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Studies of cis-trans Isomerization of Stilbene Anion Radicals by Means of a Flow-Electrolysis ESR Method

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Mechanism and kinetics of the cis-trans isomerization of stilbene anion radicals was revealed with a flow-electrolysis ESR method in N,N-dimethylformamide.

The isomerization of cis-stilbene anion radical (CS^-) produced from reduction of cis-stilbene (CS) by a suitable electron donor has been extensively investigated by Szwarc et al.1-4) They have found that CS^- quantitatively converted into the anion radical (TS^-) of the trans isomer (TS) through the rapid isomerization of the dianion (CS^{2-}). Since the isomerizing intermediate, CS^{2-}, was generated from further reduction of CS^- by the electron donor,4) this isomerization is obviously promoted by the electron donors. Therefore, for an understanding of the isomerization of CS^- itself, it is inevitable to investigate the isomerization of CS^- in a solution which does not contain electron donors.

Because the spectrophotometric observation of CS^- may induce its photoisomerization,5) an ESR technique is desirable for the study of the isomerization of CS^-. However, the observation of the ESR spectrum of CS^- is very difficult due to the fact that the isomerization of CS^- to TS^- occurs rapidly, and the full spectrum of CS^- has so far been observed only at a very low temperature of -90 °C.6)

These problems were overcome by using a flow-electrolysis ESR method which we have developed.7) This method enables us not only to observe ESR spectra of rather unstable ion radicals but also to adjust their concentrations quantitatively. Therefore, kinetic study of the cis-trans isomerization of stilbene anion radicals could be carried out using this method. Furthermore, electrochemically generated CS^- can be expected to isomerize without the possible interactions of chemical reductants. We report herein that the mechanism and kinetics of the isomerization

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of CS^- itself were revealed for the first time.

An N,N-dimethylformamide (DMF) solution containing 2 mM (1 M = 1 mol dm^{-3}) cis-stilbene and 0.1 M tetraethylammonium perchlorate in a reservoir was deoxygenated and deaerated. The solution flowed into the electrolytic flow-cell and was electrolyzed outside of the ESR cavity. The electrolyzed solution rapidly flowed into the capillary tube placed in the cavity. The dead time of the flow-cell was 10 s at a flow rate of 0.2 cm^3 min^{-1}.

The symmetric ESR spectrum observed on reduction of CS at room temperature was identical with that of TS^-. However, it changed considerably with decreasing the temperature. When CS was reduced at -10 °C, the ESR spectrum showed an asymmetric pattern, indicating that both TS^- and CS^- were present in the solution. At a lower temperature of -30 or -50 °C, the ESR spectrum became symmetric again, and it was quite different from that of TS^-. Figure 1A shows the ESR spectrum obtained at -50 °C. The ESR spectrum (Fig. 1B) simulated using the hyperfine coupling constants (hfcc's, in mT) of **a**(2H, ethylene) 0.271, **a**(2H, ortho-1) 0.198, **a**(2H, ortho-2) 0.291, **a**(2H, meta-1) 0.031, **a**(2H, meta-2) 0.090, **a**(2H,

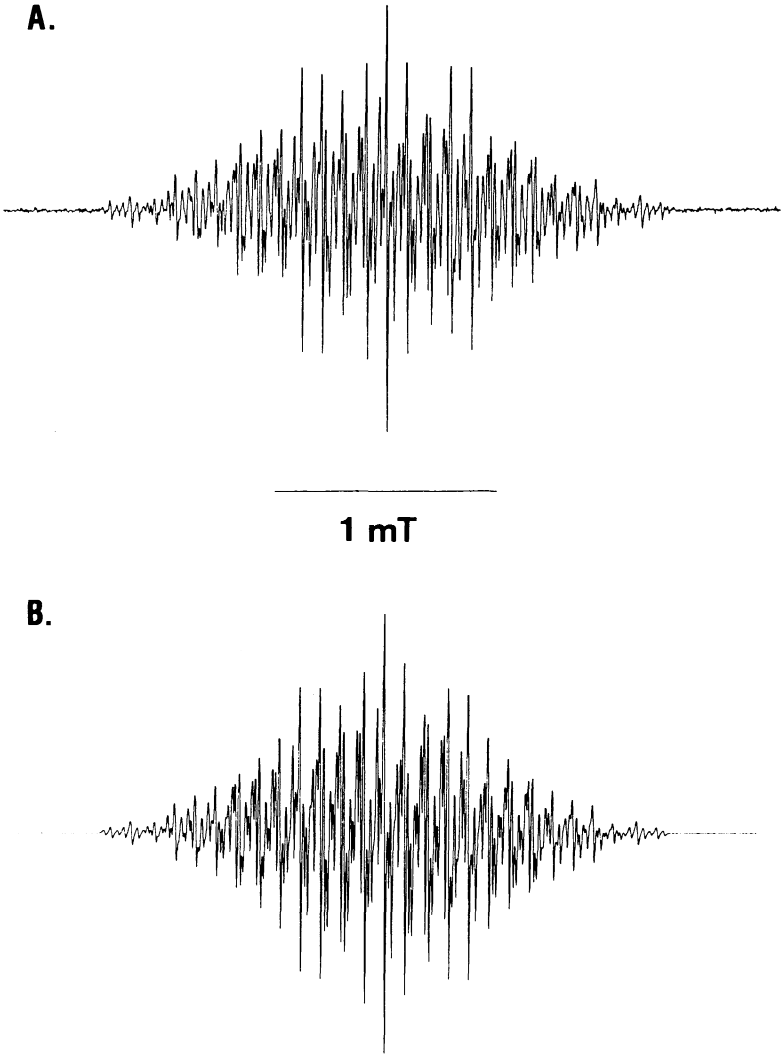

Fig. 1. (A) ESR spectrum of CS^- in DMF at -50 °C; (B) simulated spectrum of (A).

para) 0.381 is in excellent agreement with the experimental one and the hfcc values determined were almost same as those reported, i.e., **a**(2H, ethylene) 0.268, **a**(2H, ortho-1) 0.194, **a**(2H, ortho-2) 0.291, **a**(2H, meta-1) 0.030, **a**(2H, meta-2) 0.088, **a**(2H, para) 0.386.[6)] Therefore, the detected radical was assigned to be CS^-.

Because the total spectral extension of CS^- was markedly narrower than that of TS^-, the progress of the isomerization from CS^- to TS^- could be monitored by looking at the ESR signal which was not overlapped with those of CS^-. Figure 2A shows the low-field part of the ESR spectrum of CS^- which was recorded at -50 °C in the flowing solution. The signal indicated by the arrow in Fig. 2A was ascribed to that of a minute amount of TS^-. After the stop of the flow, the intensity of this signal gradually increased (Fig. 2B). The same ESR spectrum as that of TS^- was observed after the signal intensity attained to a constant value. Fig. 2C shows the low-field part of the spectrum.

It was found that the isomerization was 2nd order with respect to CS^- by analyzing the growing curves observed for the various initial concentrations of CS^- and CS. Moreover, the 2nd-order rate constants (k_2's) were independent of the concentration of CS. Therefore, the present isomerization obeys the rate equation represented by Eq. 1.

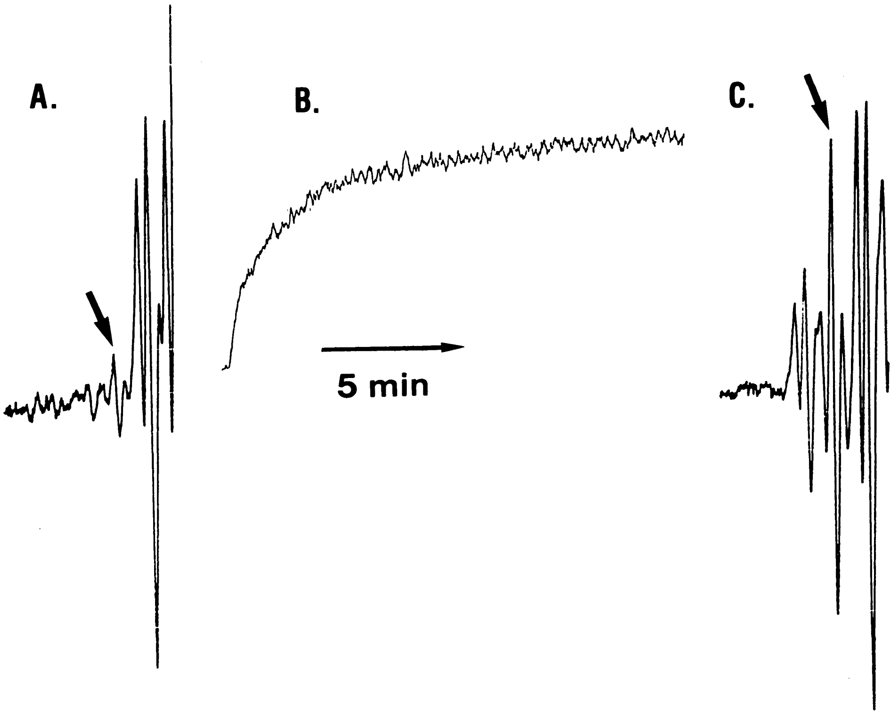

Fig. 2. (A) The low-field part of the ESR spectrum of CS^- in flowing at -50 °C; (B) the time-course of the signal indicated by the arrow in (A) after the stop of the flow; (C) the part of the spectrum observed after the signal attaining to a constant value.

$$d[CS^-]/dt = -k_2\ [CS^-]^2 \qquad (1)$$

After the consideration of possible mechanisms of the isomerization of CS^- to TS^-, it turned out that only Mechanism I could account for this rate equation.

Mechanism I

$$2CS^- \xrightarrow{k_2} CS^{2-} + CS \qquad (I\text{-}1)$$

$$CS^{2-} \xrightarrow{\text{fast}} TS^{2-} \qquad (I\text{-}2)$$

$$CS + TS^{2-} \xrightarrow{\text{fast}} CS^- + TS^- \qquad (I\text{-}3)$$

It is concluded that the isomerization of CS^- in the simplest reaction system proceeds through Mechanism I and that the rate-determining step is the disproportionation of CS^-'s (Step I-1). The rate constant of the disproportionation (k_2) was determined to be 6.5 $M^{-1}s^{-1}$ at -50 °C and 77 $M^{-1}s^{-1}$ at -30 °C in DMF.

Mechanism I exhibits that the isomerization of CS^- proceeds via CS^{2-}. Thus, it is proved that the spontaneous isomerization of CS^- is considerably unfavorable while the isomerization of CS^{2-} takes place very rapidly.

It is of interest to compare the isomerization mechanism induced by the chemical reduction1-4) with that induced by the electrochemical reduction. Although CS^{2-} involves in both cases (Step I-2), it is generated from reduction of CS by the electron donor in the former, and from the disproportionation of CS^-'s (Step I-1) in the latter. The disproportionation of CS^-'s has not so far been considered in the interpretation of the isomerization of CS^-. The details of this study will be described elsewhere.

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