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The Configurational Stability of Stilbene Anion Radicals

BO SVENSMARK JENSEN,[a] ROBERT LINES,[a] PALLE PAGSBERG[b] and
VERNON D. PARKER[a*]

[a] Electrodics Laboratory, Physical Chemistry 1, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden and [b] Danish Atomic Energy Commission Research
Establishment, Risø, Denmark

Dedicated to Professor K. A. Jensen on his 70th birthday

The anion radicals of *cis* (C) and *trans* (T) stilbene were generated electrochemically and by pulse radiolysis. Cyclic voltammetric studies showed that C^- is formed at a potential about 50 mV more cathodic than T^- and has a lifetime greater than 1 s in dimethyl formamide. Electrochemical generation of C^- in the same solvent in the ESR cavity resulted in a resolved spectrum of C^- and once again showed that the lifetime was of the order of seconds. Under the conditions of pulse radiolysis, the lifetime of C^- and T^- in tetrahydrofuran was found to be much less, *i.e.* of the order of several μs. The isomeric anion radicals were found to be spectrally distinct. T^- has an absorption maximum at 500 nm while the corresponding absorption for C^- is at 516 nm. The molar extinction of T^- at the maximum is about two times that of C^- at the maximum. Thus, for the first time, it was possible to show the configurational stability of C^- by three independent techniques. The results reported here have very strong implications on previous work in which longer lifetimes of C^- were postulated but the spectral data reported correspond to T^-.

Electron spin resonance,[1–3] ultraviolet[3] and Raman[4] spectral studies have indicated that the same radical anion species is obtained when either *cis*- or *trans*-stilbene is reduced electrochemically or by alkali metals. The latter has been interpreted to indicate that isomerization (1), where C^- and T^- refer to the *cis* and *trans* anion radicals of the corresponding stilbene, is rapid.

$$C^- \rightleftharpoons T^- \qquad (1)$$

More recently, it has been proposed that in hexamethylphosphortriamide (HMPT), in which the ions exist in the free state, reaction (1) has a relaxation time of about 650 s.[5] We now report evidence from three independent techniques which confirms the lability of C^- and shows that the spectral characteristics of the isomeric monoanions of the stilbene are indeed different.

Cyclic voltammetric reduction of both C and T in dimethylformamide (DMF) containing Bu_4NBF_4 (0.2 M) in the presence of neutral alumina[6] results in the observation of two consecutive reversible or quasi-reversible one electron redox couples.[7] The potential at which the dianion is formed, 2.700 V *vs.* SCE (Fig. 1A), was found to be independent of which of the isomers, C or T, was reduced.[8] The potentials for formation of the monoanions, on the other hand, were dependent upon which isomer was being reduced. The potential difference between the first and second charge transfers was 465 mV for the reduction of C and 515 mV for reduction of T. That is, T is reduced about 50 mV more readily than C. When the direction of voltage sweep was changed about 300 mV negative of the reduction peak for C and cycled once again the reduction peak appeared at the same potential on the second cycle (Fig. 1B). After the second cycle, the potential was held negative of the reduction peak for 15 s before reversing the direction of sweep. Under the latter conditions, the peaks for oxidation of the anion radical and for reduction of the stilbene in the diffusion layer were shifted 50 mV

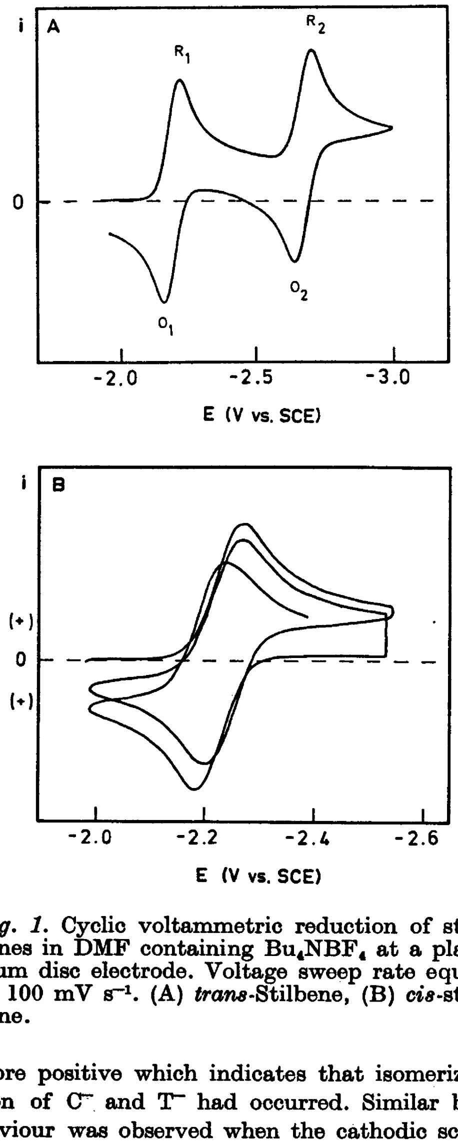

Fig. 1. Cyclic voltammetric reduction of stilbenes in DMF containing Bu_4NBF_4 at a platinum disc electrode. Voltage sweep rate equal to 100 mV s^{-1}. (A) *trans*-Stilbene, (B) *cis*-stilbene.

more positive which indicates that isomerization of C^- and T^- had occurred. Similar behaviour was observed when the cathodic scan for the reduction of C was carried out beyond the potential for reduction of C^-, showing that the stilbene dianion (S^{2-}) is oxidized to T^- under voltammetric conditions.

The ESR spectrum of C^- was obtained by reduction of C at a platinum gauze electrode in a flow cell placed in the cavity of the spectrometer. The residence time in the cell was about 1 s which indicates that under these conditions C^- has a lifetime greater than 1 s. The experimental spectrum (Fig. 2A) is nearly identical to the simulated spectrum (Fig. 2B) with coupling constants, $a^H = 3.3$ G for the ethylenic protons and $a^H = 0.8$ G for six equivalent ring protons. An interpretation consistent with the spectra is that the *ortho* and *para* protons give identical coupling while coupling to the *meta* protons is too small to be observed with the resolution obtained. The most interesting feature of the spectrum (Fig. 1A) is the unusual width, much more narrow than expected for a π-radical. The sum of the coupling constants $[(2 \times 3.3) + (6 \times 0.8) = 11.4 \text{ G}]$ is less than half of the sum of that reported for the *trans* radical.[3] The small coupling constants of the ring protons indicate that the major portion of the spin density of C^- resides on the ethylenic carbons. Following the arguments of Bernal, Rieger and Fraenkel,[11] we estimate that the spin density resides 80 % on the ethylenic carbons and 20 % in the rings. The latter corresponds to a bond angle of about 135° between the phenyl rings and the ethylenic carbons.[17]

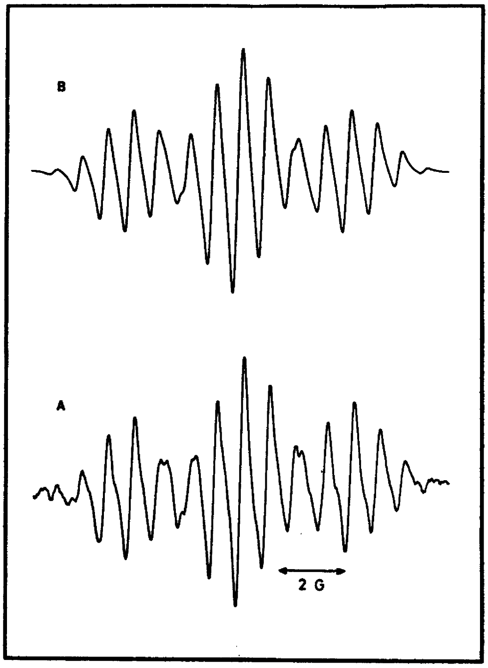

Fig. 2. ESR spectrum of *cis*-stilbene anion radical generated electrochemically in DMF (A), and the simulated spectrum (B).

Pulse radiolysis of C in THF allowed us to obtain, for the first time, the visible absorp-

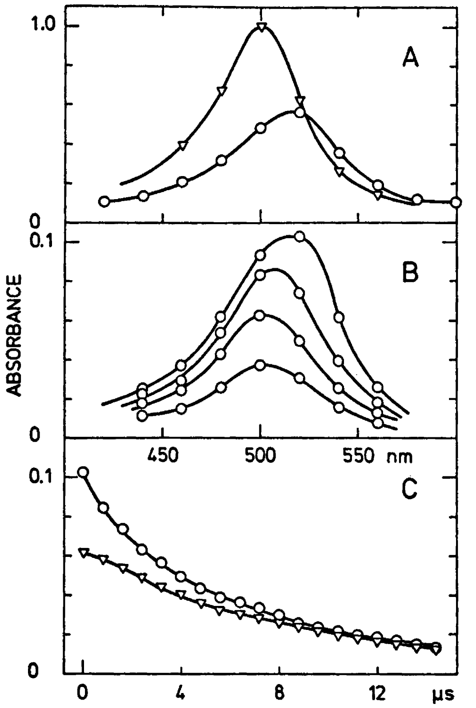

Fig. 3. Visible absorption spectra of *trans*- (upper) and *cis*-(lower) immediately after pulse radiolysis in tetrahydrofuran (A). Absorption spectra measured at various times after pulse radiolysis of *cis*-stilbene showing both decay and a blue shift of the absorption maximum (B). The decay of the visible absorption spectrum from *cis*-stilbene anion radical at various wavelengths (C).

tion spectrum of C^-. The spectra of the *cis* and *trans* radicals are shown in Fig. 3A. The absorption maximum for the *cis* anion radical appears at 516 nm as compared to 500 nm for T^-. The intensity of the absorption maximum for C^- is significantly lower than that for T^- The latter is consistent with the observations of Szwarc [5] who found an initial decrease in the absorption at 500 nm upon adding C to solutions of T^-. The latter study gave no indication of a shift in the absorption maximum which must mean that $C^-$was not formed in appreciable concentration. The radical anions generated from C by pulse radiolysis in THF at room temperature had half-lives of the order of only 6 μs. The decay of the visible absorption spectrum is illustrated in Figs. 3B and 3C. The decay of the absorption maximum is accompanied by a definite shift to lower wavelengths. The first spectrum shown, taken after 0.8 μs, is that of the nearly pure *cis* anion radical while the spectrum recorded after 12 μs revealed an absorption maximum at about 503 nm. The change in absorption maximum is most likely due to the isomerization reaction (1). If the latter is the case, we estimate that the half-life of reaction (1) under these conditions to be of the order of about 5 μs.[13]

The results presented above conclusively show that the *cis* and *trans* anion radicals of stilbenes are spectrally distinct species. The lifetime of C^- is short and dependent upon the environment in which it is generated. This work has definite bearing upon previous studies and forces one to conclude that reactions carried out with anion radicals generated from C actually had the *trans* configuration when the spectral data reported were characteristic of T^-.

EXPERIMENTAL

trans-Stilbene was reagent grade and used without further purification.

cis-Stilbene was prepared by photochemical isomerization of *trans*-stilbene and purified by column chromatography on a neutral alumina column.

DMF was distilled and passed through a column of active neutral alumina immediately before use. Cyclic voltammograms were recorded using standard equipment and neutral alumina in the cell as described previously.[6] The working electrode was made from 1 mm platinum wire sealed in soft glass and polished.

The flow cell for the ESR measurements was essentially identical to the flow cell described by Cauquis [14] with the modification that the counter electrode was placed very close to the working electrode in an arrangement similar to that published by Goldberg and Bard.[15] The solution was continuously purified by passing it through a layer of neutral alumina placed in the upper part of the cell during the experiment. This makes it possible to attain a high steady state concentration of a shortlined electrode product in the ESR cavity. The construction and performance of this cell will be published elsewhere.[16]

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17. Some doubt exists as to whether or not the spectrum shown in Fig. 2 is that of pure C^- since Professor M. Szwarc has recently informed us that a resolved spectrum of C^- much more similar to that of T^- than to Fig. 2 has been obtained in his laboratory.

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