# Electron Transfer Induced Cis–Trans Isomerization of Stilbene. The Effect of Counterions and the Existence of Two Isomeric Stilbene Dianions

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**Abstract:** We studied the kinetics of *cis*-stilbene isomerization induced in THF by electron transfer from $Li^+$, $Na^+$, $K^+$, or $Cs^+$ anthracenide. The reaction is first order in *cis*-stilbene (*cis*-St) and the pseudo-first-order rate constant, $k_{obsd}$, is proportional to $\{[A\cdot^-,Cat^+]/[A]\}^2$ provided the concentration of the unreduced anthracene [A] is sufficiently high. This implies the following mechanism of isomerization: $A\cdot^-,Cat^+ + cis\text{-St}\ (k_1) \rightleftarrows A + cis\text{-St}\cdot^-,Cat^+ (k_{-1})$; $A\cdot^-,Cat^+ + cis\text{-St}\cdot^-,Cat^+\ (k_2) \rightleftarrows A + cis\text{-St}^{2-},2Cat^+\ (k_{-2})$; $cis\text{-St}^{2-},2Cat^+\ (k_{iso}) \rightarrow trans\text{-St}^{2-},2Cat^+$, *trans*-St denoting *trans*-stilbene. At low concentration of A the concentration of $cis\text{-St}^{2-},2Cat^+$ is determined by the stationary state, *i.e.*, $\{[A\cdot^-,Cat^+]/[A]\}^2/k_{obsd} = (1/k_{iso}K_1K_2) + (1/k_{-2}K_1K_2[A])$, and thus $k_{iso}K_1K_2$, $k_{-2}K_1K_2$, and $k_{iso}/k_{-2}$ can be obtained from the kinetic data. Assuming tentatively a constant value of $\sim 10^{10}\ M^{-1}\ sec^{-1}$ for $k_{-2}$, we find $k_{iso} = 11 \times 10^6$, $5.6 \times 10^6$, $6.5 \times 10^6$, and $0.64 \times 10^6\ sec^{-1}$ for $Li^+$, $Na^+$, $K^+$, and $Cs^+$, respectively. We conclude that the association of the dianion with the cations is responsible for the hindrance of rotation causing the isomerization, the tighter the association the lower $k_{iso}$. Literature evidence is quoted to show that the association becomes tighter in the series $Li^+ < Na^+ < K^+ < Cs^+$, justifying the observed trends of $k_{iso}$ with the nature of the counterion.

Electron transfer induced isomerization of stilbene was reported first by Hoijtink and van der Meij;[1] the reaction ensued during partial reduction of *cis*-stilbene by alkali metal. Subsequently, Doran and Waack[2] studied the isomerization of *cis*-stilbene resulting from the addition of lithium to the solution of that hydrocarbon and monitored spectrophotometrically the progress of this reaction. Both groups assumed that stilbene radical anion mediates the observed isomerization.

The esr spectra of stilbene radical anions were reported by several groups,[3-5] and their complete analysis was achieved by Chang and Johnson[6] who found the odd electron to be coupled to six different pairs of protons. This implies that the rotation around the C–Ph bonds is restricted and therefore a question arose of what is the structure of the observed radical. Does the reduction produce two distinct stilbene radical anions, one being labeled as the cis and the other as the trans, or is the reduction yielding one species only? Chang and Johnson[6] reported that the esr spectra of the radical anions resulting from the reduction of the cis or the trans isomer are identical, and the structure of their esr spectrum, recorded at −60° in DME ($K^+$ counterion), leaves no doubt that the investigated solution contains one kind of radical only. The same conclusion is drawn from the examination of the esr spectrum of the stilbene radical anions formed at ambient temperature by electron transfer from sodium biphenylide to either of the isomers in hexamethylphosphoric triamide[7] (HMPA). All the numerous lines are fully accounted for by six coupling constants and this demonstrates that the other radical, if present at all, must be in proportion lower than 0.05.

Studies of the exchange between the radical anion and the two hydrocarbons convinced Chang and Johnson[6,8] that the observed radical has trans configuration, because the broadening of the esr lines, under otherwise identical conditions, was greater in the presence of the unreduced *trans*- than *cis*-stilbene. Quantitative examination of the broadened spectra[8] led to the value of $\sim 2 \times 10^9\ M^{-1}\ sec^{-1}$ for the bimolecular rate constants of the exchange

$$trans\text{-stilbenide} + trans\text{-stilbene} \rightarrow \text{exchange} \qquad \text{(a)}$$

determined at ambient temperature in DME (with $K^+$ or $Na^+$) or in THF (with $K^+$). The respective activation energies are about 2.5 kcal/mol.

The elegant work of Chang and Markgraf[9] furnished further information about this reaction. The structureless esr spectrum of potassium *trans*-stilbenide, mixed in DME with about $10^{-2}\ M$ *trans*-stilbene, revealed some structure when the solution was irradiated in the cavity of an esr spectrometer by 3200-Å light. A photostationary state should be established under these conditions, leading to the conversion of some *trans*-stilbene into the cis isomer. Therefore, the rate of exchange should be reduced on irradiation, provided reaction (b)

$$cis\text{-stilbene} + trans\text{-stilbenide} \rightarrow cis\text{-stilbenide} + trans\text{-stilbene} \qquad \text{(b)}$$

is much slower than reaction (a). After switching the light off the *cis*-stilbene re-isomerizes and the dark reaction, monitored spectrophotometrically, was found to be pseudo-first order in *cis*-stilbene. This kinetics was considered as evidence for a mechanism involving slow inverse reaction (b) followed by a rapid, unimolecular reaction (c),

$$cis\text{-stilbenide} \rightarrow trans\text{-stilbenide} \qquad \text{(c)}$$

leading therefore to a pseudo-first-order rate constant given by the product $k_b[trans\text{-stilbenide}]$ with $k_b \sim 10^3\ M^{-1}\ sec^{-1}$.

These mechanistic conclusions may be questioned. The dark relaxation of the system from its photostationary to the equilibrium state should be first order in *cis*-stilbene, regardless of the mechanism, provided that the equilibrium was only slightly perturbed by the irradiation. For example, the observed pseudo-first-order rate constant could be given by the product $k_cK_b$ if equilibrium (b) were rapidly established and reaction (c) were the rate-determining step. A more complex mechanism of this electron transfer induced cis–trans isomerization was revealed by our studies. In our work the isomerization of *cis*-stilbene into the trans isomer was induced in THF by anthracenide salts ($A\cdot^-,Cat^+$). The reaction was followed spectrophotometrically by monitoring the absorbance at 285 nm. At this wavelength the decimal extinction coefficients of the *cis*- and *trans*-stilbene are $1.02 \times 10^4$ and $2.45 \times 10^4\ M^{-1}\ cm^{-1}$, respectively, while the absorbance of the anthracenide salts is at minimum ($\epsilon \sim$

Table I. Isomerization of *cis*-Stilbene to *trans*-Stilbene Induced in THF by Lithium or Sodium Anthracenide ($T$ 22°)

| $10^3[A]$ | $10^3[A\cdot^-$,-Cat$^+]$ | $[A\cdot^-,Cat^+]/[A]$ | $10^3k_{obsd}$ | $10^3\{[A]/[A\cdot^-$,-Cat$^+]\}^2k_{obsd}$ |
|---|---|---|---|---|
| | | Counterion Li$^+$ | | |
| 5.3 | 9.3 | 1.8 | 0.12 | 0.039 (?) |
| 4.8 | 8.1 | 1.7 | 0.175 | 0.061 |
| 3.7 | 7.6 | 2.0 | 0.21 | 0.051 |
| 3.75 | 8.0 | 2.1 | 0.22 | 0.050 |
| 2.06 | 5.1 | 2.5 | 0.49 | 0.078 |
| 2.23 | 6.5 | 2.9 | 0.56 | 0.066 |
| 1.91 | 5.75 | 3.0 | 0.58 | 0.064 |
| 1.38 | 5.75 | 4.2 | 1.00 | 0.057 |
| 1.51 | 6.2 | 4.1 | 1.08 | 0.064 |
| 1.55 | 6.5 | 4.2 | 1.01 | 0.058 |
| | | Counterion Na$^+$ | | |
| 3.19 | 0.33 | 0.11 | 0.074 | 6.4 |
| 3.17 | 2.9 | 0.82 | 4.35 | 5.3 |
| 2.4 | 2.0 | 0.84 | 4.7 | 6.6 |
| 3.5 | 4.85 | 1.38 | 10.9 | 5.7 |
| 1.06 | 2.12 | 2.00 | 25.8 | 6.4 |
| 3.2 | 6.6 | 2.06 | 22.6 | 5.3 |
| 3.1 | 9.7 | 3.16 | 53.5 | 5.35 |
| 0.965 | 3.1 | 3.25 | 53.0 | 5.0 |

$0.35 \times 10^4\ M^{-1}\ \text{cm}^{-1}$). Hence, the ratio

$$\{\text{OD}(285)_t - \text{OD}(285)_\infty\}/\{\text{OD}(285)_0 - \text{OD}(285)_\infty\}$$

measures the progress of the reaction.

In a typical experiment a required amount of purified *cis*-stilbene containing about 6% of the trans isomer was added to the THF solution of the anthracenide salt kept in an evacuated all glass vessel with a quartz optical cell attached to it. The spectrum of the anthracenide salt was recorded before the addition of stilbene, during the reaction, and after its completion. It was established that in each run the concentration of anthracenide was constant, *i.e.*, this radical is not consumed by the isomerization process.

The isomerization of *cis*- to *trans*-stilbene always obeyed a first-order kinetics, *i.e.*, the plot of ln $\{\text{OD}(285)_t - \text{OD}(285)_\infty\}$ was linear, at least up to 90% conversion, its slope being denoted by $k_{obsd}$. Systematic study demonstrated that $k_{obsd}$ depends on the concentration of the anthracenide salt, $A\bullet^-$, Cat$^+$, as well as on the concentration of the unreduced anthracene, A, present in the solution. Moreover, $k_{obsd}$ depends on the nature of the counterion. At sufficiently high concentrations of the unreduced anthracene, $k_{obsd}$ was found to be proportional to $\{[A\cdot^-,Cat^+]/[A]\}^2$, as illustrated by the data pertaining to Li$^+$ and Na$^+$ cations collected in Table I and presented graphically in Figure 1. This relation suggests that the dianion of *cis*-stilbene, *cis*-St$^{2-}$,2Cat$^+$, is the isomerizing intermediate, namely

$$cis\text{-St}^{2-}, 2\text{Cat}^+ \xrightarrow{k_{iso}} trans\text{-St}^{2-}, 2\text{Cat}^+$$

its minute equilibrium concentration being maintained by the fast electron transfer reactions

$$A\cdot^-, \text{Cat}^+ + cis\text{-St} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A + cis\text{-St}\cdot^-, \text{Cat}^+ \quad (1)$$

$$A\cdot^-, \text{Cat}^+ + cis\text{-St}\cdot^-, \text{Cat}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A + cis\text{-St}^{2-}, 2\text{Cat}^+ \quad (2)$$

The symbols *cis*-St, *trans*-St, *cis*-St$\cdot^-$, *trans*-St$\cdot^-$, *cis*-St$^{2-}$, and *trans*-St$^{2-}$ denote the cis and trans isomers, their radical anions and dianions, respectively. Presence of an excess of the appropriate salt of tetraphenyl boride, sharing the common cation with $A\cdot^-$,Cat$^+$, ensures the absence of the free ions of the ionic reagents.

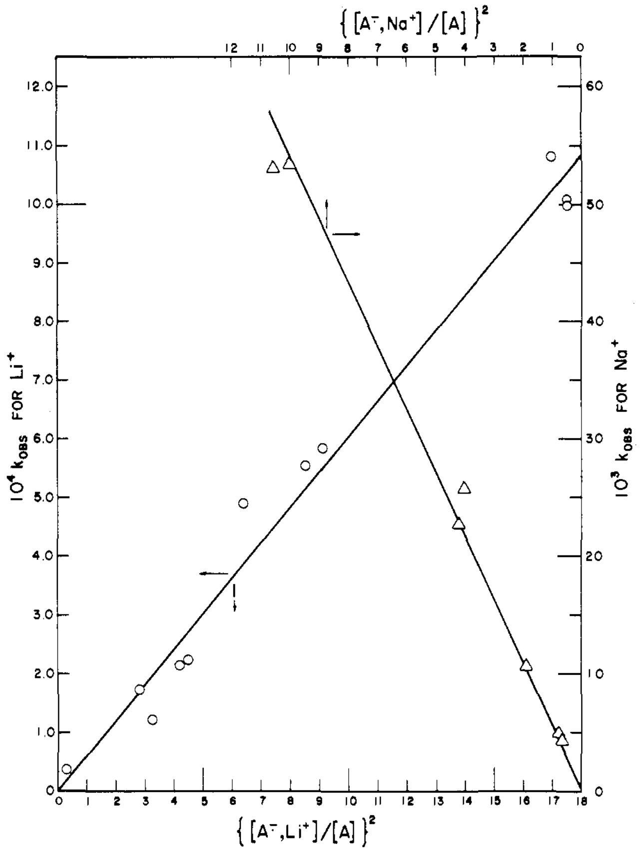

Figure 1. Plot of $k_{obsd}$ *vs.* $\{[A\cdot^-,Cat^+]/[A]\}^2$ for Li$^+$ (Δ) and for Na$^+$ (⊙).

The proposed mechanism implies that the observed pseudo-first-order rate constant $k_{obsd} = k_{iso}K_1K_2\{[A\bullet^-,Cat^+]/[A]\}^2$, $K_1$ and $K_2$ being the equilibrium constants of reactions 1 and 2. However, the constancy of $k_{obsd}\{[A]/[A\cdot^-,Cat^+]\}^2$ is maintained when the rate of *cis*-St$^{2-}$,2Cat$^+$ isomerization is much slower than the rate of the reverse reaction 2, $k_{-2}[A][cis\text{-St}^{2-},2\text{Cat}^+]$. This condition fails at low [A] and then the concentration of the dianion is maintained by the stationary state, *i.e.*

$$k_{obsd} = k_{iso}K_1K_2\{[A\cdot^-, \text{Cat}^+]/[A]\}^2/(1 + (k_{iso}/k_{-2}[A]))$$

It follows that a plot of $\{[A\cdot^-,Cat^+]/[A]\}^2/k_{obsd}$ *vs.* $1/[A]$ should be linear, its intercept giving $1/k_{iso}K_1K_2$ and its slope $1/k_{-2}K_1K_2$. Such lines are shown in Figure 2 for Li$^+$, Na$^+$, K$^+$, and Cs$^+$ counterions and the relevant constants, including the ratio $k_{iso}/k_{-2}$, are collected in Table II.

## Discussion

The data presented in the preceding section demonstrate that not only the radical anions of stilbene exist in cis and trans configuration but even the two isomeric stilbene dianions, the *cis*-St$^{2-}$,2Cat$^+$ and *trans*-St$^{2-}$,2Cat$^+$, form distinguishable species. Assuming that $k_{-2}$ is diffusion controlled and, regardless of the nature of the cation, equal to $10^{10}\ M^{-1}\ \text{sec}^{-1}$, one finds $k_{iso}$ to be in the range $10^6$-$10^7$ sec$^{-1}$ (see Table II). (The value of $k_{-2}$ probably varies with the nature of the cation; however, the variations are likely to be small.) This is a remarkably low value for an isomerization constant involving rotation around a C–C bond, the double bond character of which is virtually destroyed by the addition of two antibonding electrons. We shall discuss later a possible cause of the hindrance to the rotation, but

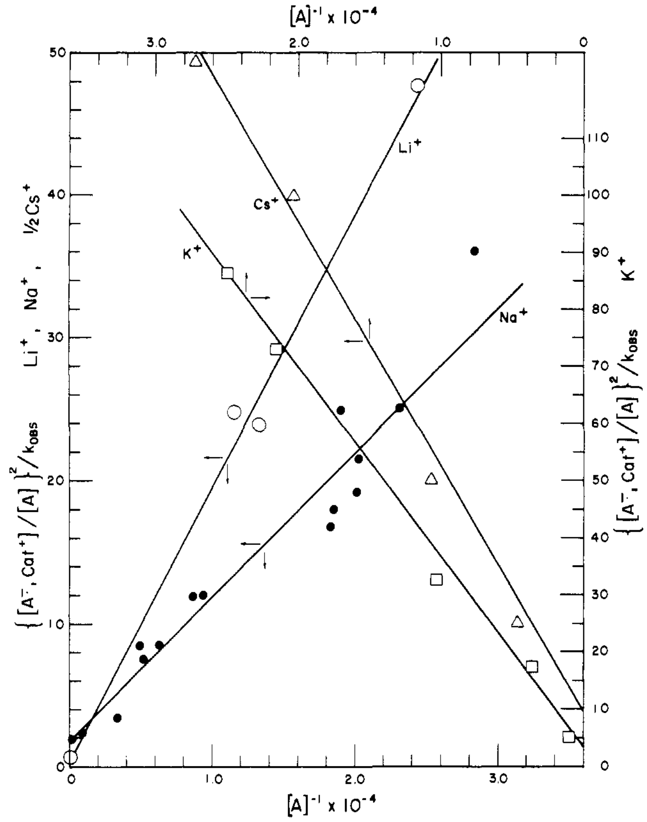

**Figure 2.** Plot of $\{[A\cdot^-,Cat^+]/[A]\}^2/k_{obsd}$ *vs.* $1/[A]$: ⊙ for $Li^+ \times 10^{-4}$, ● for $Na^+ \times 10^{-2}$, □ for $K^+ \times 10^{-3}$, △ for $Cs^+ \times 2 \times 10^{-4}$. The arrows point to the appropriate scales.

**Table II.** Electron Transfer Induced Isomerization of *cis*-Stilbene to *trans*-Stilbene in THF at 22° (Alkali Salt of Anthracenide Is the Electron Donor)

| | Counterion | | | |
|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ | $Cs^+$ |
| $k_{iso}K_1K_2 \times 10^4\ sec^{-1}$ | 0.60 | 56 | 2.0 | 0.4 |
| $k_{-2}K_1K_2 \times 10\ M^{-1}\ sec^{-1}$ | 0.54 | 100 | 3.1 | 6.25 |
| $(k_{iso}/k_{-2}) \times 10^3\ M$ | 1.11 | 0.56 | 0.65 | 0.064 |
| $k_{iso} \times 10^{-6}\ sec^{-1}$ [a] | 11.1 | 5.6 | 6.5 | 0.64 |
| $K_1K_2 \times 10^9$ [a] | 0.54 | 100 | 3.1 | 6.25 |

[a] Based on the assumed constant value of $k_{-2} = 10^{10}\ M^{-1}\ sec^{-1}$. This assumption is tentative and $k_{-2}$ may be expected to be independent of counterion's nature if the reaction is diffusion controlled.

first we wish to demonstrate that the facts reported here rule out two alternative mechanisms.

Two mechanisms could account for the proportionality of $k_{obsd}$ with $[A\cdot^-,Cat^+]^2$. Such a relation is demanded if the forward reaction 2 were the rate-determining step, *i.e.*, $k_{-2}[A] \ll k_{iso}$. However, this would make $k_{obsd}$ proportional with $[A\cdot^-,Cat^+]^2/[A]$ and not with $[A\cdot^-,Cat^+]^2/[A]^2$ as found in our study (see, *e.g.*, the second and the last results listed in Table I under the heading "counterion $Na^+$").

Alternatively, one could question the existence of the two isomeric salts of stilbene dianions. Could the isomerization result from the following reactions involving only one kind of stilbene dianions?

$$A\cdot^-, Cat^+ + cis\text{-}St\cdot^-, Cat^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} A + St^{2-}, 2Cat^+ \underset{k_4}{\overset{k_{-4}}{\rightleftarrows}} A\cdot^-, Cat^+ + trans\text{-}St\cdot^-, Cat^+$$

It may be easily proved that the pseudo-first-order rate constant governing the forward reaction consistent with this mechanism (including equilibrium 1) is given by

$$k_3K_1\{k_{-4}/(k_{-3} + k_{-4})\}[A\cdot^-, Cat^+]^2/[A]$$

*i.e.*, the $k_{obsd}$ would be again proportional with $[A\cdot^-,Cat^+]^2/[A]$ and not with $[A\cdot^-,Cat^+]^2/[A]^2$.

The effect of reversibility introduces the factor

$$\{1 - [([trans\text{-}St]/[trans\text{-}St]_e)/([cis\text{-}St]/[cis\text{-}St]_e)]\}$$

into the rate expression. This factor is virtually equal to 1 when $[trans\text{-}St]/[trans\text{-}St]_e \ll 1$ and $[cis\text{-}St]/[cis\text{-}St]_e \gg 1$, *i.e.*, when the system is far from the state of its ultimate equilibrium (subscript e refers to the ultimate equilibrium value of the reagent's concentration), and therefore its omission is justified. The difference of electron affinities of anthracene and stilbene, determined by potentiometric titration, is about 0.25 V, and hence the concentrations of the stilbenes radical anions and dianions are negligible when compared with those of the respective hydrocarbons.

Further evidence supporting the proposed mechanism is provided by the experiments involving sodium pyrenide, $\pi\cdot^-,Na^+$, as the electron donor. The isomerization was much faster but retained all the kinetic features of the reaction induced by sodium anthracenide. Thus, the respective pseudo-first-order rate constant, $k_{obsd,\pi}$, was found to be proportional with $\{[\pi\cdot^-,Na^+]/[\pi]\}^2$, implying that

$$k_{obsd,\pi} = k_{iso}K_{1,\pi}K_{2,\pi}\{[\pi\cdot^-, Na^+]/[\pi]\}^2$$

Here $K_{1,\pi}$ and $K_{2,\pi}$ are the equilibrium constants of the electron transfers

$$\pi\cdot^-, Na^+ + cis\text{-}St \rightleftarrows \pi + cis\text{-}St\cdot^-, Na^+$$

and

$$\pi\cdot^-, Na^+ + cis\text{-}St\cdot^-, Na^+ \rightleftarrows \pi + cis\text{-}St^{2-}, 2Na^+$$

while $k_{iso}$ refers again to the reaction

$$cis\text{-}St^{2-}, 2Na^+ \xrightarrow{k_{iso}} trans\text{-}St^{2-}, 2Na^+$$

participating in the isomerization induced by the anthracenide salt. It follows that $k_{iso}K_{1,\pi}K_{2,\pi}/k_{iso}K_1K_2 = K_{\pi,A}{}^2$, where $K_{\pi,A}$ is the equilibrium

$$\pi\cdot^-, Na^+ + A \rightleftarrows \pi + A\cdot^-, Na^+$$

$K_{\pi,A}$ was determined;[10] its value is 110 while $(k_{obsd,\pi}/k_{obsd})^{1/2} = 140$. The agreement is most satisfactory.

We return to the question why the value of $k_{iso}$ is relatively low although the double bond character and therefore the rigidity of the stilbene system is virtually destroyed by the addition of two antibonding electrons. Apparently, the two phenyl groups of the cis dianion are linked through cations associated with both. Such an association stabilizes the cis configuration and hinders the rotation of one phenyl group in respect to the other reducing, therefore, the value of $k_{iso}$. The nature of the counterion may exert a large influence on $k_{iso}$ and this seems to be revealed by the data collected in Table II, namely, the value of $k_{iso}/k_{-2}$ for the $Li^+$ system is 20 times greater than that found for the $Cs^+$. Although $k_{-2}$ may vary with the nature of counterion, the variations are expected to be small if the reaction is diffusion controlled, and could not account for such a large change of $k_{iso}/k_{-2}$. Indeed, the data obtained for a similar system,[11] *viz.*, $A^{2-},2Cat^+ + A$ $(k_{-3}) \rightarrow 2A\cdot^-,Cat^+$, show $k_{-3}$ to be only slightly affected by the counterion and to be virtually diffusion limited (A denotes anthracene).

The stronger the association of the cation with the anion the smaller $k_{iso}$ should be. This trend, reflected by the data listed in Table II, agrees with the behavior of other alkali salts in THF. For example, lithium polystyryl is more dissociated and its ion pair is more reactive in THF than other polystyryl salts[12] because of the high tendency of the small $Li^+$ cation to be solvated by molecules of THF. Studies of living polystyryls[12] revealed also the striking difference between $K^+$ and $Cs^+$ salts; the latter is 4 times less reactive and about 20 times less dissociated than the former.

The importance of counterions is further emphasized by the kinetics of *cis*-stilbene isomerization in HMPA.[13] In that solvent the ion pairs are quantitatively dissociated,[14] and hence the isomerization proceeds through the intermediacy of free ions. The rate of such an isomerization, induced by the *trans*-stilbenide *free* ions, was found to be proportional to the ratio $[trans\text{-St}\cdot^-]/[trans\text{-St}]$ and not to its square. Thus, the stilbene radical anions isomerize sufficiently fast when the association with the cations is avoided and the route through dianion is thus circumvented.

Finally, the effect of cations on the value of $K_1K_2$ deserves some comments. Reaction 2 resembles the disproportionation of radical anions and the extent of such a disproportionation usually is much greater for the cesium salts than for those of lithium.[15] The results obtained for the sodium salt may appear strange. However, the exceptional behavior of the sodium salt was noted also in studies of disproportionation of sodium anthracenide in THF.[16] The disproportionation constants of $Li^+$, $Na^+$, $K^+$, and $Cs^+$ anthracenide ion pairs in THF were found to be $2.9 \times 10^{-7}$, $158 \times 10^{-7}$, $7.6 \times 10^{-7}$, and $34 \times 10^{-7}$, respectively, a pattern similar to that reported here for $K_1K_2$.

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## Appendix

**Disproportionation of *cis*-Stilbene Radical Anions.** The literature data[17] indicate that the electron affinity of *cis*-stilbene is slightly lower than that of *trans*-stilbene. The difference of electron affinities of anthracene and *trans*-stilbene, determined potentiometrically,[10] is about −0.30 V, and hence the equilibrium constant of

$$A\cdot^- + trans\text{-St} \rightleftharpoons A + trans\text{-St}\cdot^- \qquad K_1'$$

is about $10^{-5}$. Therefore, $K_1$ (referring to *cis*-St) is smaller than $10^{-5}$. Our data, summarized in Table II, lead to $K_1K_2 \sim 10^{-7}$ for the sodium system, implying that $K_2 > 10^{-2}$

$$A\cdot^-, Na^+ + cis\text{-St}\cdot^-, Na^+ \rightleftharpoons A + cis\text{-St}^{2-}, 2Na^+ \qquad K_2$$

since for the

$$A + cis\text{-St}\cdot^-, Na \rightleftharpoons A\cdot^-, Na^+ + cis\text{-St}$$

the equilibrium constant is $>10^5$, the disproportionation

$$2cis\text{-St}\cdot^-, Na^+ \rightleftharpoons cis\text{-St}^{2-}, 2Na^+ + cis\text{-St} \qquad K_{\text{dispr}}$$

has an equilibrium constant $K_{\text{dispr}} > 10^3$. The high value of this disproportionation constant is remarkable and its significance will be discussed in a future publication.

This high value of that disproportionation explains why the stationary concentration of $cis\text{-St}^{2-},2Cat^+$ is determined by $k_{-2}$ (the reaction of the dianion with A) and not by its reaction with stilbene. The latter is slower than the former even when the concentration of the stilbenes greatly exceeds that of A.

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