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The Dianion of 9,9′-Bixanthenylidene and Its Reaction with Oxygen. A Contribution to Photochromism

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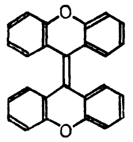
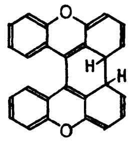
The anion produced by the reduction of 9,9′-bixanthenylidene with sodium or potassium metal was identified with the dianion by pulse radiolysis. It appears that the dianion is twisted around the central ethylenic bond. The dianion reacts with oxygen at 100 K to produce a colored form, the spectrum of which is in accord with that of the transient species observed in the flash photolysis of 9,9′-bixanthenylidene. The colored form is expected to be produced *via* a twisted 9,9′-bixanthenylidene, because the oxygen is considered to remove electrons from the twisted dianion. This twisted intermediate may also participate in the photochromic or thermochromic reaction in which the same-colored form is produced.

9,9′-Bixanthenylidene is known to be one of the thermochromic ethylenes, and the structure of the colored form has been assumed to be a dihydro-form of a species, A, which is obtained as the stable photoproduct.[1,2)]



Species A



Dihydro- form of A

The same color is observed on UV irradiation at low temperatures, and it fades reversibly in the dark in a few minutes.[3)] The above structure of the colored form was assumed by analogy from the facts that *cis*-stilbene, which has the same ethylenic bond, shows photochromism in a deaerated solution and, that its colored form is considered to be the dihydro-form of phenanthrene.[4,5)]

A similar dihydro-form has been assumed for the colored form of thermochromic 10,10′-bianthrone. It has been found that, in the presence of oxygen, helianthrone and *meso*-naphthobianthrone are produced; the dihydro-forms of these stable photoproducts are produced in the absence of oxygen.[6–8)]

It seems, therefore, that in many cases the colored form of the thermochromic ethylenes is a dihydro-form of the stable photoproducts.

In 1959, Woodward and Wasserman[9)] showed that the reaction of the anion of 10,10′-bianthrone with methanol gave rise to the formation of the colored form. We ourselves have found that the colored form of 9,9′-bixanthenylidene is produced by the reaction of its anion with oxygen at low temperatures. The mechanism of this reaction has now been studied by using flash photolysis and pulse radiolysis with the aim of elucidating the mechanism of the photochromic reactions.

Experimental

9,9′-Bixanthenylidene was prepared by the reduction of xanthone with zinc powder and acetic acid in the presence of hydrochloric acid. The purification was done by recrystallization from a methanolic solution. The tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MTHF) were stored on the metallic alloy of potassium and sodium *in vacuo*. The benzene and ethanol were extra-pure reagents from Wako Pure Chemical Industries.

The details of the flash photolysis apparatus have been described previously.[10)] The photolysis flash consisted of two xenon lamps, 80 J in power and 50 μs in duration.

The pulse radiolysis was carried out by using 2.7 MeV pulsed electrons, 0.5 or 1.0 μs in duration, generated from a Van de Graaff accelerator; the details have been described elsewhere.[11)]

The absorption spectra of stable products were recorded on a Cary 14 R spectrophotometer.

Results and Discussion

Flash Photolysis. Figure 1 shows the transient absorption spectrum observed immediately after the flash photolysis of 9,9′-bixanthenylidene in a deaerated benzene solution. The spectrum had an absorption peak at 620 nm and decayed with a first-order rate constant of $1.8 \times 10^4\ \mathrm{s}^{-1}$ at room temperature. In an aerated solution, the same spectrum was observed; the amount of intermediate species produced (at 620 nm) per flash and the decay rate were identical with those in a deaerated solution within the limits of experimental errors. These results indicate that the transient species may be produced *via* the excited singlet state.

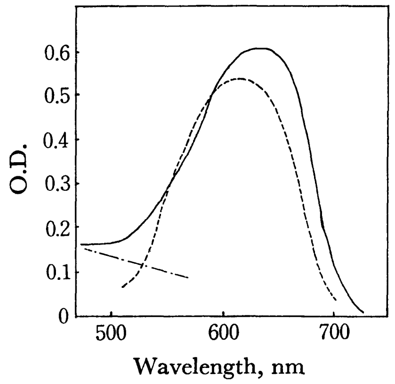


Fig. 1. Absorption spectra of the colored substance.
------: The transient species formed upon flash photolysis in benzene at room temperature;
——: The colored substance produced by the reaction of the dianion of 9,9′-bixanthenylidene with oxygen at low temperature (100 K) in MTHF.

On the other hand, Hirshberg and Fischer[3] found that the colored form is produced on the UV irradiation of 9,9′-bixanthenylidene at low temperatures. The spectrum is in accord with the transient spectrum obtained by the present flash photolysis. They also studied the dependence of the decay rate of the colored form on the temperature, and evaluated the kinetic parameters of a "critical increment" [12] and a frequency factor over the temperature range from −150 to −170 °C. Using these parameters, one can estimate the rate constant of the decay at room temperature to be $2.5 \times 10^4\ \mathrm{s}^{-1}$; this value is in agreement with that obtained for the transient species by the flash photolysis.

From these results, it may be concluded that the transient absorption in the flash photolysis is due to the colored form of 9,9′-bixanthenylidene produced by UV irradiation at low temperatures.

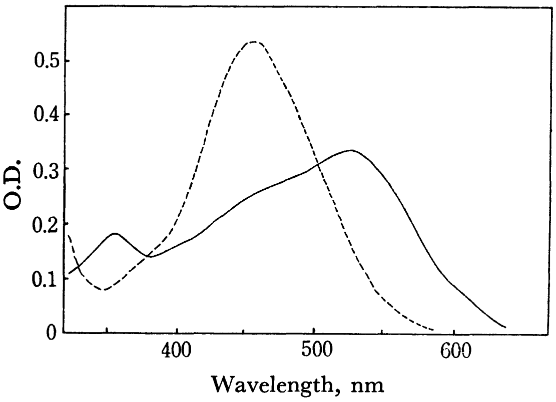


Fig. 2. Absorption spectra of the dianion of 9,9′-bixanthenylidene (——) and potassium xanthenylide (------) in MTHF at room temperature.

Reaction of Dianion with Oxygen. When 9,9′-bixanthenylidene was reduced in a MTHF solution by metallic sodium or potassium, the solution turned reddish-brown and had an absorption peak at 520 nm, as is shown in Fig. 2. The colored species may be regarded as a monoanion or a dianion because the color of the solution fades rapidly upon the introduction of air. It was identified with the dianion by pulse radiolysis, as will be described in the next section.

The solution turned brilliant blue and had an absorption peak at 630 nm when the dianion was in contact with the air at a low temperature (100 K). The resulting spectrum is similar to that of the transient species produced by the flash photolysis, as is shown in Fig. 1, indicating that the two species are identical. The colored form was stable so long as the solution was kept at 77 K, but it disappeared rapidly with an increase in the temperature. This suggests that the viscosity of the solution plays an important role in the reversion reaction (colored→colorless).

Hirshberg and Fischer[3] found that photochromism occurs above −120 °C in the mixed glassy media of methanol and ethanol. They also mentioned that the phenomenon takes place only in a fluid solution.

Pulse Radiolysis of 9,9′-Bixanthenylidene. Figure 3 shows the transient spectrum of the monoanion of 9,9′-bixanthenylidene produced by pulsed electron irradiation in a MTHF solution at room temperature. The ion is produced according to:

$$\mathrm{MTHF} \rightsquigarrow e^- + \mathrm{MTHF}^+$$

$$e^- + \mathrm{M} \longrightarrow \mathrm{M}^- \quad (\mathrm{M}\text{: solute}).$$

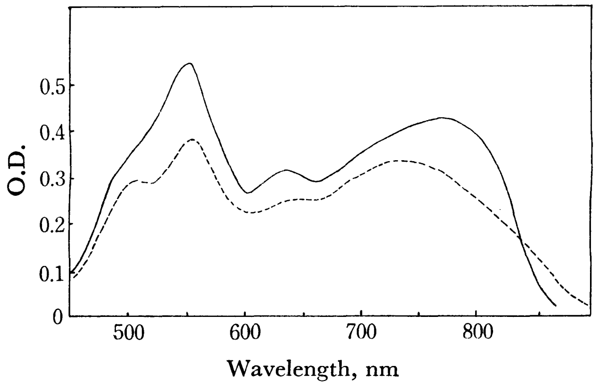


Fig. 3. Absorption spectra of the monoanion of 9,9′-bixanthenylidene.
——: Produced by γ-ray irradiation at 77 K;
------: Produced by pulse radiolysis at room temperature.

A similar spectrum of the monoanion was observed by the steady Co^{60}-γ rays irradiation of 9,9′-bixanthenylidene in MTHF at 77 K.

In view of the difference between the spectrum of this monoanion and that of the ion produced by the reduction of 9,9′-bixanthenylidene with alkali metals, the latter one may possibly be regarded as being due to the dianion.

It is also noted that the monoanion does not appear to change in structure in going from 77 K to room temperature, because the electronic spectra are similar at both temperatures.

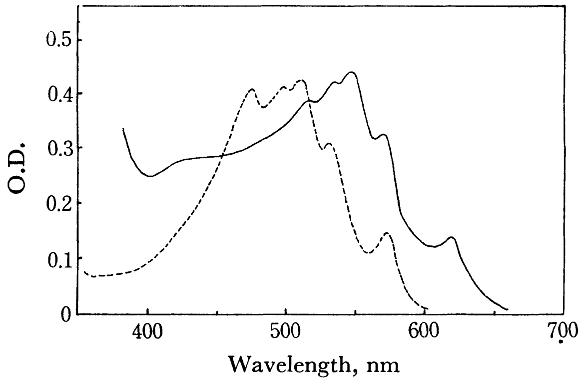


Fig. 4. Absorption spectra of the dianion of 9,9′-bixanthenylidene (——) and potassium xanthenylide (------) at 77 K in MTHF.

Structure of the Dianion. In Fig. 4, the absorption spectrum of the dianion is compared with that of potassium xanthenylide, both of which were obtained in MTHF solutions at 77 K.

If the dianion is assumed to be twisted around the ethylenic bond, the spectrum is expected to be similar to that of the xanthenyl carbanion. Although the absorption band of the dianion is located in a longer wavelength region compared with that of the carbanion, the same vibrational progression is found in both spectra. It is, therefore, reasonable to assume that the dianion has a twisted structure at 77 K. The slight shift of the absorption band of the dianion to longer wavelengths may be interpreted in terms of the bathochromic effect due to the substituted xanthenyl moiety.

The structure of the stilbene dianion was discussed by Garst *et al.*,[13] who proposed a geometry in which the two benzylidene moieties are rotated around the central ethylenic bond to an angle of 90°. Suzuki *et al.*[14] studied the twisted forms of the dianion of stilbene derivatives and interpreted the absorption spectra on the basis of the MO calculation.

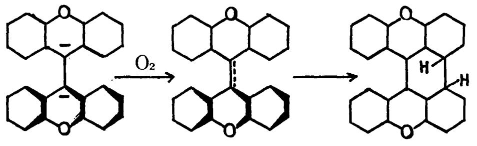
The dianion with a central ethylenic bond is likely to be twisted around the bond.

Intermediate as a Precursor of the Colored Form. The reaction of oxygen with anions of aromatic molecules is considered to give rise to the formation of the original molecules:

$$M^{-} \text{ (or } M^{2-}) + O_2 \longrightarrow M \text{ (M: aromatic molecule)}$$

where oxygen is assumed to act simply as an electron acceptor.

In the case of the 9,9′-bixanthenylidene dianion, the reaction with oxygen at low temperatures has been shown to produce a colored compound, not original 9,9′-bixanthenylidene. This result may be explained by assuming that the elimination of two electrons from the twisted dianion gives rise to the formation of a metastable intermediate which is also twisted and which immediately forms the colored compound:



(Twisted intermediate)

In view of the fact that the same colored substance is formed in either the photochromic or thermochromic reaction, this intermediate is formed in both cases, although it could not be detected by the flash photolysis.

We wish to thank Miss. Yuriko Moribe for her assistance with the flash photolysis study, and Dr. Tadamasa Shida and Dr. Shigeyoshi Arai for thier enlightening discussions.

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