Kinetics of Isomerization of the Free *cis*-Stilbene Radical Anion into Its Trans Isomer in Hexamethylphosphoric Triamide. Spectroscopic and Electron Spin Resonance Identification of *cis*-Stilbene Radical Anion in Tetrahydrofuran

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Abstract: The optical spectrum of *cis*-stilbene radical anions, $C^{-}\cdot,Na^{+}$, in THF was determined by flash photolysis and pulse radiolysis, λ_{max} 500 nm, ϵ 3.3×10^4, compared with λ_{max} 495 nm and ϵ 5.2×10^4 for *trans*-stilbene radical anion, $T^{-}\cdot,Na^{+}$. Flash photolysis permitted us also to determine the constant of the electron-transfer equilibrium, $T^{-}\cdot$, $Na^{+} + C \rightleftarrows T + C^{-}\cdot$, Na^{+} in THF, $K_{tr} = 0.2$. The ESR spectrum of $C^{-}\cdot$ in HMPA was recorded too. It differs only slightly from that of $T^{-}\cdot$; the respective coupling constants are similar, but the distinction is unequivocal. Hence, the free $C^{-}\cdot$ radical anion and its sodium salt unquestionably form species different from $T^{-}\cdot$ and its sodium salt. The kinetics of spontaneous isomerization of the free *cis*-stilbene radical anions, $C^{-}\cdot$, in HMPA into their trans isomer, $T^{-}\cdot$, was investigated. The reaction is accelerated by electron transfer from triphenylide radical ion, $Trph^{-}\cdot$. Mechanisms (see Scheme I) are proposed to account for the results. Apparently only one kind of free stilbene dianion is formed, namely X^{2-}, that becomes transformed into $T^{-}\cdot$ (probability γ) or $C^{-}\cdot$ (probability $1 - \gamma$) as the second electron is removed, γ being close to unity. In terms of interpretation a or b $k_3 = 40 \pm 3$ $M^{-1}\,s^{-1}$ and $K_3 \approx 4 \times 10^{-9}$; i.e., the second reduction potential of *cis*-stilbene is at least by 0.7 V higher than the first.

Electron transfer induced isomerization of *cis*-stilbene (C) into its trans isomer (T) proceeding in hexamethylphosphoric triamide (HMPA) was described in a previous paper.[1] The results suggest the following mechanism for that process

$$T^{-}\cdot + C \rightleftarrows T + C^{-}\cdot \qquad (1)$$

$$C^{-}\cdot \rightleftarrows T^{-}\cdot \qquad (2)$$

where $T^{-}\cdot$ and $C^{-}\cdot$ denote the free radical anions derived from the respective hydrocarbons. The first step converts C into T, while the $T^{-}\cdot$ radical anion, responsible for the chain isomerization, is regenerated in the second step.

Analysis of the kinetics in terms of the above mechanism led to the equilibrium constant $K_1 = 0.6$ and to the relaxation time of the second step $\tau_2 \approx 10^3$ s. The relatively long relaxation time implies a relatively long lifetime for the free $C^{-}\cdot$ radical anion which eventually becomes converted into $T^{-}\cdot$. Nevertheless, when *cis*-stilbene was reduced in HMPA by the addition of an equimolar amount of biphenylide, or by electrolytic reduction taking place in the cavity of an ESR spectrometer (see ref 1), the resulting ESR spectrum examined in a time much shorter than 1000 s appeared to be that of $T^{-}\cdot$. The discrepancy between the kinetic conclusions and the apparent ESR findings casts doubt about the postulated existence of $C^{-}\cdot$ as a distinct species from $T^{-}\cdot$. Further work was, therefore, needed.

In the present paper we report the results of four studies.

(1) Kinetics of spontaneous isomerization of free $C^{-}\cdot$ radical anions into $T^{-}\cdot$ in HMPA. This reaction may be accelerated by electron transfer from a suitable electron donor, say triphenylide, $Trph^{-}\cdot$, to $C^{-}\cdot$ converting the latter into the respective dianion. It is this acceleration that led to apparent contradictions between the previously mentioned kinetic and ESR results.

(2) Determination of the optical spectrum of $C^{-}\cdot,Na^{+}$ in tetrahydrofuran (THF). The results yielded λ_{max} as well as the respective ϵ. The reliability of the technique was tested by determining the known optical spectrum of $T^{-}\cdot,Na^{+}$.

(3) Determination of the equilibrium constant of the electron transfer reaction, $T^{-}\cdot,Na^{+} + C \rightleftarrows T + C^{-}\cdot,Na^{+}$ in THF.

(4) Recording the ESR spectrum of $C^{-}\cdot$ in HMPA and its turn into the spectrum of $T^{-}\cdot$ while the investigated solution was left for about 0.5 h.

Again, the reliability of the technique was tested by using *trans*-stilbene instead of cis isomer and recording the ESR spectrum of $T^{-}\cdot$.

Experimental Section

Purification of *cis*-stilbene, of HMPA, and the preparation of solutions of radical anions are reported in the previous publication.[1] The reagents, a 10^{-3} M solution of triphenylide, $Trph^{-}\cdot$, containing the unreduced hydrocarbon, Trph, and a solution of C, both in HMPA, were placed in the two bulbs of a "flip apparatus." This device and its mode of operation are reported elsewhere.[2] Suffice to say that the reagents could be rapidly mixed, the mixture poured into a 2-mm optical cell with a spacer reducing the optical path, and the ensuing reaction monitored by recording the absorbance at 500 nm with a Beckman Acta MV1 spectrometer. The monitoring began at about 15 s after mixing the reagents.

Two techniques were used in determining the optical spectrum of $C^{-}\cdot$ in THF: flash photolyses and pulse radiolysis. The details of flash photolyses are reported by Rämme et al.,[3] who described also the procedure by which a highly dilute (10^{-6} M or less) solution of reagents can be prepared reliably and reproducibly without adding a fresh solvent. The details of pulse radiolysis technique were published by Dorfman.[4]

The HMPA solutions of $Trph^{-}\cdot$ ($\sim 10^{-4}$ M) mixed with Trph and solutions of *cis*-stilbene ($\sim 10^{-4}$ M) were prepared as previously described. By pressurizing them with purified, rigorously dried, and oxygen-free nitrogen they were forced to flow through a glass mixing chamber and then through a flat cell placed in the cavity of a Varian ESR spectrometer.

Discussion

Kinetics of the Reaction $C^{-}\cdot \rightarrow T^{-}\cdot$ in HMPA. Results of a previous study[1] implied that the absorbance of $C^{-}\cdot$ at 500 nm is weaker than that of $T^{-}\cdot$. Therefore, changes of the absorbance at this wavelength monitor the conversion of $C^{-}\cdot$ into $T^{-}\cdot$.

$Trph^{-}\cdot$ was initially in excess to stilbene and hence, as shown by spectrophotometric analysis, the latter was quantitatively

Table I. Kinetics of Isomerization of $C^{-}\cdot$ into $T^{-}\cdot$ in HMPA

10^4 [Trph$^{-}\cdot$], M	10^2 [Trph], M	10^4 [T$^{-}\cdot$]$_\infty$, M	10^3 k_u, s^{-1}
0.32	0.45	5.06	3.13
0.49	0.20	5.32	3.46
0.60	1.76	6.76	4.04
1.07	0.12	4.89	5.77
1.22	0.53	5.31	5.24
1.32	3.36	5.11	2.89 (?)[b]
1.95	0.51	4.25	7.84[a]
2.38	3.22	5.29	8.05
3.40	0.28	13.4	15.6
3.42	0.30	6.01	20.2
3.61	1.41	5.89	18.1
3.70	0.77	5.84	19.3
3.74	0.56	3.46	20.1
4.21	0.52	3.03	21.7
4.52	1.42	3.30	25.1
5.25	0.28	5.86	47 (?)[b]
5.29	0.30	2.70	31.1

[a] Na,BPh$_4$ added: [Na,BPh$_4$] = 4.5×10^{-3} M. [b] These results are omitted in the graph and rejected in the calculation of k_3.

converted into stilbene radical anions, the conversion being completed in a time shorter than 10 s. Thereafter, the absorbance at 415 nm (λ_{max} of Trph$^{-}\cdot$) remained constant throughout the duration of each run. The composition of each of the investigated mixtures is given in Table I. The concentrations of the stilbene radical anions, i.e., [C$^{-}\cdot$] + [T$^{-}\cdot$], of the residual Trph$^{-}\cdot$, and of Trph remained constant during the studied isomerization. [Trph$^{-}\cdot$] was determined from the absorbance at 415 nm (λ_{max} Trph$^{-}\cdot$, ϵ 1.3×10^4), [stilbene$^{-}\cdot$] = [C$^{-}\cdot$] + [T$^{-}\cdot$] was obtained from the final absorbance at 500 nm given by [T$^{-}\cdot$]$_\infty$ since all C$^{-}\cdot$ was converted into T$^{-}\cdot$ at that time, and [Trph] was calculated from its concentration in the original solution. It was established that the total concentration of radical anions was not affected either by mixing the reagents or by the isomerization, i.e., [Trph$^{-}\cdot$]$_0$ = [Trph$^{-}\cdot$]$_\infty$ + [T$^{-}\cdot$]$_\infty$.

In each experiment a plot of ln (abs(500)$_\infty$ − abs(500)$_t$) against time resulted in a perfect straight line. The slopes of such lines give the apparent first-order rate constants, k_u, listed in the last column of Table I. Inspection of this table shows that k_u is affected by the concentration of [Trph$^{-}\cdot$] and therefore the isomerization $C^{-}\cdot \rightarrow T^{-}\cdot$ cannot be a simple unimolecular reaction.

Several mechanisms may account for these observations:

(a)
$$C^{-}\cdot \xrightarrow{k_2} T^{-}\cdot \qquad (2)$$

$$C^{-}\cdot + \mathrm{Trph}^{-}\cdot \rightleftarrows C^{2-} + \mathrm{Trph}; \quad K_3 \qquad (3)$$

$$C^{2-} \xrightarrow{k_i} T^{2-} \qquad (4)$$

$$T^{2-} + \mathrm{Trph} \rightleftarrows T^{-}\cdot + \mathrm{Trph}^{-}\cdot \qquad (5)$$

According to this scheme reactions 3 and 4 maintain an extremely low stationary concentration of C^{2-}, while reaction 5 rapidly converts the produced T^{2-} into $T^{-}\cdot$ regenerating the minute amount of Trph$^{-}\cdot$ consumed in reaction 3.

The following rate expression is then derived:

$$k_u = -\mathrm{d}\ln[C^{-}\cdot]/\mathrm{d}t = k_2 + k_iK_3([\mathrm{Trph}^{-}\cdot]/[\mathrm{Trph}])/(1 + k_i/k_{-3}[\mathrm{Trph}])$$

Therefore, at sufficiently high concentrations of Trph and at constant concentration of Trph$^{-}\cdot$ the observed $k_u - k_2$ should be proportional to 1/[Trph]. The data collected in Table I show, however, that k_u is independent of [Trph] for a constant [Trph$^{-}\cdot$]. Either k_i is very high ($>10^{10}$ s^{-1}) or the reduction of C$^{-}\cdot$ produces only one kind of dianions, denoted by X^{2-}. The latter are converted by the backward reaction 3 either into T$^{-}\cdot$ with probability γ, or into C$^{-}\cdot$ with probability $1 - \gamma$. Most probably $\gamma \approx 1$.

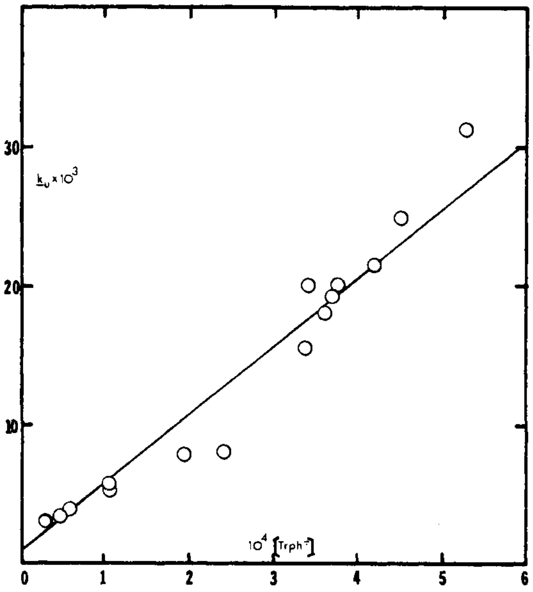
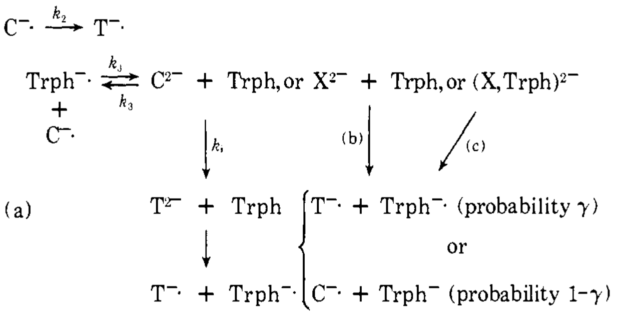


Figure 1. Plot of k_u vs. [Trph$^{-}\cdot$].

Scheme I



The above modification of mechanism a (Scheme I) is embodied in mechanism b

$$\text{(b)}\quad \mathrm{Trph}^{-}\cdot + C^{-}\cdot \underset{1-\gamma}{\overset{k_3}{\rightleftarrows}} \mathrm{Trph} + X^{2-} \overset{\gamma}{\rightleftarrows} \mathrm{Trph}^{-}\cdot + T^{-}\cdot$$

and such a scheme leads to the rate expression

$$k_u = -\mathrm{d}\ln[C^{-}\cdot]/\mathrm{d}t = k_2 + \gamma k_3[\mathrm{Trph}^{-}\cdot]$$

A plot of k_u vs. [Trph$^{-}\cdot$] shown in Figure 1 is linear. Its slope gives $\gamma k_3 = (40 \pm 3)$ M^{-1} s^{-1} and the intercept $k_2 = 1.1 \times 10^{-3}$ s^{-1}.

In proposing the third mechanism (c) we assume that the lifetime of X^{2-} is so short that the two alternative reactions reverting it into radical anions take place before the interacting reagents become separated, i.e.,

$$\mathrm{Trph}^{-}\cdot + C^{-}\cdot \overset{K_{enc}}{\rightleftarrows} (\mathrm{Trph}^{-}\cdot, C^{-}\cdot) \underset{1-\gamma}{\overset{k_r}{\rightleftarrows}} (\mathrm{Trph},X)^{2-}$$

$$\overset{\gamma}{\rightleftarrows} (\mathrm{Trph}^{-}\cdot, T^{-}\cdot) \rightleftarrows \mathrm{Trph}^{-}\cdot + T^{-}\cdot$$

In this last scheme the parentheses symbolize encounter complexes, while (Trph,X)$^{2-}$ represents a state of the system in which the isomerization may take place. In this interpretation k_3 of mechanism b is replaced by $K_{enc}k_r\gamma \simeq K_{enc}k_r$, i.e., the frequency of the *effective* encounters.

Treatment c slightly differs from b. In the latter the second electron may be removed by Trph molecule *different* from that

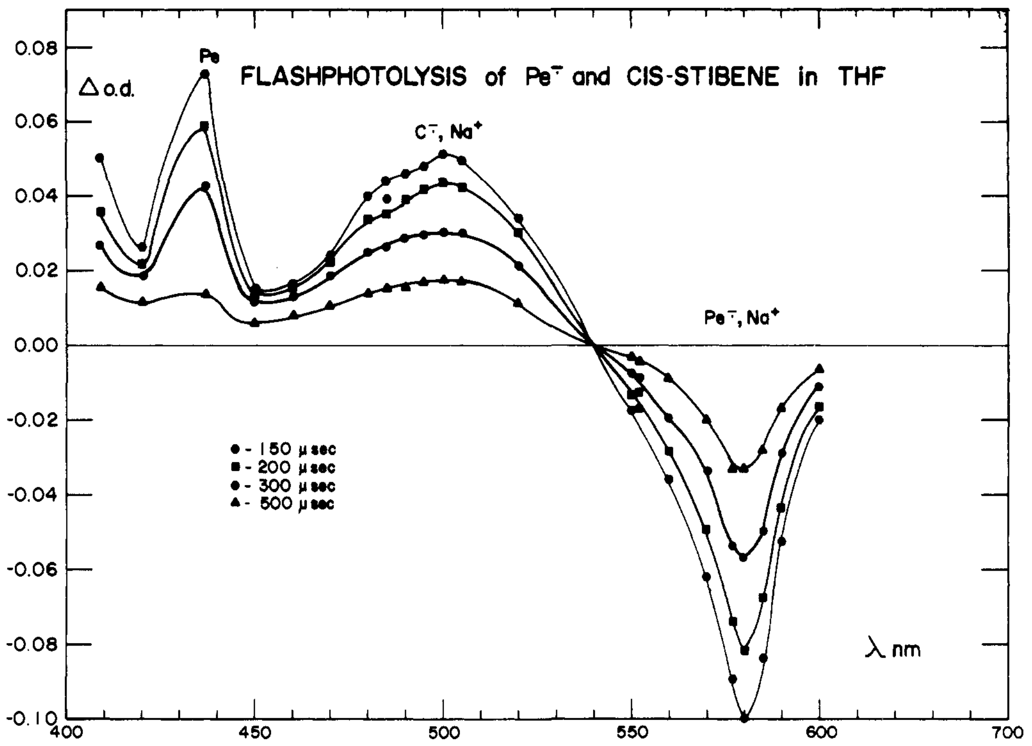


Figure 2. Difference spectrum of flash-photolyzed solution of $Pe^{-}\cdot,Na^{+}$ and C in THF, 100 μs after flash. The bleaching at 580 nm arises from the temporary destruction of $Pe^{-}\cdot,Na^{+}$, the absorbance at 437 nm manifests the formation of Pe, and the absorbance at 500 nm is attributed to $C^{-}\cdot,Na^{+}$.

formed in the effective encounter, whereas the *same* Trph molecule has to be involved in both reactions if interpretation c is correct. In that case the existence of stilbene dianions as an independent species is not required. The effective encounter of $Trph^{-}\cdot$ and $C^{-}\cdot$ may be treated as an event catalyzing the conversion of $C^{-}\cdot$ into $T^{-}\cdot$, presumably by momentary sharing of the extra electrons. Of course, all three mechanisms become kinetically indistinguishable from each other when k_i, the rate of isomerization of the hypothetical C^{2-} into T^{2-}, becomes much greater than $k_{-3}[Trph]$, e.g., for $k_i \geq 10^{11}\ s^{-1}$.

In terms of mechanisms a and b the backward reaction (3) is expected to be diffusion controlled, i.e., k_{-3} is probably of the order $10^{10}\ M^{-1}\ s^{-1}$. This interpretation requires $K_3 \simeq 4 \times 10^{-9}$ and the second reduction potential of *cis*-stilbene, i.e., $C^{-}\cdot \rightarrow stilbene^{2-}$, to be greater than the first one at least by 0.7 V.

Could the association of C^{2-} with a cation prolong its lifetime and make it distinct from T^{2-}? Such an association takes place in THF and apparently it is responsible for the relatively long lifetime of (C^{2-}, Cat^{+}) or $(C^{2-}, 2Cat^{+})$ in that solvent. Indeed, the previous results[5] unequivocally show that two distinct salts of dianions, one derived from C and the other from T, are present in that system. We investigated therefore the effect of added sodium tetraphenylboride on the rate of isomerization. The result was negative, as shown by the data listed in Table I. Apparently, the oppositely charged ions are not paired in HMPA, even in the presence of an excess of Na^{+}.

The puzzling features of the absorbance observed in the previous study[1] when *cis*-stilbene was mixed with sodium biphenylide become now explicable. The reaction $B^{-}\cdot + C^{-}\cdot$ greatly accelerated the isomerization of $C^{-}\cdot$ into $T^{-}\cdot$.

Absorption Spectrum of *cis*-Stilbene Radical Anions. The existence of two isomeric stilbene radical anions, $C^{-}\cdot$ and $T^{-}\cdot$, was unequivocally demonstrated in the preceding section. The *trans*-stilbene radical anion, $T^{-}\cdot$, is a stable and well-known species. The absorption spectrum of its sodium salt in THF was first reported by Zabolotny and Garst,[6] λ_{max} 480 nm, ϵ 6.2 × 10^4. In HMPA the λ_{max} of $T^{-}\cdot$ appears at 500 nm, ϵ 6.0 × 10^4 (ref 1) and our own results have shown λ_{max} of the sodium salt in THF to be at 494 nm with ϵ 5.5 × 10^4. In contrast, *cis*-stilbene radical anion, $C^{-}\cdot$, is a labile species, spontaneously isomerizing into $T^{-}\cdot$. Its absorption spectrum was obtained now by the following strategem.

An excess of highly purified *cis*-stilbene, C ([C] ~ 10^{-4} M), was added to a solution of ~2 × 10^{-6} M sodium perylenide, $Pe^{-}\cdot,Na^{+}$, in THF. Isomerization, C $\rightleftarrows$ T, does not occur under these conditions because electron affinity of perylene is too high. Indeed, from the results reported in ref 5 we calculate the rate of isomerization induced by $Pe^{-}\cdot,Na^{+}$ to be 10^{10} times slower than that induced by sodium anthracenide, i.e., immeasurably slow. Thus prepared solution is placed in a 10 cm long cylindrical quartz cell, equipped with optically flat windows and flashed with visible light. As shown previously[7] flash of light ejects electrons from $Pe^{-}\cdot$ and, under our conditions, some of them are captured by the *cis*-stilbene. The difference spectrum of the irradiated solution is shown in Figure 2. The bleaching at 580 nm arises from the destruction of $Pe^{-}\cdot$ ($Pe^{-}\cdot + h\nu \rightarrow Pe + e^{-}$), the absorbance at 437 nm manifests the formation of an equivalent amount of Pe, and the absorbance at 500 nm is attributed to the formation of $C^{-}\cdot$. The bleached $Pe^{-}\cdot$ is re-formed in about 1 ms, i.e., $C^{-}\cdot + Pe \rightarrow C + Pe^{-}\cdot$; however, although the absorbance and bleaching decay, the ratio ΔOD(500)/ΔOD(580) remains constant within the time of observation. Thus the spectrum of $C^{-}\cdot,Na^{+}$ was constructed, its molar absorbance at 500 nm calculated as 3.3 × 10^4 based on ϵ of $Pe^{-}\cdot$ at 580 nm of 5.9 × 10^4. To test the reliability of the method, these experiments were repeated using, however, *trans*-stilbene instead of its cis isomer. The resulting difference spectrum is shown in Figure 3; λ_{max} of $T^{-}\cdot,Na^{+}$ was observed at 495 nm, ϵ 5.2 × 10^4, in fair agreement with the direct determination. Both spectra (corrected for the absorbance of Pe) are shown in Figure 4.

The results of the above experiments permitted us to de-

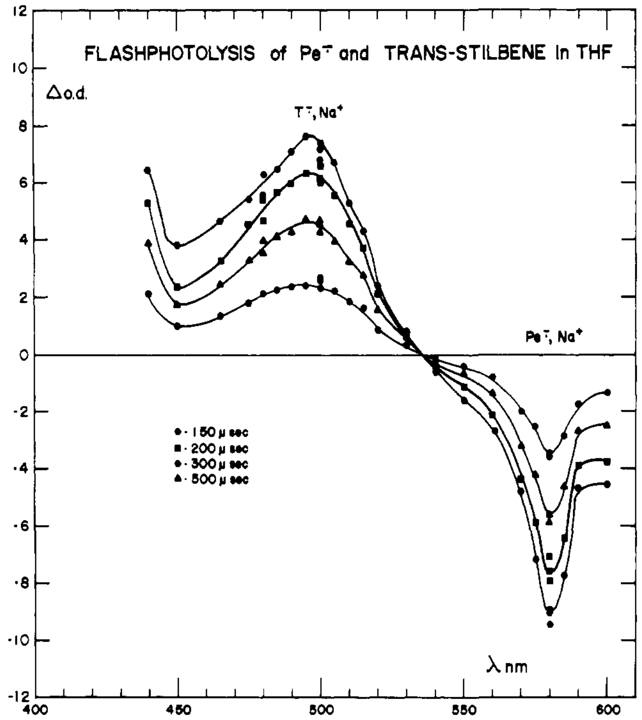


Figure 3. Difference spectrum of flash-photolyzed solution of $Pe^{-}\cdot,Na^{+}$ and T in THF, 100 μs after flash. The bleaching at 580 nm arises from the temporary destruction of $Pe^{-}\cdot,Na^{+}$, the absorbance at 437 nm manifests the formation of Pe, and the absorbance at 495 nm is attributed to $T^{-}\cdot,Na^{+}$.

termine the rate constants of the following electron transfers taking place in THF:

$$C^{-}\cdot,Na^{+} + Pe \rightarrow C + Pe^{-}\cdot,Na^{+} \quad k = 1.5 \times 10^{10}\ M^{-}\ s^{-1}$$

$$T^{-}\cdot,Na^{+} + Pe \rightarrow T + Pe^{-}\cdot,Na^{+} \quad k = 1.8 \times 10^{10}\ M^{-1}\ s^{-1}$$

The absorption spectrum of $C^{-}\cdot,Na^{+}$ was determined also by pulse-radiolysis technique. In cooperation with Professor L. M. Dorfman and Dr. Bockrath[8] we pulsed a 10^{-2} M THF solution of *cis*-stilbene containing 7×10^{-3} M sodium tetraphenylboride. The absorption spectrum of the resulting $C^{-}\cdot$, Na^{+} had a maximum at 498 nm and width at half-height of ~50 nm, in fair agreement with our findings (λ_{max} 500 nm, width ~60 nm). Unfortunately, no attempt was made to determine accurately the molar absorbance, but the results indicate a value of $2\text{-}3 \times 10^4$ for the ϵ, again comparable to that derived from flash photolysis. The absorption spectrum of *trans*-stilbene$^{-}\cdot$ was determined previously by pulsing a solution of *trans*-stilbene in 2-propanol.[4] The λ_{max} was found at 490 nm but unfortunately the respective ϵ was not reported. Thus, a slight hypsochromic shift is observed in both studies, although it should be noted that a spectrum of the free $T^{-}\cdot$ in 2-propanol was recorded by Dorfman, whereas we report the spectrum of $T^{-}\cdot,Na^{+}$ in THF.

The similarity of the absorption spectra of $C^{-}\cdot$ and $T^{-}\cdot$ should not be interpreted as evidence for their identity. The molar absorbances are different. Moreover, even 2000 pulses, each producing ~10^{-5} M concentration of the radical ions in a 10^{-2} M solution of *cis*-stilbene, did not lead to any measurable conversion of the cis into trans isomer. This clearly proves that $C^{-}\cdot,Na^{+} - e^{-} \rightarrow C$, i.e., $C^{-}\cdot,Na^{+}$ is *different* from $T^{-}\cdot,Na^{+}$.

Electron-Transfer Equilibrium $T^{-}\cdot,Na + C \rightleftarrows T + C^{-}\cdot,Na^{+}$ in THF. Having established the molar absorbances of $C^{-}\cdot,Na^{+}$ and $T^{-}\cdot,Na^{+}$ in THF, we proceeded further and determined the equilibrium constant of the reaction $T^{-}\cdot,Na^{+} + C \rightleftarrows T + C^{-}\cdot,Na^{+}$. This was achieved by flash photolyzing mixtures of C and T of known proportions added to solutions of $Pe^{-}\cdot,Na^{+}$. The ratio of ΔOD at 500 nm (or 495 nm) to ΔOD at 580 nm provides the average molar absorbance, ϵ_{av}, of the resulting mixture of $C^{-}\cdot,Na^{+}$ and $T^{-}\cdot,Na^{+}$, the latter being given by $x\epsilon_{C^{-}\cdot} + (1 - x)\epsilon_{T^{-}\cdot}$ where x denotes the mole fraction of $C^{-}\cdot,Na^{+}$ in the mixture of $C^{-}\cdot,Na^{+}$ and $T^{-}\cdot,Na^{+}$. Thus, the sought equilibrium constant K_{tr} is given by

$$K_{tr} = (x/(1 - x))([T]/[C])$$

The pertinent data are listed in Table II. The ratio $[C^{-}\cdot$,

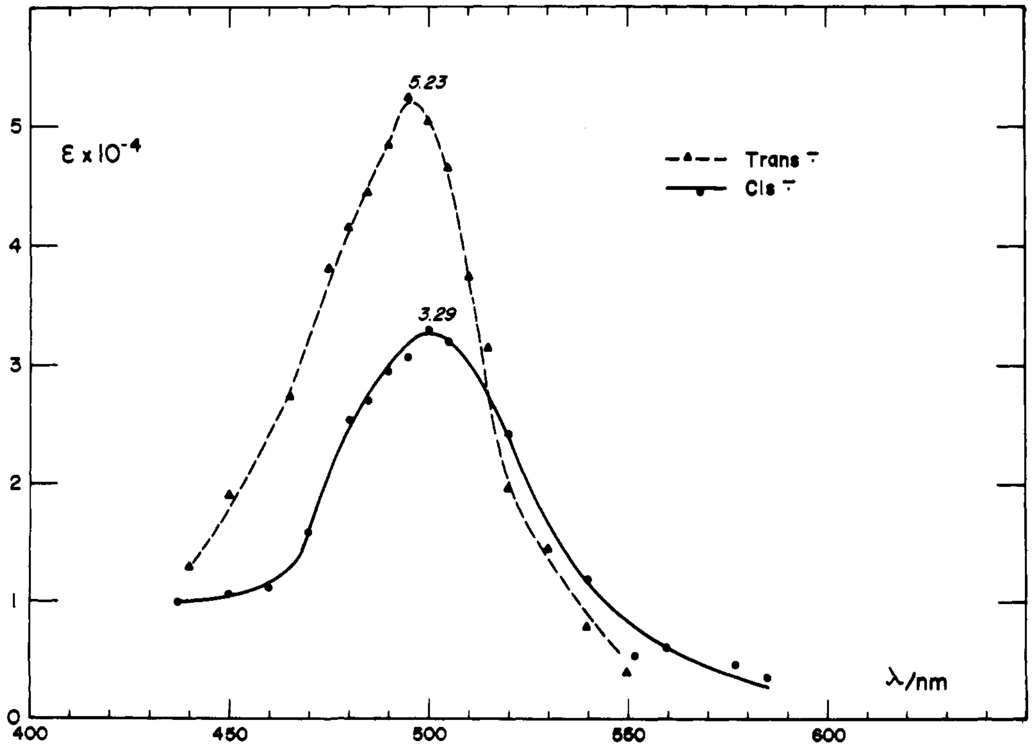


Figure 4. The absorption spectra of $C^{-}\cdot,Na^{+}$ and $T^{-}\cdot,Na^{+}$ in THF.

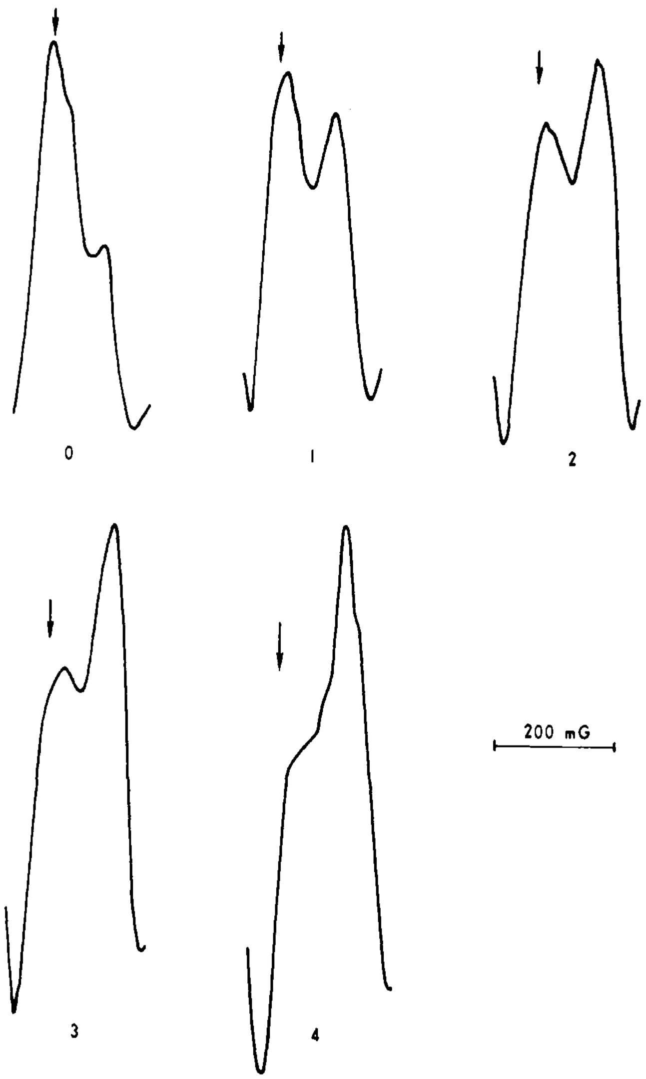


Figure 5. The ESR line (5th from the center) of $C^{-}\cdot$ in THF. (0) in flow, (1) 3 min after stopping the flow, (2) 6 min after stopping the flow, (3) 9 min after stopping the flow, (4) 24 min after stopping the flow. The arrows are at the distance of 830 mG from the center. Note the decay of the original line (840 mG from the center) and the appearance of a new line (1000 mG from the center). It arises from $s = \frac{1}{2}$ for proton 4 (a = 3.93 G) and $s = \frac{1}{2}$ for proton 6 (a = 2.93 G).

$Na^{+}]/[T^{-}\cdot,Na^{+}]$ shows a trend with time which is exaggerated by its high sensitivity to experimental errors in ΔOD's. If this trend is genuine it would indicate that *trans*-stilbene captures electrons more readily than *cis*-stilbene and thence the initial composition of the $C^{-}\cdot,Na^{+} - T^{-}\cdot,Na^{+}$ mixture is determined by the kinetics of the electron-capture process and not by equilibrium. However, in view of the relatively high concentration of the hydrocarbons ($\sim 10^{-4}$ M) and the length of the time interval between the flash and the observation (150 μs), it seems unlikely that the equilibrium is not established yet.

In spite of some scatter of the results the value of K is well established corresponding to $\Delta\epsilon$ = 47 mV. It is particularly reassuring to find the ratio $[C^{-}\cdot,Na^{+}]/[T^{-}\cdot,Na^{+}]$ proportional to the ratio [C]/[T]. The higher value (0.6) of the electron-transfer equilibrium in HMPA[1] may imply that the association of $T^{-}\cdot$ with Na^{+} in THF is weaker than that of $C^{-}\cdot$ with Na^{+}.

Disproportionations $2C^{-}\cdot \rightleftarrows C + X^{2-}$ and $2T^{-}\cdot \rightleftarrows T + X^{2-}$. Our data permit us to compare the disproportionations of the free $C^{-}\cdot$ or $T^{-}\cdot$ radical ions into the common dianions X^{2-} having, most probably, a skewed conformation. The following data are now available:

Table II. Equilibrium $T^{-}\cdot,Na^{+} + C \rightleftarrows T + C^{-}\cdot,Na^{+}$ in THF. $K = [C^{-}\cdot,Na^{+}][T]/[C][T^{-}\cdot,Na^{+}]$

[C]/[T]	Time, μs	ΔOD(500)/ ΔOD(580)	$[C^{-}\cdot,Na^{+}]/[T^{-}\cdot,Na^{+}]$	K
2.46	150	0.755 (0.771)[a]	0.38 (0.37)	0.15 (0.15)
2.46	200	0.735 (0.737)	0.52 (0.56)	0.21 (0.23)
2.46	250	0.744 (0.747)	0.45 (0.50)	0.18 (0.20)
2.88	150	0.749 (0.757)	0.42 (0.44)	0.15 (0.15)
2.88	200	0.723 (0.731)	0.62 (0.60)	0.21 (0.21)
2.88	250	0.716 (0.722)	0.68 (0.67)	0.24 (0.23)
2.97	150	0.752 (0.766)	0.39 (0.39)	0.13 (0.13)
2.97	200	0.756 (0.759)	0.37 (0.43)	.012 (0.14)
2.97	250	0.737 (0.733)	0.50 (0.60)	0.13 (0.20)
5.18	150	0.709 (0.699)	0.75 (0.86)	0.14 (0.17)
5.18	200	0.709 (0.710)	0.75 (0.77)	0.14 (0.15)
5.18	250	0.733 (0.724)	0.53 (0.65)	0.10 (0.13)
8.44	150	0.668 (0.649)	1.31 (1.50)	0.16 (0.18)
8.44	200	0.672 (0.643)	1.24 (1.60)	0.15 (0.19)
8.44	250	0.667 (0.647)	1.34 (1.72)	0.16 (0.20)

[a] Results in parentheses were obtained from the absorbance measured at 495 nm.

$$\text{(a)}\quad C^{-}\cdot + Trph^{-}\cdot \rightleftarrows X^{2-} + Trph \qquad K_3 \approx 4 \times 10^{-9}$$

$$\text{(b)}\quad T^{-}\cdot + Trph \rightleftarrows T + Trph^{-}\cdot \qquad K_{T\text{-}Trph} \approx 10^{-4}$$

$$\text{(c)}\quad C^{-}\cdot + T \rightleftarrows T^{-}\cdot + C \qquad K_{C^{-}\cdot,T} = 1.5$$

The value for a was obtained from the results of this work, for b from the potentiometric titrations, and for c from the previously reported study.[1] On addition these equations yield

$$2C^{-}\cdot \rightleftarrows C + X^{2-} \qquad K_{\text{dispr},C^{-}\cdot} \approx 6 \times 10^{-13}$$

The disproportionation constant of the free $T^{-}\cdot$ radical ions is even lower. The ratio $K_{\text{dispr},T^{-}\cdot}/K_{\text{dispr},C^{-}\cdot}$ is given by the equilibrium constant of

$$2T^{-}\cdot + C \rightleftarrows T + 2C^{-}\cdot$$

which in turn is equal to the ratio of the equilibrium constants

$$2(T^{-}\cdot + C \rightleftarrows T + C^{-}\cdot) \qquad 1/K^{2}_{C^{-}\cdot,T} = 0.36$$

and

$$C \rightleftarrows T \qquad K_{CT}$$

Hence, $K_{\text{dispr},T^{-}\cdot}/K_{\text{dispr},C^{-}\cdot} = 0.4/K_{CT}$. Although the value of K_{CT} at ambient temperature is not known, there is no doubt that it is >100.

The significance of this result is self-evident. Apparently the steric hindrance between the Ph groups in $C^{-}\cdot$ radical anions is comparable, or even slightly greater, than in the *cis*-stilbene. On disproportionation one of the $C^{-}\cdot$ radical ions is converted into a skewed, nonhindered dianion X^{2-}, and thus the steric hindrance is released. This favors the disproportionation of $C^{-}\cdot$.

However, such a gain does not take place in the disproportionation of the nonhindered $T^{-}\cdot$, and hence $K_{\mathrm{dispr},T^{-}\cdot}$ is by a corresponding factor lower than $K_{\mathrm{dispr},C^{-}\cdot}$. The assumption of the skewed form of the dianion is basic for this argument.

The skewed structure of the dianions seems to contradict the previous claim[13] of the existence of two distinct salts $C^{2-},2Cat^{+}$ and $T^{2-},2Cat^{+}$. Such a contradiction could be avoided. Let us assume that the cations are associated with a single side of phenyl groups and that such an association is retained during the rotation around the C–C axis. The skewed form of the $C^{2-},2Cat^{+}$ and $T^{2-},2Cat^{+}$ would be then different if the cations have to find themselves on the opposite sides of a planar trans or cis form of stilbene. The skewed form derived from $C^{2-},2Cat^{+}$ would have either each cation associated with a phenyl group placed in the vicinity of the other phenyl, or each separated from the other phenyl group, whereas in $T^{2-},2Cat^{+}$ one cation associated with a phenyl would be placed in the vicinity of the other phenyl while the second cation would be separated from the alternative phenyl group. Thus the difference between $C^{2-},2Cat^{+}$ and $T^{2-},2Cat^{+}$ could be retained even for the skewed structure.

ESR Spectrum of *cis*-Stilbene Radical Anions. Our study of the optical spectrum of $C^{-}\cdot$ was supplemented by ESR investigation with the intention of differentiating the ESR spectra of $C^{-}\cdot$ and $T^{-}\cdot$. Past attempts to record the ESR spectrum of $C^{-}\cdot$ were in vain,[1,9,10] although some indirect evidence for the existence of $C^{-}\cdot$ was derived by Chang[11] from his ESR observations. The previous work of our group demonstrated that the intensity of an overmodulated ESR signal does not vary as $C^{-}\cdot$ is converted into $T^{-}\cdot$; i.e., the isomerization does not destroy radicals.[1]

In our present study the ESR spectrum of $C^{-}\cdot$ in HMPA was examined by flowing an HMPA solution of triphenylene$^{-}\cdot$ + triphenylene mixed with a slight excess of C through a flat cell placed in the cavity of an ESR spectrometer. Segments of the spectrum were recorded as the mixture was flown through the cell; thereafter the flow was stopped and the recording of a chosen segment of the spectrum repeated every 3 min for about 0.5 hr. Some definite and reproducible changes were observed in the central part of the spectrum. The central line ($m = 0$) became sharper with time, apparently owing to a small difference in g values (the center line of $T^{-}\cdot$ appears to be shifted by 70 mG upfield from that of $C^{-}\cdot$). The fifth line from the center was split into two, and on stopping the flow the weak line grew and the stronger one decayed. These changes are shown in Figure 5. No attempt was made to record and analyze the full spectrum because of the limited amount of solution available for this study, but the observed differences and changes with time leave no doubt that the ESR spectra of $C^{-}\cdot$ and $T^{-}\cdot$ are not identical.

Final Conclusions

We demonstrated that free *cis*-stilbene, $C^{-}\cdot$, as well as its sodium salt, $C^{-}\cdot,Na^{+}$, are distinct species from *trans*-stilbene, $T^{-}\cdot$, radical anions and its sodium salt. The labile $C^{-}\cdot$ was characterized by its optical absorption. The kinetics of its conversion into $T^{-}\cdot$ was investigated and the pertinent rate constants determined.

The *free* dianions of C and T formed in HMPA probably cannot be treated as distinct species, although in THF their association with counterions makes $C^{2-},2Cat^{+}$ a distinct species from $T^{2-},2Cat^{+}$.

The disproportionation of $2C^{-}\cdot \rightarrow X^{2-} + C$ is favored when compared with the disproportionation $2T^{-}\cdot \rightarrow X^{2-} + T$, because the steric hindrance in one $C^{-}\cdot$ is released on formation of the skewed X^{2-}. This gain in energy is not taking place in the disproportionation of the nonhindered $T^{-}\cdot$.

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