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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- and T2-, were characterized spectrophotometrically and electrochemically. The disproportionation 2T-,Na+ = T + T2-,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 × 107 M-1 s-1. The cis-trans isomerization was studied in THF at ambient temperature in three systems: T + Na+, C, T2-,2Na+, and B-,Na+ + C, B denoting biphenyl. In the first two systems the reaction is governed by the three interrelated equilibria, namely, C + T-,Na+ = T + C-,Na+ (k1), C + T2-,2Na+ = C-,Na+ + T-,Na+, (k2 = Kd/Kdissol), and 2T-,Na+ = T + T2-,2Na+ (ksolv). The rate-determining step being C-,Na+ → T-,Na+ (k2). The results give k1,k1 or k2. In the last system the rapid electron transfer B-,Na+ + C → B + C-,Na+ produces momentarily high concentration of C-,Na+ and, since its disproportionation is favored, a relatively large amount of C2-,2Na+. The latter rapidly isomerizes into T2-,2Na+. Thus, in early stages of the reaction, the concentration of T2-,2Na+ exceeds that expected for the disproportionation equilibrium had the reaction with B-,Na+ formed only C-,Na+ and then T-,Na+. This observation provides the evidence for the existence of C2-,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 at elevated temperatures exceeding 300 °C. Photoisomerization was extensively investigated; it leads to photostationary state. In a recent series of papers 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− = cis-stilbene + cis-stilbene2−. 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:

\[ T-,Na^+ + C \rightleftharpoons T + C-,Na^+ \]
\[ T2-,2Na^+ + C \rightleftharpoons T-,Na^+ + C-,Na^+ \]
\[ 2T-,Na^+ \rightleftharpoons T + T2-,2Na^+ \]

A more powerful reducing agent, viz., sodium biphenylide, B-,Na+, converts some C into C2-,2Na+, and then the spontaneous reaction

\[ C2-,2Na^+ \rightleftharpoons T2-,2Na^+ \]

produces T2-,2Na+ in excess of what would be expected in disproportionation of equivalent amounts of T-,Na+. The distinction between C2-,2Na+ and T2-,2Na+ is not required to account for that result. In fact, C2-,2Na+ may be identical with T2-,2Na+.

Reagents and Their Characterization

trans-4,4’-Diphenylstilbene, subsequently referred to as T, was acquired commercially. The purchased material was...
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. The UV spectrum agrees with that reported in the literature, the UV molar absorbance at 340 nm is 0.16 with those reported by Baroni, although our product showed a substantially lower melting point than that reported by the Russian workers. The 'H NMR spectrum of C recorded in benzene). Extensive reduction on a sodium mirror of the THF solution of T yields the respective diamagnetic dianions, T2-. The first redox potential of T was determined potentiometrically by combining the couple T-:,Na+ with T + T-:,Na+ with T + T-:,Na+ with T - Na+. The results led to \( \Delta_{E,\text{pe}} = 266 \text{ mV} \). A cyclic voltamogram of T in THF on a platinum electrode shows two reversible peaks at \( \epsilon_{1/2} = -2.07 \) and \(-2.27 \text{ V (vs. SCE)} \) and similar potentials were observed potentiographically in DMF at a mercury electrode, namely, \(-2.13 \) and \(-2.36 \text{ V (vs. SCE)} \). Since the polarographic \( \epsilon_{1/2} \) of perylene was found to be \(-1.81 \text{ V (corrected to SCE)} \) in THF, the respective \( \Delta_{E,\text{pe}} \) is 260 mV, in agreement with the potentiometric study.

The second redox potential of T was measured potentiometrically by combining the couple T-:,Na+ with T + T-:,2Na+ with T + T-:,Na+ with T - 2Na+. The results led to \( \Delta_{E,\text{pe}2} = 80 \text{ mV} \). A cyclic voltamogram of T in THF on a platinum electrode shows two reversible peaks at \( \epsilon_{1/2} = -2.07 \) and \(-2.27 \text{ V (vs. SCE)} \) and similar potentials were observed potentiographically in DMF at a mercury electrode, namely, \(-2.13 \) and \(-2.36 \text{ V (vs. SCE)} \). Since the polarographic \( \epsilon_{1/2} \) of perylene was found to be \(-1.81 \text{ V (corrected to SCE)} \) in THF, the respective \( \Delta_{E,\text{pe}} \) is 260 mV, in agreement with the potentiometric study.

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**Kinetics of Cis-Trans Isomerization Induced by T-:,Na+**

A rigorously dried THF solution of T was partially reduced on sodium mirror. Its initial concentration, \([T]_0\), was determined previously by spectrophotometric technique. After reduction, spectrophotometric analysis allowed us to determine the concentration of T-:,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 isomerization is induced by T-:,Na+ (\([T]_0=[T]_0\)) and is followed by monitoring the optical densities 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-:,2Na+ and the concentration of the latter was determined spectrophotometrically. This gives \([C]_0 + [T]_0\)
and by subtracting the previously determined \([T]_0\) one gets \([C]_0\).

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

\[
C + T^- + Na^+ \overset{k_1}{\underset{k_1}{\rightleftharpoons}} C^- + Na^+ + T
\]

is maintained during its course, and the observed isomerization governed by the reaction \(C^- + Na^+ \rightarrow T^- + Na^+\), with \(k_1 \ll k_1\)[[T]]. Hence

\[
-d\ln [C]/dt = k_1 [T^- + Na^+]/[T]
\]

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

\[
-a \ln ([C]/[C]_0) + [C] - [C]_0 = k_1 [T^- + Na^+]
\]

Plots of the left side of that equation vs. time are shown in Figure 3. Their slopes divided by \([T^- + Na^+]/[T]\) give \(k_1/k_1\[T]\), namely, 1.0, 1.3, and 1.1 in units \(10^{10} \text{ s}^{-1}\).

Polarographic data indicate that the electrode affinity of \(T\) is greater than that of \(C\). The rate of electron transfer from \(C^- + Na^+\) to \(T\) is expected, therefore, to be very fast; i.e., \(k_1\) is probably in the range \(10^8 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}\). Since \(k_1 \ll k_1\[T\], \(k_1\) is estimated to be smaller than \(10^8 \text{ s}^{-1}\).

**Figure 3.** Plot of \([C] - [C]_0 - a_0 \ln ([C]/[C]_0)\) vs. time: \(\delta\), \([C]_0 = 9.3 \times 10^{-4} \text{ M}, [T^- + Na^+] = 2.88 \times 10^{-4} \text{ M}, a = 1.06 \times 10^{-4} \text{ M}; \delta\), \([C]_0 = 11.5 \times 10^{-4} \text{ M}, [T^- + Na^+] = 2.31 \times 10^{-4} \text{ M}, a = 1.41 \times 10^{-4} \text{ M}; \delta\), \([C]_0 = 11.4 \times 10^{-4} \text{ M}, [T^- + Na^+] = 1.78 \times 10^{-4} \text{ M}, a = 1.54 \times 10^{-4} \text{ M}. The \(\Delta\) and \(\delta\) lines are displaced upward by 1 and 2 units, respectively. It seems that \([C]_0\) in the \(\Delta\) line is slightly underestimated.

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

**Figure 5.** Typical plot of \([C], [T], [T^- + Na^+],\) and \([T^- + 2Na^+]\) as functions of time.

**Table I**

<table>
<thead>
<tr>
<th>Run</th>
<th>([C]_0, M)</th>
<th>([T^- + 2Na^+]_0, M)</th>
<th>([C]_0)</th>
<th>([T^+])</th>
<th>([T^- + Na^+])</th>
<th>([T^- + 2Na^+])</th>
<th>(k_1/k_2, s^{-1})</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>9.80</td>
<td>36.53</td>
<td>3.73</td>
<td>3.21</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>9.62</td>
<td>16.41</td>
<td>1.71</td>
<td>2.62</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.45</td>
<td>39.95</td>
<td>7.33</td>
<td>2.97</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>5.07</td>
<td>18.21</td>
<td>3.59</td>
<td>3.00</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>5.0</td>
<td>9.49</td>
<td>1.90</td>
<td>3.26</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>4.93</td>
<td>19.46</td>
<td>3.55</td>
<td>3.15</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>4.80</td>
<td>17.85</td>
<td>3.72</td>
<td>2.50</td>
<td>10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>9.62</td>
<td>25.56</td>
<td>2.84</td>
<td>10^{-4}</td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) \(10^4[B^- + Na^+] / M\).

**Kinetics of Cis–Trans Isomerization Induced by \(T^- + 2Na^+\)**

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

\[T + T^- + 2Na^+ = 2T^- + Na^+ + 1/K_{\text{dispr}}\]

reducing \([T^- + 2Na^+]\) and yielding equivalent amounts of \([T^- + Na^+]\). 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 \([T^- + Na^+]\) and \([T^- + 2Na^+]\) were determined as functions of time. It was gratifying to find the sum \(2[T^- + 2Na^+] + [T^- + Na^+]\) to be constant and equal to \(2[T^- + 2Na^+]_0\). Concentration of \(T\) was calculated from the relation \([T] = K_{\text{dispr}} [T^- + Na^+]^2/[T^- + 2Na^+]\) using the previously determined value of 0.04 for \(K_{\text{dispr}}\), and the concentration of \(C\) was obtained from the balance equation \([C] = [C]_0 - [T] - \frac{1}{2}[T^- + 2Na^+]\). Typical results giving \([C], [T], [T^- + Na^+],\) and \([T^- + 2Na^+]\) as functions of time are shown in Figure 5. From plots of \(\ln [C]/\text{vs. time}\) 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 \(C^- + Na^+ \rightarrow T^- + Na^+\), \(k_1\) the concentration of \(C^- + Na^+\) being determined by the rapidly established equilibrium

\[C + T^- + 2Na^+ \overset{k_2}{\underset{k_2}{\rightleftharpoons}} C^- + Na^+ + T^- + Na^+\]
This mechanism leads to Since these three equilibria are interrelated, give the values of 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 (λ_max of T−,Na+) and at 606 nm (λ_max of T−,Na+) were determined, and thereafter the spectrum of the reacting solution was recorded at fixed time intervals. Figure 7 illustrates thus recorded spectra.

Biphenylide reacted within seconds, and the recorded spectra showed only the presence of T−,2Na+ and T−,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−,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−,2Na+]/[T−,Na+]. The plot of −d ln [C]/dt vs. [T−,2Na+]/[T−,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−,2Na+ and T−,Na+. Had the reaction followed the scheme discussed previously, namely

\[ B−,Na+ + C \rightarrow B + C−,Na+ \text{ (rapid) } \]

\[ C−,Na+ \rightarrow T−,Na+ \text{ (rapid) } \]

and

\[ T−,Na+ + C \rightarrow C−,Na+ + T \text{ (slow) } \]

the dianions would have been formed by the disproportionation of T−,Na+ radical anions. Let us assume that all B−,Na+ (9.6 × 10−4 M) was converted into C−,Na+ and subsequently into T−,Na+. The rapidly established disproportionation equilibrium would produce some T−,2Na+ and the ratio of [T−,2Na+]/[T−,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−,2Na+ was formed by a reaction different from disproportionation. The reaction T−,Na+ + B−,Na+ → T−,2Na+ + B is unlikely, because C, being in excess (25.6 × 10−4 M), efficiently competes with any formed T−,Na+ for B−,Na+. One has to conclude that the initially formed C−,Na+ rapidly disproportionates into C−,2Na+ and the latter is either identical with T−,2Na+ or extremely rapidly converted into T−,2Na+. Alternatively, but less likely, C−,Na+ formed by electron transfer from B−,Na+ could react with the remaining B−,Na+ giving C−,2Na+. Whatever the explanation, we have to infer from our observation that C−,2Na+ which may or may not be identical with T−,2Na+, is readily formed and rapidly converted into T−,2Na+ if not identical with it. Apparently the disproportionation of C−,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, calculated to be ±2, with the previously described polarographic studies of C reduction.

![Figure 6](image_url)

Figure 6. Plots of ln [C]/dt vs. [T−,2Na+]/[T−,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.

![Figure 7](image_url)

Figure 7. Typical spectra of THF solution of C + B−,Na+.
Kinetics of Disproportionation of T^-;Na^+

In the earlier discussion we assumed that the disproportionation equilibrium, \(2T^-;Na^+ \rightleftharpoons T + T^2-;2Na^+\), 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

\[
2T^-;Na^+ \xrightleftharpoons[k_3]{k_1} T + T^2-;2Na^+ \quad K_{disp} = \frac{k_3}{k_1 - 3}
\]

is perturbed by flash of visible light. Some electrons photoejected from T^-;Na^+ are captured by the unphotolyzed T^-;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^-;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 of T^2-;2Na^+ and of T increases after the flash while the concentration of T^-;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^2-,2Na^+ into T^-;Na^+ or by isomerization of C^2-,2Na^+ into T^2-;2Na^+. The ratio \([C^2-,2Na^+]/[C^-;Na^+] = \text{const} [C^-;Na^+]/[C]\). In experiments involving T^-;Na^+ or T^2-;2Na^+ as the donors, the equilibrium concentration of C^-;Na^+ determined by \(K_1\) or \(K_2\) is very low and consequently the ratio of \([C^2-,2Na^+]/[C^-;Na^+]\) is also very small. Hence, virtually all the observed isomerization proceeds via C^-;Na^+ and not C^2-,2Na^+. However, in the experiments involving B^-;Na^+ as a donor, the initial concentration of C^-;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 \(k_1K_1\) and \(k_1K_2\) allow us to calculate \(K_{disp}\) from kinetic data leading to \(K_{disp} = 0.038\). This value compares well with the one determined potentiometrically, viz., 0.04.

Finally, our work demonstrated the high degree of disproportionation of C^-;Na^+ radical anions in THF justifying the polarographic observations.

Acknowledgment. The financial support of this study by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) (a) State University of New York; (b) The University of Texas at Austin.
(11) The referee inquires whether the reactions

\[
\begin{align*}
C^- + T^- & \rightarrow C^2- + T \\
C^2- & \rightarrow T^2- \quad \text{fast} \\
T^2- + T & \rightarrow 2T^- \\
\end{align*}
\]

should be considered. Apparently not: (1) C^- + 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^-.

Hence, the reaction with C is much more likely than with C^-; notwith-