m/e (P) 241.0705. Found: *m/e* 241.0708. Anal. ($C_{12}H_{15}DOS_2$) C, H, D, S.

Acknowledgment. R.B.G. thanks Dr. E. W. Yankee for helpful discussions during the course of this study.

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Electron Transfer Induced Isomerization of *cis*-4,4′-Diphenylstilbene into Its Trans Form

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Abstract: The 4,4′-diphenylstilbenes, denoted by C and T for the cis and trans isomers, as well as $T^{-}\cdot$ and T^{2-}, were characterized spectroscopically and electrochemically. The disproportionation $2T^{-}\cdot,Na^{+} \rightleftarrows T + T^{2-},2Na^{+}$ has equilibrium constant in THF 0.04, ΔH = 18.2 kcal/mol, and ΔS = 54 cal/mol·deg, and its rate constant is 9.0×10^{8} M^{-1} s^{-1}. The cis–trans isomerization was studied in THF at ambient temperature in three systems: $T + T^{-}\cdot,Na^{+} + C$, $T^{2-},2Na^{+} + C$, and $B^{-}\cdot,Na^{+} + C$, B denoting biphenyl. In the first two systems the reaction is governed by the three interrelated equilibria, namely, $C + T^{-}\cdot,Na^{+} \rightleftarrows T + C^{-}\cdot,Na^{+}$ (K_1), $C + T^{2-},2Na^{+} \rightleftarrows C^{-}\cdot,Na^{+} + T^{-}\cdot,Na^{+}$, ($K_2 = K_1/K_{\mathrm{dispr}}$), and $2T^{-}\cdot,Na^{+} \rightleftarrows T + T^{2-},2Na^{+}$ (K_{dispr}), the rate-determining step being $C^{-}\cdot,Na^{+} \rightarrow T^{-}\cdot,Na^{+}$ (k_i). The results give k_iK_1 or k_iK_2. In the last system the rapid electron transfer $B^{-}\cdot,Na^{+} + C \rightarrow B + C^{-}\cdot,Na^{+}$ produces momentarily high concentration of $C^{-}\cdot,Na^{+}$ and, since its disproportionation is favored, a relatively large amount of $C^{2-},2Na^{+}$. The latter rapidly isomerizes into $T^{2-},2Na^{+}$. Thus, in early stages of the reaction, the concentration of $T^{2-},2Na^{+}$ exceeds that expected for the disproportionation equilibrium had the reaction with $B^{-}\cdot,Na^{+}$ formed only $C^{-}\cdot,Na^{+}$ and then $T^{-}\cdot,Na^{+}$. This observation provides the evidence for the existence of $C^{2-},2Na^{+}$.

Several routes lead to conversion of *cis*-stilbene to its trans isomer. A direct thermal reaction is too slow to be observed at ambient temperature; it was studied[2a,b] at elevated temperatures exceeding 300 °C. Photoisomerization was extensively investigated;[2c,d] it leads to photostationary state. In a recent series of papers[3] we reported an isomerization process catalyzed by electron transfer. Reduction of *cis*-stilbene to its radical anion or dianion is followed by their spontaneous isomerization to the respective radical anion or dianion of *trans*-stilbene. Electron transfer from the latter to the unreduced *cis*-stilbene generates the original cis radical anions or dianions and continues the process.

Spontaneous isomerization of *cis*-stilbene radical anions, or their ion pairs, is slow, whereas the dianions, or their aggregates with cations, isomerize rapidly. Which of these two contributes more to the overall isomerization depends on the extent of disproportionation, 2 *cis*-stilbene$^{-}\cdot$ ⇄ *cis*-stilbene + *cis*-stilbene^{2-}. For example, in hexamethylphosphoric triamide the radical anions are not associated with cations and the disproportionation constant is very low. Thus, virtually all the isomerization proceeds via radical anions. In contrast, in THF the radical anions are coupled with cations into ion pairs and the disproportionation constant is high. Under these conditions the dianions are the intermediates responsible for the isomerization.

We extended these studies to a derivative of stilbene, namely, the *p,p*′-diphenylstilbenes. Our results revealed again that isomerization of *cis-p,p*′-diphenylstilbene (C) may be induced by the radical anions or dianions of *trans-p,p*′-diphenylstilbene (T). Three equilibria are maintained in this system:

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

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

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

A more powerful reducing agent, viz., sodium biphenylide, $B^{-}\cdot,Na^{+}$, converts some C into $C^{2-},2Na^{+}$, and then the spontaneous reaction

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

produces $T^{2-},2Na^{+}$ in excess of what would be expected in disproportionation of equivalent amounts of $T^{-}\cdot,Na^{+}$.

The distinction between $C^{2-},2Na^{+}$ and $T^{2-},2Na^{+}$ is not required to account for that result. In fact, $C^{2-},2Na^{+}$ may be identical with $T^{2-},2Na^{+}$

Reagents and Their Characterization

trans-4,4′-Diphenylstilbene, subsequently referred to as T, was acquired commercially. The purchased material was

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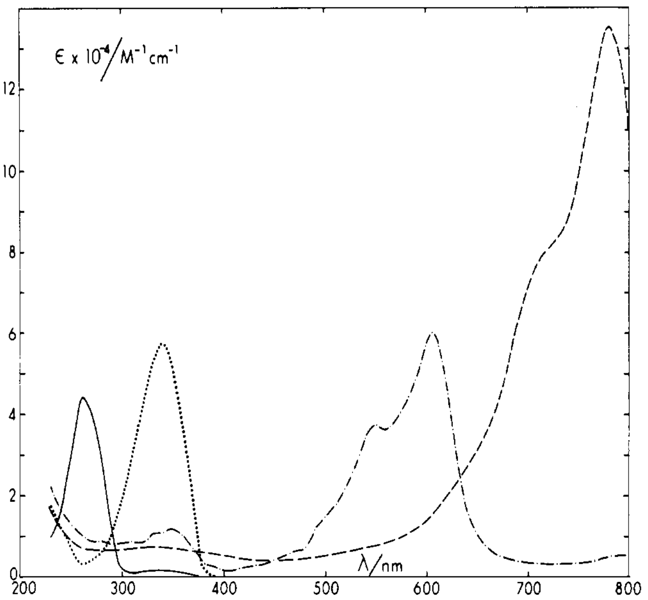
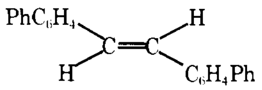
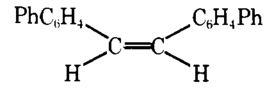


Figure 1. Optical absorption of C (solid line), T (dotted line), T$^{-}\cdot$,Na^{+} (dash-dot line), and T^{2-},2Na^{+} (dashed line), all in THF solution.



T



C

crystallized from benzene, dried under vacuum, and finally sublimed under high vacuum into sealed tubes equipped with break-seals. Thus purified material melts sharply at 304 °C, its mass spectrum reveals the molecular ion at *m/e* 332, the IR spectrum agrees with that reported in the literature,[4a] the UV spectrum in THF (see Figure 1) shows absorption maximum at 340 nm (ϵ 5.74 × 10^{4}), and the molar absorbance at 260 nm (λ_{max} of the cis isomer) is 0.33 × 10^{4}. The λ_{max} agrees with that reported by Baroni et al.[4b] and by Suzuki,[5] although the reported molar absorbances are slightly different from those determined by us (4.99 × 10^{4} in benzene).

The cis isomer, referred to as C, was prepared by photoisomerization of a deaerated THF suspension of T using a high-pressure mercury lamp as the light source and a thick Pyrex tube as a filter. Toward the end of the photolysis the suspension turns into a clear solution owing to higher solubility of the cis isomer. After evaporation of the solvent the solid residue is extracted with hot benzene and the dissolved cis isomer crystallized. On recrystallization the absorption at 340 nm virtually disappeared. The resulting spectrum, attributed to C, is also shown in Figure 1, λ_{max} 260 nm (ϵ 4.43 × 10^{4}), and molar absorbance at 340 nm is 0.16 × 10^{4}. These data agree with those reported by Baroni,[4a] although our product showed a substantially lower melting point than that reported by the Russian workers. The ^{1}H NMR spectrum of C recorded in deuterated benzene differs from that of T in the resonance of the olefinic protons, viz., δ 4.60 and 7.12 for C and T, respectively, while the aromatic multiplets, although of different patterns, appear in the same region, viz., 7.1–7.5 ppm for C and 7.1–7.6 ppm for T.

Extensive reduction on a sodium mirror of the THF solution of T yields the respective diamagnetic dianions, T^{2-}. Their spectrum, also shown in Figure 1, has the absorption maximum at 780 nm (ϵ 13.50 × 10^{4}); the molar absorbance at 606 (λ_{max} of T$^{-}\cdot$) is 1.47 × 10^{4}. The T^{2-} is converted into T$^{-}\cdot$ by adding tenfold excess of rigorously dried T. The radical anions absorb at λ_{max} 606 nm (ϵ 6.0 × 10^{4}); their molar absorbance at 780 nm is 0.55 × 10^{4}, at 340 nm 1.0 × 10^{4}, and at 260 nm 1.03 × 10^{4}. Neither C$^{-}\cdot$ nor C^{2-} could be prepared owing to their rapid isomerization.

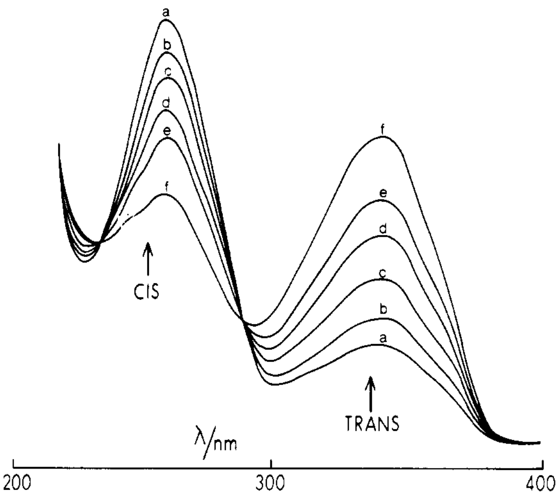


Figure 2. Typical spectra of THF solution of C + T$^{-}\cdot$ recorded over a period of about 24 h. The isomerization is induced by T$^{-}\cdot$,Na^{+} ([T$^{-}\cdot$,Na^{+}] = const). Note the isosbestic points at 290 and 238 nm.

Reduction Potentials and Disproportionation of T$^{-}\cdot$,Na^{+}

First reduction potential of T was determined potentiometrically in THF by the technique described elsewhere.[5] The couple T + T$^{-}\cdot$,Na^{+} was combined with perylene–perylene$^{-}\cdot$,Na^{+} and the results led to $\Delta\epsilon_{T,Pe}$ = 266 mV. A cyclic voltammogram of T in THF on a platinum electrode shows two reversible peaks at $\epsilon_{1/2}$ = −2.07 and −2.27 V (vs. SCE) and similar potentials were obtained polarographically in DMF at a mercury electrode, namely, −2.13 and −2.36 V (vs. SCE). Since the polarographic $\epsilon_{1/2}$ of perylene was found[7] to be −1.81 V (corrected to SCE) in THF, the respective $\Delta\epsilon_{T,Pe}$ is 260 mV, in agreement with the potentiometric study.

The second redox potential of T was measured potentiometrically by combining the couple T$^{-}\cdot$,Na^{+} + T^{2-},2Na^{+} with T + T$^{-}\cdot$,Na^{+}. The results led to $\Delta\epsilon_{dispr}$ = 80 mV compared with $\Delta\epsilon_{dispr}$ = 200 mV obtained through cyclic voltammetry in THF. Potentiometric work utilized Na^{+} as the counterion, whereas Bu$_4$N^{+} was the counterion in the cyclic voltammetry. This accounts for the different findings. The sodium ions solvated by THF become desolvated on association with dianions making the disproportionation constant high, while this effect does not appear when large cations neutralize the anions.[10] Thus the observed different $\Delta\epsilon_{dispr}$'s agree with the general pattern observed for such reactions.

Kinetics of Cis–Trans Isomerization Induced by T$^{-}\cdot$,Na^{+}

A rigorously dried THF solution of T was partially reduced on sodium mirror. Its initial concentration, [T]$_{00}$, was determined previously by spectrophotometric technique. After reduction, spectrophotometric analysis allowed us to determine the concentration of T$^{-}\cdot$,Na^{+} and, by difference, the concentration of the residual, unreduced T. The latter is denoted by [T]$_0$. The partially reduced solution is introduced into one bulb of an apparatus described in ref 8b, while an approximately known amount of crystallinic C is placed in the other bulb. The C hydrocarbon is dissolved by distilling some of the solvent from the first bulb into the second, and then both solutions are mixed and poured into an optical cell, and the progress of isomerization is followed by monitoring the optical densities at 260 (λ_{max} of C) and at 340 nm (λ_{max} of T). All the operations were performed on a high-vacuum line using the standard high-vacuum technique.[8a] Typical spectra recorded at consecutive times are shown in Figure 2 and reveal the expected isosbestic point at 290 nm.

After completion of the reaction the ingredients were reduced to T^{2-},2Na^{+} and the concentration of the latter was determined spectrophotometrically. This gives [C]$_0$ + [T]$_{00}$

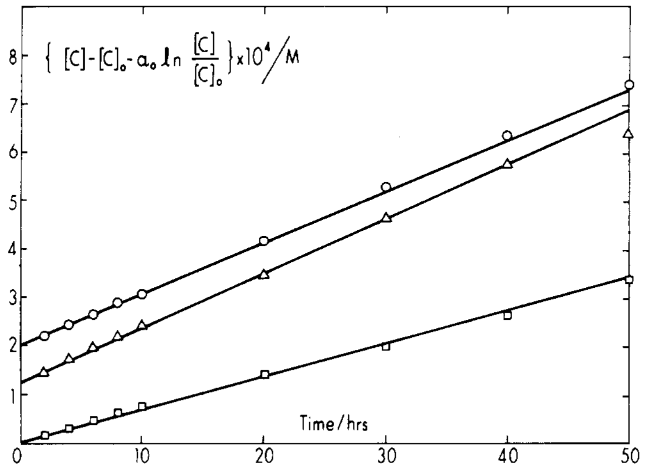


Figure 3. Plot of $\{[\mathrm{C}] - [\mathrm{C}]_0 - a_0 \times \ln([\mathrm{C}]/[\mathrm{C}]_0)\}$ vs. time: ○, $[\mathrm{C}]_0 = 9.3 \times 10^{-4}$ M, $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}] = 2.88 \times 10^{-4}$ M, $a = 10.6 \times 10^{-4}$ M; △, $[\mathrm{C}]_0 = 11.5 \times 10^{-4}$ M, $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}] = 2.31 \times 10^{-4}$ M, $a = 16.1 \times 10^{-4}$ M; □, $[\mathrm{C}]_0 = 11.4 \times 10^{-4}$ M, $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}] = 1.78 \times 10^{-4}$ M, $a = 15.4 \times 10^{-4}$ M. The △ and ○ lines are displaced upward by 1 and 2 units, respectively. It seems that $[\mathrm{C}]_0$ in the △ line is slightly overestimated.

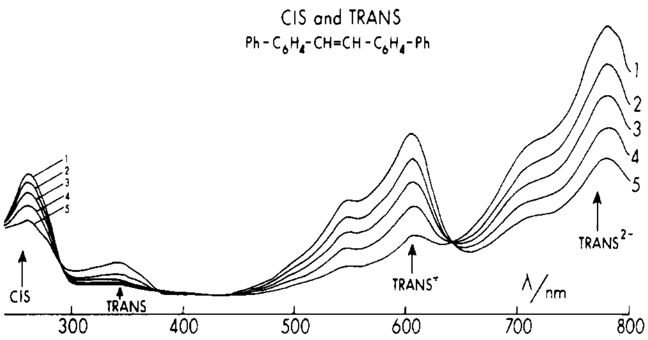


Figure 4. Typical spectra of reacting solution in which the C → T isomerization is induced by $\mathrm{T}^{2-},2\mathrm{Na}^{+}$. The reaction is monitored at 780 ($\lambda_{\max}$ of $\mathrm{T}^{2-},2\mathrm{Na}^{+}$) and at 606 nm ($\lambda_{\max}$ of $\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$). Note the isosbestic point at 644 nm expected for the 1:2 stoichiometry. The variable OD of $\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$ and $\mathrm{T}^{2-},2\mathrm{Na}^{+}$ makes it impossible to determine [C] and [T] from their absorbances.

and by subtracting the previously determined $[\mathrm{T}]_{00}$ one gets $[\mathrm{C}]_0$.

Since the reaction takes a few hours, it is plausible to assume that the equilibrium

$$\mathrm{C} + \mathrm{T}^{-}\cdot,\mathrm{Na}^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{C}^{-}\cdot,\mathrm{Na}^{+} + \mathrm{T} \qquad K_1$$

is maintained during its course, and the observed isomerization governed by the reaction $\mathrm{C}^{-}\cdot,\mathrm{Na}^{+} \rightarrow \mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$, k_i, with $k_i \ll k_{-1}[\mathrm{T}]$. Hence[11]

$$-\mathrm{d}\ln[\mathrm{C}]/\mathrm{d}t = k_iK_1[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]/[\mathrm{T}]$$

The concentration of $\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$ remains constant during each run, while the concentration of T varies, being given by $[\mathrm{C}]_0 + [\mathrm{T}]_0 - [\mathrm{C}]$. Denoting $[\mathrm{C}]_0 + [\mathrm{T}]_0$ by a, we find

$$-a\ln\{[\mathrm{C}]/[\mathrm{C}]_0\} + [\mathrm{C}] - [\mathrm{C}]_0 = k_iK_1[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]t$$

Plots of the left side of that equation vs. time are shown in Figure 3. Their slopes divided by $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$ give k_iK_1, namely, 1.0, 1.3, and 1.1 in units 10^{-5} s^{-1}.

Polarographic data indicate that the electron affinity of T is greater than that of C. The rate of electron transfer from $\mathrm{C}^{-}\cdot,\mathrm{Na}^{+}$ to T is expected, therefore, to be very fast; i.e., k_{-1} is probably in the range 10^8–10^{10} M^{-1} s^{-1}. Since $k_i \ll k_{-1}[\mathrm{T}]$, k_i is estimated to be smaller than 10^4 s^{-1}.

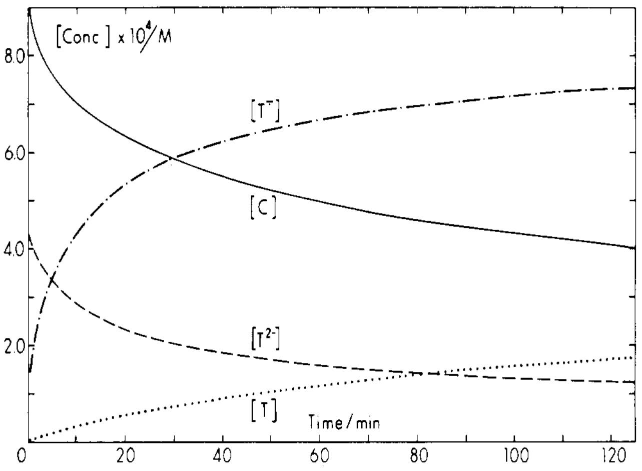


Figure 5. Typical plot of [C], [T], $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$, and $[\mathrm{T}^{2-},2\mathrm{Na}^{+}]$ as functions of time.

Table I

run	$10^4[\mathrm{T}^{2-},2\mathrm{Na}^{+}]$, M	$10^4[\mathrm{C}]_0$, M	$[\mathrm{C}]_0$, $[\mathrm{T}^{2-},2\mathrm{Na}^{+}]_0$	slope = k_iK_2, s^{-1}
A	9.80	36.53	3.73	3.21×10^{-4}
B	9.62	16.41	1.71	2.62×10^{-4}
C	5.45	39.95	7.33	2.97×10^{-4}
D	5.07	18.21	3.59	3.00×10^{-4}
E	5.0	9.49	1.90	3.26×10^{-4}
F	4.93	19.46	3.55	3.15×10^{-4}
G	4.80	17.85	3.72	2.50×10^{-4}
				av $(2.96 \pm 0.29) \times 10^{-4}$
H	9.62[a]	25.56		2.84×10^{-4}

[a] $10^4[\mathrm{B}^{-}\cdot,\mathrm{Na}^{+}]$/M.

Kinetics of Cis–Trans Isomerization Induced by $\mathrm{T}^{2-},2\mathrm{Na}^{+}$

Addition of $\mathrm{T}^{2-},2\mathrm{Na}^{+}$ to C also induces the isomerization of that hydrocarbon revealed by decrease of concentration of $\mathrm{T}^{2-},2\mathrm{Na}^{+}$ and increase of concentration of $\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$. The isomerization converts C into T, and accumulation of the latter hydrocarbon affects the disproportionation equilibrium

$$\mathrm{T} + \mathrm{T}^{2-},2\mathrm{Na}^{+} \rightleftarrows 2\mathrm{T}^{-}\cdot,\mathrm{Na}^{+} \qquad 1/K_{\mathrm{dispr}}$$

reducing $[\mathrm{T}^{2-},2\mathrm{Na}^{+}]$ and yielding equivalent amounts of $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$. The progress of the reaction was monitored by scanning the spectra every few minutes, and a typical result, shown in Figure 4, reveals the expected isosbestic point at 644 nm (for the 1:2 stoichiometry). From the spectra the concentrations of $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$ and $[\mathrm{T}^{2-},2\mathrm{Na}^{+}]$ were determined as functions of time. It was gratifying to find the sum $2[\mathrm{T}^{2-},2\mathrm{Na}^{+}] + [\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$ to be constant and equal to $2[\mathrm{T}^{2-},2\mathrm{Na}^{+}]_0$. Concentration of T was calculated from the relation $[\mathrm{T}] = K_{\mathrm{dispr}}[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]^2/[\mathrm{T}^{2-},2\mathrm{Na}^{+}]$ using the previously determined value of 0.04 for K_{dispr}, and the concentration of C was obtained from the balance equation $[\mathrm{C}] = [\mathrm{C}]_0 - [\mathrm{T}] - \frac{1}{2}[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$. Typical results giving [C], [T], $[\mathrm{T}^{-}\cdot,\mathrm{Na}^{+}]$, and $[\mathrm{T}^{2-},2\mathrm{Na}^{+}]$ as functions of time are shown in Figure 5. From plots of ln [C] vs. time the momentary values of d ln [C]/dt were obtained by graphical procedure.

Table I gives the initial conditions of seven experiments. It is assumed that the isomerization is due to the conversion of $\mathrm{C}^{-}\cdot,\mathrm{Na}^{+} \rightarrow \mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$, k_i, the concentration of $\mathrm{C}^{-}\cdot,\mathrm{Na}^{+}$ being determined by the rapidly established equilibrium

$$\mathrm{C} + \mathrm{T}^{2-},2\mathrm{Na}^{+} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{C}^{-}\cdot,\mathrm{Na}^{+} + \mathrm{T}^{-}\cdot,\mathrm{Na}^{+}$$

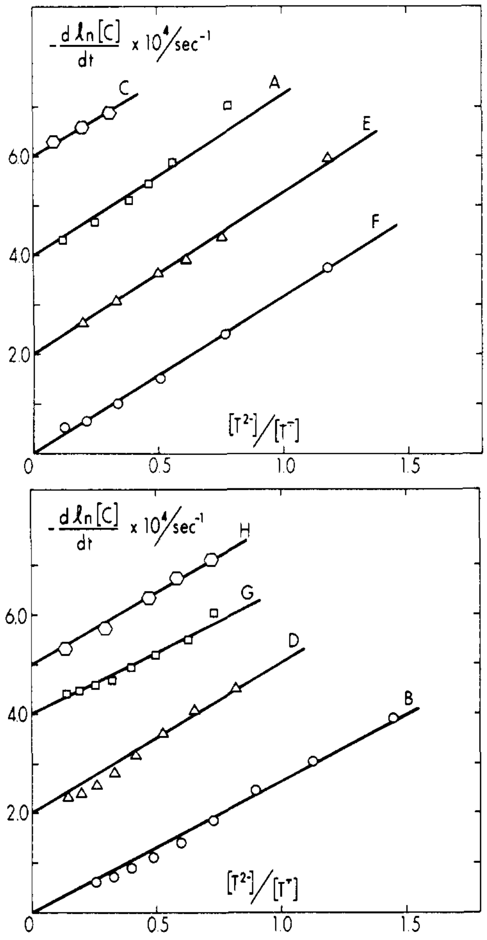


Figure 6. Plots of d ln [C]/dt vs. [T^{2-},2Na^+]/[$T^-\cdot$,Na^+] (see Table I). Lines A, C, D, E, G, and H are displaced vertically by adding 4.0, 6.0, 2.0, 2.0, 4.0, and 5.0, respectively, to the appropriate values of −d ln [C]/dt.

Table II

$10^7[T]_0$, M	$10^7[T^{-}\cdot$, $Na^+]_0$, M	$10^7[T^{2-}$, $2Na^+]_0$, M	slope, s^{-1} [c]	$10^{-8}k_{-3}$, M^{-1} s^{-1} [d]
3.97[a]	13.4	0.05	280	13
1.29[b]	14.1	1.85	170	8.9
1.10[b]	12.9	6.03	290	8.3
0.04[b]	4.18	5.03	238	8.6

[a] $[T]_0$ was determined spectrophotometrically. [b] $[T]_0$ was calculated on the basis of $K_{\text{dispr}} = 0.012$. [c] Slope of the plot ln $\{[T]_0 + [T^{2-},2Na^+]_0 + 4K_{\text{dispr}}[T^-\cdot,Na^+] + (1 - 4K_{\text{dispr}})X\}/X$ vs. time; $2X$ denotes the change of $[T^-\cdot,Na^+]$ after flash (ref 10). [d] $k_{-3} = 2 \times \text{slope}/([T]_0 + [T^{2-},2Na^+]_0 + 4K_{\text{dispr}}[T^-\cdot,Na^+])$.

maintained simultaneously with the equilibria $T^-\cdot,Na^+ + C \rightleftarrows T + C^-\cdot,Na^+,K_1$, and $2T^-\cdot,Na^+ \rightleftarrows T + T^{2-},2Na^+,K_{\text{dispr}}$. Since these three equilibria are interrelated, $K_1/K_2 = K_{\text{dispr}}$. This mechanism leads to

$$-d\ln[C]/dt = k_iK_2[T^{2-},2Na^+]/[T^-\cdot,Na^+]$$

Plots of d ln [C]/dt vs.[T^{2-},2Na^+]/[$T^-\cdot$,Na^+] are shown in Figure 6 and their slopes, listed in the last column of Table I, give the values of k_iK_2.

Kinetics of Cis–Trans Isomerization Induced by Sodium Biphenylide

A THF solution of sodium biphenylide ($B^-\cdot$,Na^+) of known concentration was placed in one bulb of an apparatus described in ref 8b, while a known amount of crystallized, rigorously dried C was introduced into the other bulb. Since the whole unit was evacuated, some THF could be distilled from the first bulb into the second and the solid C dissolved; then both solutions were rapidly mixed and poured into an optical cell. Within 0.5 min after mixing the absorbances at 780 ($\lambda_{\max}$ of T^{2-},2Na^+) and at 606 nm ($\lambda_{\max}$ of $T^-\cdot$,Na^+) were determined, and thereafter the spectrum of the reacting solution was recorded at fixed time intervals. Figure 7 illustrates thus recorded spectra.

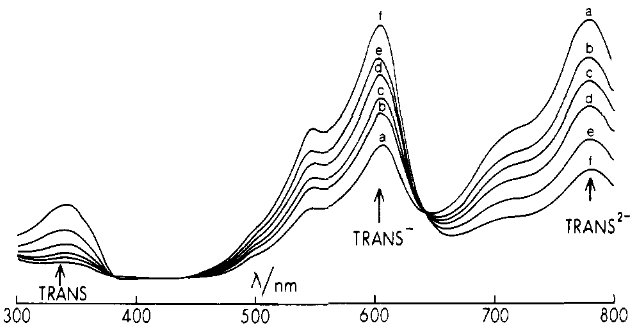


Figure 7. Typical spectra of THF solution of C + $B^-\cdot$,Na^+.

Biphenylide reacted within seconds, and the recorded spectra showed only the presence of T^{2-},2Na^+ and $T^-\cdot$,Na^+. The concentration of the former gradually decreased, while that of the latter increased, and hence the system was apparently identical with that resulting from the addition of T^{2-},2Na^+ to C. Indeed, the kinetics discussed in the preceding section applies to this reaction, i.e., −d ln [C]/dt was proportional to [T^{2-},2Na^+]/[$T^-\cdot$,Na^+]. The plot of −d ln [C]/dt vs. [T^{2-},2Na^+]/[$T^-\cdot$,Na^+] is included in Figure 6, its slope being in the range of those found in the previous experiments.

The significance of the biphenylide system arises from the consideration of the initial concentrations of T^{2-},2Na^+ and $T^-\cdot$,Na^+. Had the reaction followed the scheme discussed previously, namely

$$B^-\cdot,Na^+ + C \rightarrow B + C^-\cdot,Na^+ \text{ (rapid)}$$

$$C^-\cdot,Na^+ \xrightarrow{k_i} T^-\cdot,Na^+ \text{ (rapid)}$$

and

$$T^-\cdot,Na^+ + C \rightarrow C^-\cdot,Na^+ + T \text{ (slow)}$$

the dianions would have been formed by the disproportionation of $T^-\cdot$,Na^+ radical anions. Let us assume that all $B^-\cdot$,Na^+ (9.6 × 10^{-4} M) was converted into $C^-\cdot$,Na^+ and subsequently into $T^-\cdot$,Na^+. The rapidly established disproportionation equilibrium would produce some T^{2-},2Na^+ and the ratio of [T^{2-},2Na^+]/[$T^-\cdot$,Na^+] could not be greater than 0.2. Its value subsequently should decrease as T is formed by isomerization of C. However, the initially determined ratio was 1.54—substantially larger than the calculated one.

One has to conclude that at least some of the T^{2-},2Na^+ was formed by a reaction different from disproportionation. The reaction $T^-\cdot,Na^+ + B^-\cdot,Na^+ \rightarrow T^{2-},2Na^+ + B$ is unlikely, because C, being in excess (25.6 × 10^{-4} M), efficiently competes with any formed $T^-\cdot$,Na^+ for $B^-\cdot$,Na^+. One has to conclude that the initially formed $C^-\cdot$,Na^+ rapidly disproportionates into C^{2-},2Na^+ and the latter is either identical with T^{2-},2Na^+ or extremely rapidly converted into T^{2-},2Na^+. Alternatively, but less likely, $C^-\cdot$,Na^+ formed by electron transfer from $B^-\cdot$,Na^+ could react with the remaining $B^-\cdot$,Na^+ giving C^{2-},2Na^+. Whatever the explanation, we have to infer from our observation that C^{2-},2Na^+, which may or may not be identical with T^{2-},2Na^+, is readily formed and rapidly converted into T^{2-},2Na^+ if not identical with it. Apparently the disproportionation of $C^-\cdot$,Na^+ is high, its equilibrium constant probably being larger than 2.5. This estimate agrees with the value of the disproportionation constant of *cis*-stilbene radical anions,[9] calculated to be ≥2, with the previously described polarographic studies of C reduction.

Kinetics of Disproportionation of $T^{-}\cdot,Na^{+}$

In the earlier discussion we assumed that the disproportionation equilibrium, $2T^{-}\cdot,Na^{+} \rightleftarrows T + T^{2-},2Na^{+}$, is maintained in the course of isomerization. To prove it we studied the kinetics of this reaction using the flash-photolysis technique reported earlier.[10] The equilibrium

$$2T^{-}\cdot,Na^{+} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} T + T^{2-},2Na^{+} \qquad K_{\mathrm{disp}} = k_3/k_{-3}$$

is perturbed by flash of visible light. Some electrons photoejected from $T^{-}\cdot,Na^{+}$ are captured by the unphotolyzed $T^{-}\cdot,Na^{+}$, reducing it to $T^{2-},2Na^{+}$. Hence, the concentration of $T^{2-},2Na^{+}$ and of T increases after the flash while the concentration of $T^{-}\cdot,Na^{+}$ decreases. In the dark period following the flash, the system relaxes to its equilibrium state and kinetics of the relaxation can be studied by monitoring the absorbance at 606 or 780 nm. The results are summarized in Table II and demonstrate that the relaxation time is of the order of milliseconds.

Final Conclusions

Electron-transfer isomerization of C into T may proceed by isomerization of $C^{-}\cdot,Na^{+}$ into $T^{-}\cdot,Na^{+}$ or by isomerization of $C^{2-},2Na^{+}$ into $T^{2-},2Na^{+}$. The ratio $[C^{2-},2Na^{+}]/[C^{-}\cdot,Na^{+}] = \mathrm{const}[C^{-}\cdot,Na^{+}]/[C]$. In experiments involving $T^{-}\cdot,Na^{+}$ or $T^{2-},2Na^{+}$ as the donors, the equilibrium concentration of $C^{-}\cdot,Na^{+}$ determined by K_1 or K_2 is very low and consequently the ratio of $[C^{2-},2Na^{+}]/[C^{-}\cdot,Na^{+}]$ is also very small. Hence, virtually all the observed isomerization proceeds via $C^{-}\cdot,Na^{+}$ and not $C^{2-},2Na^{+}$. However, in the experiments involving $B^{-}\cdot,Na^{+}$ as a donor, the initial concentration of $C^{-}\cdot,Na^{+}$ is relatively high, resulting in a rather large concentration of $C^{2-},2Na^{+}$. In such experiments the isomerization of $C^{2-},2Na^{+}$ into $T^{2-},2Na^{+}$ contributes to the overall process and is responsible for the initially high concentration of $T^{2-},2Na^{+}$.

The experimentally determined constants k_iK_1 and k_iK_2 allow us to calculate K_{dispr} from kinetic data leading to $K_{\mathrm{dispr}} = 0.038$. This value compares well with the one determined potentiometrically, viz., 0.04.

Finally, our work demonstrated the high degree of disproportionation of $C^{-}\cdot,Na^{+}$ radical anions in THF justifying the polarographic observations.

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(11) The referee inquires whether the reactions

$$C^{-}\cdot + T^{-}\cdot \rightarrow C^{2-} + T \text{ (slow)}$$

$$C^{2-} \rightarrow T^{2-} \text{ (fast)}$$

$$T^{2-} + T \rightarrow 2T^{-}\cdot$$

should be considered. Apparently not: (1) $C^{-}\cdot + T^{-}$ should give $C + T^{2-}$ rather than $C^{2-} + T$. In this case there is no contribution to the isomerization. (2) The concentration of C is enormously greater than that of $C^{-}\cdot$. Hence, the reaction with C is much more likely than with $C^{-}\cdot$, notwithstanding the fact that intrinsically the latter would be slower than the former. (3) If one accepts this route, then k_1K_1 calculated from the performed experiments would be not constant, viz., 0.34, 0.56, and 0.61 in units 10^{-1} s^{-1}, whereas constant values, namely, 1.0, 1.3, and 1.1×10^{-5} s^{-1}, are obtained on the basis of our mechanism.