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Laser-Induced Photoconversion of *trans*-Stilbene Dianions into *cis*-Stilbene Radical Anions

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Abstract: Laser-pulse photolysis of the sodium salt of *trans*-stilbene dianions induced by tunable dye laser leads to electron ejection. The ejected electron is captured by biphenyl present in a large excess and a transient absorbance at 400 nm (λ_{max} of the formed biphenylide) monitors the electron ejection process. The formation of *trans*-stilbene radical anions, resulting from the electron photoejection, should be revealed by a transient absorbance at 480 nm, but at high light intensity this transient is weaker than needed for the 1:1 stoichiometric ratio biphenylide:*trans*-stilbenide. Moreover, under these conditions the 480-nm transient grows for a period of 8–10 μs, the growth obeying a first-order law with the first-order rate constant proportional to the concentration of the dianions present in large excess in the solution. We conclude that *cis*-stilbenide is formed in the photolysis and the reaction *cis*-stilbenide + trans dianion → cis dianion + *trans*-stilbenide, followed by the extremely fast conversion, cis dianion → trans dianion, is responsible for the observed growth of the 480-nm transient, because at this wavelength the molar absorbance of *trans*-stilbenide is higher than that of *cis*-stilbenide. The electron transfer biphenylide + *trans*-stilbenide → biphenyl + trans dianion eventually restores the system to its initial state. The fraction of trans dianions converted into *cis*-stilbenide instead of *trans*-stilbenide increases with light intensity. The cause of this effect is discussed.

Radical anions and even the dianions of the stilbenes exist in two distinct forms referred to as the cis, $C^{-\cdot}$ and C^{-2}, and trans, $T^{-\cdot}$ and T^{2-}. This designation does not necessarily imply the conventional difference in geometry of these isomers. Rather it is used in operational meaning. The cis radical anion of stilbene is the one that is formed on attachment of an electron to *cis*-stilbene, C, and is converted back into *cis*-stilbene when the electron is removed. Similar definition applies to the term *trans*-stilbene radical anion, i.e.,

$$C + e^- \rightleftarrows C^{-\cdot} \text{ and } T + e^- \rightleftarrows T^{-\cdot}$$
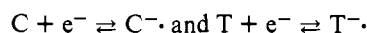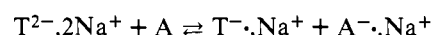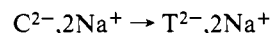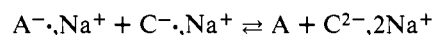
A radical anion may be formed from the respective dianion by electron photodetachment. One would anticipate the electron photodetachment from *trans*-stilbene dianions to yield *trans*-stilbene radical anions but, as will be shown later, laser pulse photolysis of T^{2-},2Na$^+$ yields, at least partially, the *cis*-stilbene radical anions.

In this paper we wish to present the experimental results leading to this conclusion and discuss their significance. It is advisable, however, first to review briefly the evidence for the existence of the distinct *cis*- and *trans*-stilbene radical anions and dianions and to describe their optical spectra.

Radical Anions and Dianions of the Stilbenes. The results reported in the past by various workers[1-3] led to the belief that radical anions of the stilbenes exist in one form only or, if there are two isomers, the one derived from *cis*-stilbene converts extremely rapidly into the known and stable species derived from *trans*-stilbene. The work carried out in our laboratory[4-6] showed this not to be the case. Kinetic studies of electron transfer induced isomerization of *cis*-stilbene into the trans isomer conclusively demonstrated the presence of *cis*-stilbene

radical anions, $C^{-\cdot}$, that only slowly isomerize into *trans*-stilbene radical anions. In fact, for the free radical anions not associated with cations the direct isomerization, $C^{-\cdot} \rightarrow T^{-\cdot}$, proceeds very slowly with a rate constant of about 5×10^{-3} s^{-1}. Such a reaction was studied in hexamethylphosphoric triamide.[6] In tetrahydrofuran the radical anions are associated with counterions into pairs, e.g., $C^{-\cdot}$,Na$^+$ and $T^{-\cdot}$,Na$^+$. The direct isomerization, $C^{-\cdot}$,Na$^+ \rightarrow T^{-\cdot}$,Na$^+$, cannot be observed under these conditions because an alternative faster route leads to the transformation of $C^{-\cdot}$,Na$^+$ into $T^{-\cdot}$,Na$^+$. In the presence of a suitable electron donor, say $A^{-\cdot}$,Na$^+$, the $C^{-\cdot}$,Na$^+$ radical anions are reduced to the C^{2-},2Na$^+$ dianions and the latter isomerize with a rate constant of about 10^6–10^7 s^{-1} into T^{2-},2Na$^+$. Thus the following sequence of reactions takes place,[4]

$$A^{-\cdot},Na^+ + C^{-\cdot},Na^+ \rightleftarrows A + C^{2-},2Na^+$$

$$C^{2-},2Na^+ \rightarrow T^{2-},2Na^+$$

$$T^{2-},2Na^+ + A \rightleftarrows T^{-\cdot},Na^+ + A^{-\cdot},Na^+$$

the isomerization C^{2-},2Na$^+$ into T^{2-},2Na$^+$ being the rate-determining step. This work proved the existence not only of two different radical anions of the stilbenes but also of two different dianions, provided that the latter are associated with cations. The absorption spectra of $C^{-\cdot}$,Na$^+$ and $T^{-\cdot}$,Na$^+$ in tetrahydrofuran were eventually recorded by application of flash photolysis.[6] The absorption maxima are close to each other, namely, at 498 nm for $C^{-\cdot}$,Na$^+$ and 490 nm for $T^{-\cdot}$,Na$^+$; however, the molar absorbances are different, viz., 3.3 $\times 10^4$ and 5.2 $\times 10^4$, respectively. These results have been confirmed recently by pulse-radiolytic studies of Levanon and
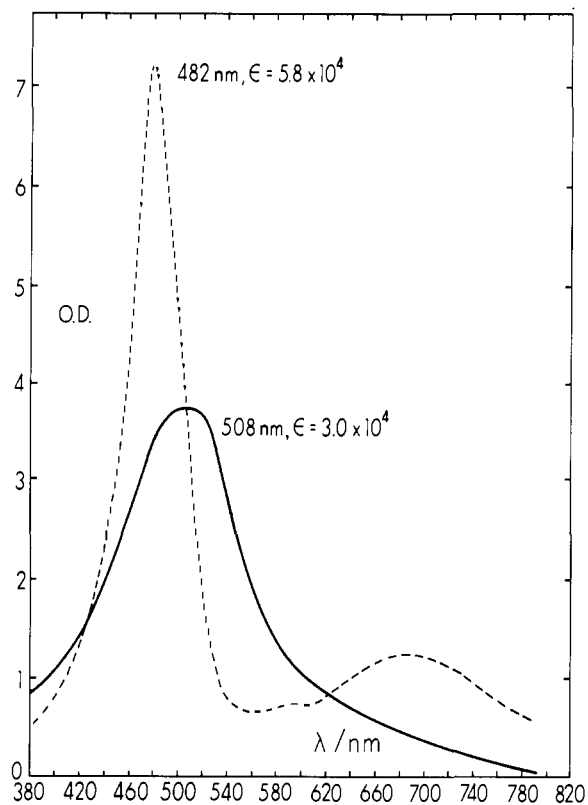
Figure 1. Absorption spectrum of sodium salts of *trans*-stilbenide and *trans*-stilbene dianions in tetrahydrofuran: (- - -) T$^-$·,Na$^+$; (—) T^{2-},2Na$^+$.

Figure 2. Oscilloscope tracer of the 400-nm transient showing the electron attachment to biphenyl, virtually completed within 4 μs, followed by a slow electron transfer, biphenylide + stilbenide → biphenyl + stilbene dianion, leading to the decay of the transient. Scales: 2 μs/div; 20 mV/div.

Figure 3. Oscilloscope tracers of the 480-nm transient (λ_{max} of *trans*-stilbenide) showing its growth over 8–10 μs to an asymptotic value corresponding to the concentration of *trans*-stilbenide equivalent to that of the formed biphenylide. Scales: 2 μs/div; 10 mV/div.

Neta[7] and they agree with the findings derived from studies of radiolysis of the stilbenes in 2-MeTHF glasses.[8]

Finally, knowing the behavior of these systems it was possible to design conditions under which the *cis*-stilbene radical anions were sufficiently stable to allow recording of their ESR spectrum.[9] This spectrum is distinct from that of *trans*-stilbene radical anion, and eventually it slowly converts to the latter. In conclusion, two distinct radical anions of the stilbenes exist as well as the respective dianions, provided that the latter are associated with cations.

Absorption Spectra of T$^-$·,Na$^+$ and T^{2-},2Na$^+$ in THF. Absorption spectra of T$^-$·,Na$^+$ and T^{2-},2Na$^+$ were first reported by Zabolotny and Garst.[10] The λ_{max} of T$^-$·,Na$^+$ was found at 480 nm (ϵ 6.2 × 10^4) and of T^{2-},2Na$^+$ at ~505 nm (ϵ ~3.0 × 10^4). We redetermined these values and our spectra of T$^-$·,Na$^+$ and T^{2-},2Na$^+$ are shown in Figure 1. The absorption maxima appear at 482 (ϵ 5.8 × 10^4) and at 508 nm (ϵ 3.0 × 10^4) for T$^-$·,Na$^+$ and T^{2-},2Na$^+$, respectively. Thus determined molar absorbance of T$^-$·,Na$^+$ is by 10% higher than that obtained by the flash-photolytic technique.[6] In view of the experimental difficulties encountered in flash photolysis, the directly obtained ϵ is more reliable.

Inspection of both spectra shown in Figure 1 is instructive. An isosbestic point is seen at ~510 nm, i.e., a process converting T^{2-},2Na$^+$ into an equivalent amount of T$^-$·,Na$^+$, e.g., T^{2-},2Na$^+$ + $h\nu$ → T$^-$·,Na$^+$ + e$^-$,Na$^+$, should not affect the optical density of the system at this wavelength.

Photolysis of Sodium Salt of *trans*-Stilbene Dianions by Pulse of Laser Light. Visible light induced photodetachment of electrons from radical anions or dianions of aromatic hydrocarbons was reported by various workers.[11] This phenomenon is also observed in the photolysis of T^{2-},2Na$^+$. The following photochemical reaction is expected,

$$T^{2-},2Na^+ \xrightarrow{h\nu} T^-·,Na^+ + e^-,Na^+ \qquad (a)$$
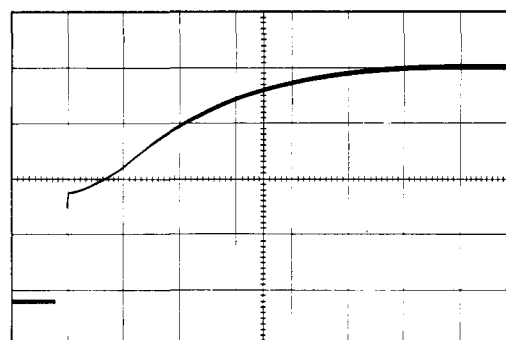
and it should manifest itself by the appearance of transient absorbance at 480 nm because the absorbance of T$^-$·,Na$^+$ is much stronger at this wavelength than that of T^{2-},2Na$^+$ (see Figure 1).

The subsequent reactions of the electron–sodium pairs (e$^-$,Na$^+$) complicate the investigation of this system. To avoid them, and to provide a more reliable method of gauging the extent of electron photoejection, biphenyl, B, at ~10^{-3} M concentration was added to ~10^{-5} M solution of T^{2-},2Na$^+$ in THF. Such a solution was photolyzed by a pulse of tunable dye laser (λ 482 nm) of about 100 ns duration. Under these conditions the photoejected electrons were rapidly scavenged by biphenyl, and the reduction of biphenyl is revealed by a transient absorbance at 400 nm (λ_{max} of B$^-$·,Na$^+$) that appeared after each pulse. This is illustrated by the oscillogram shown in Figure 2. The 400-nm transient reaches its maximum in about 4 μs, a time needed for the reaction

$$e^-,Na^+ + B \rightarrow B^-·,Na^+ \qquad (b)$$
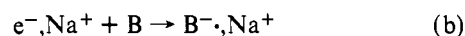
and thereafter it slowly decays. The decay is attributed to the reaction

$$B^-·,Na^+ + \text{the stilbenide} \rightarrow B + T^{2-},2Na^+ \qquad (c)$$
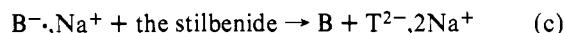
regenerating the original dianions and eventually, after each pulse, the system returns to its original state.

The behavior of the 480-nm transient is more complex than expected. Its intensity is lower than calculated on the basis of the concentration of the formed B$^-$·,Na$^+$ (gauged by the 400-nm transient), provided that the intensity of the laser light is sufficiently high. Moreover, the too "weak" 480-nm transient grows over a period of 8–10 μs, as manifested by the oscillogram shown in Figure 3, and thereafter slowly decays.

The growth of the 480-nm transient obeys a first-order law,
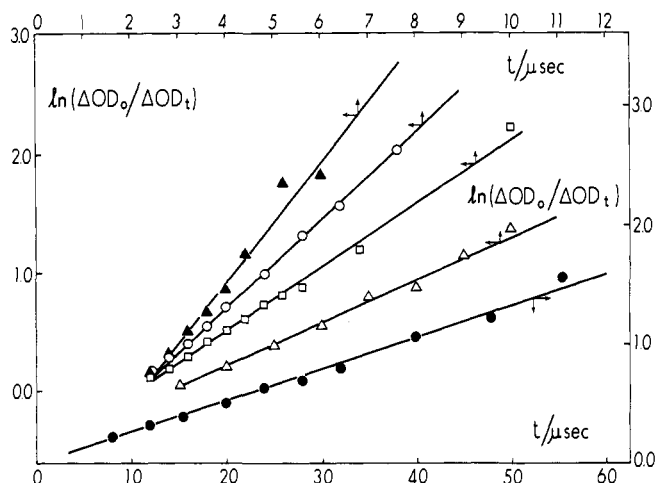
Figure 4. First-order plot of the growth of the 480-nm transient at various, virtually constant concentrations of *trans*-stilbene dianions [T^{2-},$2Na^+$]: ▲, [T^{2-},$2Na^+$] = 3.6 × 10^{-5} M; O, [T^{2-},$2Na^+$] = 2.8 × 10^{-5} M; □, [T^{2-},$2Na^+$] = 1.6 × 10^{-5} M; △, [T^{2-},$2Na^+$] = 0.7 × 10^{-5} M; ●, [T^{2-},$2Na^+$] = 0.35 × 10^{-5} M.

Figure 6. Oscilloscope tracers of the 480-nm transients obtained at different intensities of laser light. Note the flatness of the trace at low light intensity and its rising which becomes steeper with increasing intensity of laser light. Scale: 2 μs/div; 20 mV/div.

Table I. Pseudo-First-Order Constant of the 480-nm Transient Increase

$10^5[T^{2-},2Na^+]$, M	$10^{-5}k_u$, s	$10^5[T^{2-},2Na^+]$, M	$10^{-5}k_u$, s
0.35	0.26	2.8	3.90
0.70	1.50	3.6	5.30
1.6	2.68		

which shows a series of oscillograms obtained by exposing the same solution to several laser pulses of increasing intensity.

Discussion

The facts summarized in the preceding section leave us with the following two questions: (1) What is the species responsible for the observed absorbance at 480 nm? (2) What reaction accounts for the growth of the 480-nm transient observed during the first 8–10 μs after a pulse?

The product responsible for the 480-nm transient should be related to a stilbene radical anion. Detachment of an electron from T^{2-},$2Na^+$ yielding any other product than the stilbene radical anion is highly improbable. However, the resulting radical anion need not be the *trans*-stilbenide; it might be the *cis*-stilbenide.

Could an electron photodetachment from $T^-\cdot$,Na^+, that is from the primary product of the photolysis, account for the initially lower absorbance observed at 480 nm and for its subsequent growth in the period following the pulse? This is contrary to the observations. The proposed scheme implies two reactions: (1) A primary photochemical act converting some T^{2-},$2Na^+$ into $T^-\cdot$,Na^+ and subsequently some $T^-\cdot$,Na^+ into T. The ejected electrons would be captured by B and form $B^-\cdot$,Na^+. This would bleach initially the absorbance in the 570–580 nm range (see Figure 1). (2) The dark reaction in which the remaining T^{2-},$2Na^+$, present in a large excess and at a much higher concentration than the formed $B^-\cdot$,Na^+, would reduce the formed T as well as $T^-\cdot$,Na^+. Such a process should lead to a further *decrease* in the absorbance in the 570–580 nm range caused by $T + T^{2-} \rightarrow 2T^-\cdot$,$Na^+$ (see again Figure 1). Instead, a small *increase* in the absorbance following the initial bleaching was observed in this region. On the other hand, the explanation given below accounts for these observations.

Provided that *cis*-stilbenide is formed in the photolysis, a lower transient absorbance at 480 nm is expected, because the molar absorbance of the cis radical anion is smaller than that of the trans radical anion (see the preceding section). In the presence of T^{2-},$2Na^+$ a pseudo-first-order reaction could take place (the concentration of T^{2-},$2Na^+$ is relatively high when compared with the products of photolysis), namely,

$$C^-\cdot,Na^+ + T^{2-},2Na^+ \rightarrow C^{2-},2Na^+ + T^-\cdot,Na^+$$

Figure 5. Plot of the observed pseudo-first-order rate constant vs. [T^{2-},$2Na^+$].

as can be seen from Figure 4. The kinetic results are summarized in Table I, and the observed pseudo-first-order rate constants are proportional to the concentration T^{2-},$2Na^+$, as shown by Figure 5. It seems that the growth of the transient is due to a bimolecular reaction

$$X + T^{2-},2Na^+ \rightarrow Y + Z \qquad (d)$$
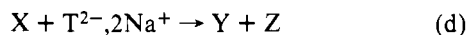
that proceeds with a rate constant of 1.5 × 10^{10} M^{-1} s^{-1}. The asymptotic value reached by the 480-nm transient corresponds to that expected for the formation of *trans*-stilbenide in an amount equimolar to that of the formed biphenylide (λ_{max} 400 nm).

At low laser light intensity the 480-nm transient appears to be stationary for about 14 μs; however, as the intensity of laser light increases growth of the transient in time becomes apparent. This behavior of the system is illustrated by Figure 6,

followed by the rapid conversion of $C^{2-},2Na^+$ into $T^{2-},2Na^+$. The latter, as was pointed out earlier, proceeds with a rate constant of $\sim 10^7 s^{-1}$. The conversion of $C^-\cdot,Na^+$ into $T^-\cdot,Na^+$ increases the absorbance at 480 nm and accounts for our observation, namely, for the first-order kinetics governing the growth of the 480-nm transient and the dependence of the observed first-order constant on the concentration of the unphotolyzed $T^{2-},2Na^+$.

The proposed partial photoconversion of $T^{2-}2Na^+ + B$ into $C^-\cdot,Na^+ + B^-\cdot,Na^+$ accounts for our observations. However, all the findings could equally well be explained by postulating formation of some hypothetical isomer X of $T^-\cdot,Na^+$, different from $C^-\cdot,Na^+$, that eventually is converted into $T^-\cdot,Na^+$. Specific evidence for formation of $C^-\cdot,Na^+$ comes from the following calculation.

At 4 μs all the ejected electrons are captured by B and hence the intensity of the 400-nm transient at that time gives $[B^-\cdot,Na^+] = [T^-\cdot,Na^+] + [X]$. The sum $[T^-\cdot,Na^+] + [X]$ could also be calculated from the intensity of the 480-nm transient measured at the same time had the amount of [X] present at that time and its molar absorbance been known. At about 10 μs all of the X is converted into $T^-\cdot,Na^+$ and the concentration of $T^-\cdot,Na^+$ could be deduced then from the intensity of either the 400- (ϵ_{eff} 3.8 × 10^4) or the 480-nm transient (ϵ_{eff} 2.7). The agreement between both values is fair, e.g., 4.3 × 10^{-6} and 4.6 × 10^{-6}, 4.9 × 10^{-6} and 4.7 × 10^{-6}, etc. The increase in the intensity at 480 nm occurring between 4 and 10 μs gives the concentration of X at 4 μs that is converted into $T^-\cdot,Na^+$ at 10 μs. Assuming X to be $C^-\cdot,Na^+$, we can calculate the required concentration of $C^-\cdot,Na^+$ at 4 μs ($\epsilon_{eff} = \epsilon_{T^-\cdot,Na^+} - \epsilon_{C^-\cdot,Na^+} = 1.9 \times 10^4$), and by difference the corresponding concentration of $T^-\cdot,Na^+$. Thus we may calculate the optical density of the 480-nm transient at 4 μs and compare the calculated value with the observed one. The results agree within 30–40%. In view of the uncertainties in the employed molar absorbances ($\sim$10% for each) we consider this agreement satisfactory indicating that the molar absorbance at 480 nm of X is the same as that of $C^-\cdot,Na^+$. This provides a supporting evidence to our suggestion that $T^{2-},2Na^+ + B$ is partially photoconverted into $C^-\cdot,Na^+ + B^-\cdot,Na^+$.

The photoconversion of $T^{2-},2Na^+$ into *cis*-stilbenide calls for further consideration. Figure 6 clearly demonstrates that the fraction of $T^{2-},2Na^+$ photochemically converted into $C^-\cdot,Na^+$ increases with increasing intensity of laser light. Two tentative explanations may be offered to account for this observation.

The equilibrium constant $C^-\cdot,Na^+ \rightleftarrows T^-\cdot, Na^+$, $K_{C^-\cdot,T^-\cdot}$, may be calculated by adding two equilibria:

$$C \rightleftarrows T, K_{C,T}, \text{ and } C^-\cdot,Na^+ + T \rightleftarrows C + T^-\cdot,Na^+, K_{e,exch}$$

i.e., $K_{C^-\cdot,T^-\cdot} = K_{C,T}K_{e,exch}$. The value of the latter was determined[6] to be about 5, while that of the former, although still unknown, has to be greater, and presumably much greater than 100. Hence, $K_{C^-\cdot,T^-\cdot} > 500$, implying that the energy content of $C^-\cdot,Na^+$ is greater than that of $T^-\cdot,Na^+$. Hence, electron detachment from $T^{2-},2Na^+$ leading to the formation of $T^-\cdot,Na^+$ may be a monophotonic process, whereas a simultaneous absorption of two photons might be needed for the formation of $C^-\cdot,Na^+$. The effect of light intensity is then accounted for.

Alternatively, one may hypothesize that a monophotonic process leads to electron ejection from $T^{2-},2Na^+$ with formation of an excited state of stilbene radical ion, let us say $X^-\cdot,Na^+$. The latter may be either spontaneously converted into $T^-\cdot,Na^+$ or absorb another photon and be transformed into $C^-\cdot,Na^+$. Again increasing intensity of laser light should favor the formation of *cis*-stilbenide. The possibility that a second photon converts $T^-\cdot,Na^+$ into $T + e^-,Na^+$ was ruled out by evidence discussed earlier.

Direct Photoisomerization of Sodium *trans*-Stilbenide into Sodium *cis*-Stilbenide. Several attempts to observe a direct photoisomerization of $T^-\cdot,Na^+$ into $C^-\cdot,Na^+$ were not conclusive. We flash photolyzed $T^-\cdot,Na^+$ mixed with an excess of T using visible light as an actinic agent. It was hoped that electron photoejection, $T^-\cdot,Na^+ \rightarrow T + e^-,Na^+$, would be compensated by the rapid reverse electron capture, and thus a decrease in absorbance around 500 nm would manifest the isomerization. However, the reaction $T^-\cdot,Na^+ + e^-,Na^+ \rightarrow T^{2-},2Na^+$ could also account for the observed bleaching and unfortunately, within the accessible spectral region, the differences in the absorbances of $2T^-\cdot,Na^+$ and $T^{2-},2Na^+$ are similar to the differences in the absorbances of $T^-\cdot,Na^+$ and $C^-\cdot,Na^+$. Similar difficulties were encountered in laser photolysis.

We are inclined to believe that visible light does not induce photoisomerization of $T^-\cdot,Na^+$ into $C^-\cdot,Na^+$, and UV light causes some other reactions that interfere with our study. It is not clear why $C^-\cdot,Na^+$ could be formed by photolysis of $T^{2-},2Na^+$ and not by photolyzing $T^-\cdot,Na^+$. It may be that the excited state leading to isomerization is reached by irradiation of $T^{2-},2Na^+$ and not $T^-\cdot,Na^+$. Whatever the reason, further study of this subject is desired.

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