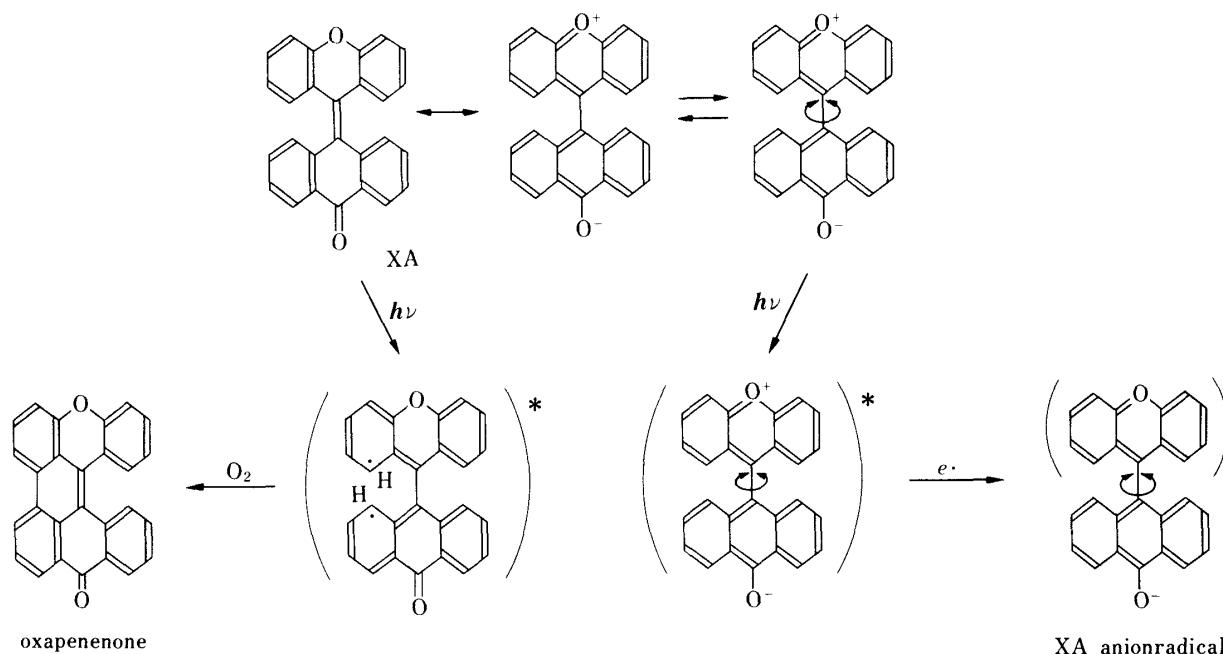
Each curve shows the time-dependent change of the ESR signal at a different temperature. The value A' is relative. a, 20°C; b, 7°C; c, -1°C; d, -15°C.

quantum yield. Figure 3 shows that the quantum yield (the solid line) decreases remarkably at higher temperatures. This negative temperature effect suggests that the population of the planar conformation of I in solution decreases at higher temperatures so that positions 1' and 8 are not in appropriate locations for the dehydrogenation.

On the other hand, the reaction rate of the photo-induced radical formation increases at higher temperatures. Figure 4 shows the radical formation followed in terms of the peak of the ESR signal. Figure 5 shows the time-dependent change of the signal intensity measured at various temperatures. It is clear from the log plot of the curve that it is not a simple first-order

reaction, but the formation rate of the anion radical definitely increases at higher temperatures. This positive temperature effect is in contrast to the negative temperature effect on the photo-cyclization rate in solution.

The above-mentioned results indicate that the process of the photochemical reaction is affected by O_2 , namely, that the excited reactive state (probably triplet) of I generated in non-deoxygenated solvent by light irradiation interacts with O_2 in the solvent to result in dehydrogenative cyclization, while that of I generated in deoxygenated solvent by light irradiation takes an electron from the solvent to form the anion radical. This is illustrated in the following scheme.



When compound I in the crystal state was irradiated at *ca.* 380 nm, it also changed to II as confirmed by the increase of absorbance of II. In this case, however, no temperature effect on the reaction rate could be recognized over a wide temperature range from 20 to 80 °C. It appears that the molecule in the crystal state is stabilized in a planar structure.

It may be concluded that the planar structure of the molecule I in solution changes with increasing temperature to a twisted structure which may hinder the intramolecular dehydrogenation because of an inappropriate distance between positions 1' and 8, whereas the planar structure of the molecule I in the crystal state is predominant over a wide range of temperature.

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References and Notes

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