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Electron-Transfer Induced Isomerization of *cis*-Stilbene in Hexamethylphosphoramide. Isomerization Mediated by the Free Ions of Stilbenides Radicals

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Abstract: Isomerization of *cis*-stilbene in HMPA mediated by the free ions of stilbenides is governed by the mechanism.

$$T\cdot^- + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T + C\cdot^- \quad (1) \qquad C\cdot^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} T\cdot^- \quad (2)$$

Here the letters C and T refer to *cis*- and *trans*-stilbenes, respectively. The kinetic data demonstrate that $K_1 = k_1/k_{-1} = 0.6$ and $k_2 + k_{-2} = 1.5 \times 10^{-3}$ sec^{-1}. Literature data indicate that k_{-1} is very large, at least 10^8 M^{-1} sec^{-1}. Hence, the composition of the stilbenide radical ions is virtually maintained by equilibrium (1) and the spontaneous isomerization (2) is the slow rate-determining step, its relaxation time being ~650 sec.

Isomerization of stilbene induced by electron transfer was reported first by Hoijtink and van der Meij[1] who observed this reaction in the course of partial reduction of *cis*-stilbene by alkali metal. The isomerization caused by the addition of lithium to THF solution of *cis*-stilbene was studied by Doran and Waack[2] who monitored spectrophotometrically its progress. In both studies it was tacitly assumed that the stilbene radical anions mediate the isomerization, i.e., the reaction results from

$$T\cdot^- + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T + C\cdot^- \qquad (1)$$

followed by

$$C\cdot^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} T\cdot^- \qquad (2)$$

where the symbols C and T refer to *cis*- and *trans*-stilbene, respectively.

Detailed kinetic studies of *cis*-stilbene isomerization induced in THF by various salts of anthracenide anions, viz., $Li^+,A\cdot^-$, $Na^+,A\cdot^-$, $K^+,A\cdot^-$, and $Cs^+,A\cdot^-$, were reported recently by our group.[3,4] Those reactions were found to be first order in *cis*-stilbene but otherwise more complex than originally anticipated. The $C\cdot^-,Cat^+$ pairs present in THF are too stable to contribute significantly to the isomerization and the reaction proceeds through step 3, because the

$$C^{2-},\ 2Cat^+ \longrightarrow T^{2-},\ 2Cat^+ \qquad (3)$$

dianions are more readily isomerized than the radical anions. The facile disproportionation of the latter[4] maintains a reasonable concentration of the former and therefore a measurable rate of isomerization.

The reported results imply that the cations bind together the adjacent phenyl groups of the cis form and thus hinder its isomerization. It became interesting, therefore, to investigate the isomerization involving free ions only. Since the ionic aggregates such as $C\cdot^-,Cat^+,C^{2-},2Cat^+$, etc., are likely to be fully dissociated in hexamethylphosphoramide[5] (HMPA), we investigated the electron-transfer-induced isomerization of *cis*-stilbene in that solvent. Neither anthracenide nor pyrenide induces any observable reaction in HMPA, and we studied therefore the process initiated by a more powerful electron donor, viz., sodium biphenylide ($Na^+,B\cdot^-$). This donor reacts instantly and quantitatively with the stilbenes yielding stilbenide radical ions. Hence, the investigated isomerization does not involve any other ions but those derived from the stilbenes.

Experimental Section

Commercial *cis*-stilbene (Aldrich Chemicals) was purified on a silicon column operating at 200° and then dried by CaH_2 in an evacuated bulb. Drying was facilitated by dilution of the hydrocarbon with THF, and the dried stilbene was filtered and stripped off the diluent before being dissolved in the required amount of HMPA and sealed in evacuated ampoules equipped with break seals. Although the peak of *trans*-stilbene seen in the chromatogram is well separated from that of the cis isomer, the purified material, as verified by the subsequent VPC analysis, contained still 6-10% of the trans isomer. Apparently some isomerization occurs on the column.

HMPA was four times vacuum distilled from ampoules covered by sodium mirror and then once again from a clean ampoule. The distillation took place at 70°.

Sodium biphenylide ($Na^+,B\cdot^-$) was prepared in the conventional way in THF, the solvent distilled off in vacuum, and the residue redissolved in HMPA. The concentration of $Na^+,B\cdot^-$ was determined spectrophotometrically.

Two ampoules, one containing *cis*-stilbene solution and the other the solution of $Na^+,B\cdot^-$, were sealed to a mixing bulb linked to an optical quartz cell. After crushing the break seals the solutions were mixed and poured into the cell, and the progress of the ensuing reaction was followed, ~20 sec after mixing, by monitoring the absorbance at 325 nm. At this wavelength the decimal extinction coefficient of *cis*-stilbene is 0.186×10^4 and of the trans isomer is 1.79×10^4. The isomerization was slow and proceeded for thousands of seconds.

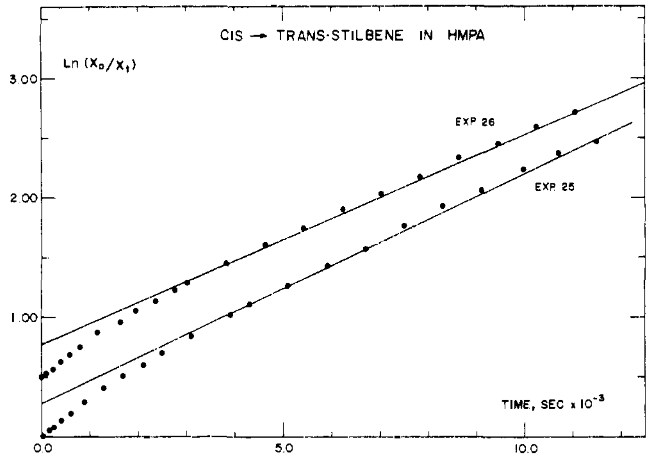

Figure 1. Plot of ln (x_0/x_t) versus time: $a = 24 \times 10^{-4}\ M$; $b = 128$ or $122 \times 10^{-4}\ M$. The ln (x_0/x_t) axis in experiment 26 is shifted upwards by 0.5 unit. Note the reliability of the asymptotes. $x_0/x_t = [\mathrm{OD}_0(325) - \mathrm{OD}_\infty(325)]/[\mathrm{OD}_t(325) - \mathrm{OD}_\infty(325)]$.

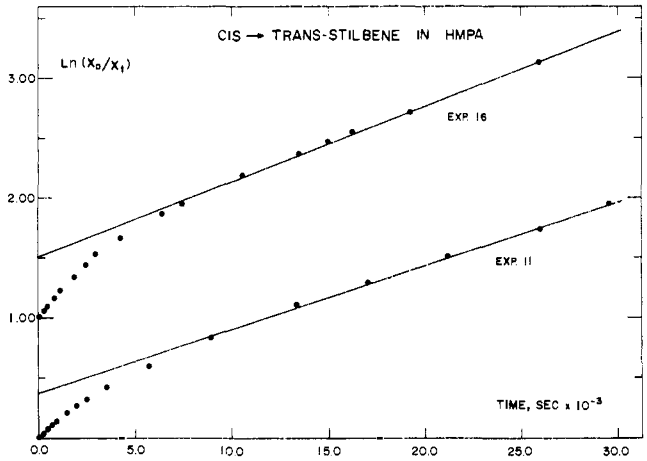

Figure 2. Plot of ln (x_0/x_t) versus time. Note the difference of $a = 0.25$ or $9.8 \times 10^{-4}\ M$; $b = 3.2$ or $136 \times 10^{-4}\ M$, but the similarity of $a/b = 0.077$ or 0.072. The asymptotes are nearly superimposed. The ln (x_0/x_t) axis in experiment 16 is shifted upwards by 1.0 unit. $x_0/x_t = [\mathrm{OD}_0(325) - \mathrm{OD}_\infty(325)]/[\mathrm{OD}_t(325) - \mathrm{OD}_\infty(325)]$.

Results

The extent of isomerization is measured by $[\mathrm{OD}_0(325) - \mathrm{OD}_\infty(325)]/[\mathrm{OD}_t(325) - \mathrm{OD}_\infty(325)]$. The plots of ln of this ratio versus time are *not* linear, as seen from Figures 1 and 2, but the resulting curves eventually merge with their asymptotes. Figure 1 exemplifies the reproducibility of the experiments, while Figure 2 demonstrates that experiments performed at greatly different initial conditions yield parallel asymptotes provided that the ratio (total concentration of radical anions)/(total concentration of the stilbenes) = $([\mathrm{C}\cdot^-] + [\mathrm{T}\cdot^-])/([\mathrm{C}] + [\mathrm{T}])$ is kept constant. Of course, $[\mathrm{C}\cdot^-] + [\mathrm{T}\cdot^-] = [\mathrm{Na}^+,\mathrm{B}\cdot^-]_0$.

Additional information about the character of the reaction was obtained by studying changes in the absorbance at 500 nm as exemplified by Figure 3. At this wavelength *trans*-stilbenide has an absorption maximum ($\epsilon = 6.02 \times 10^4$). The addition of *cis*-stilbene to a solution of *trans*-stilbenide ($\mathrm{T}\cdot^-$) in HMPA (a solution of $\mathrm{T}\cdot^-$ is prepared by mixing equivalent amounts of T and $\mathrm{Na}^+,\mathrm{B}\cdot^-$, the identity of the resulting radical ion is established through its ESR spectrum; see Table II) leads to an abrupt decrease in the absorbance at 500 nm; however, its intensity slowly rises, reaching its initial value as the cis isomer becomes converted into the trans. Surprisingly, this change in the absorbance is not accompanied by the appearance of any new absorption peak in the visible part of the spectrum. A similar increase in the absorbance at 500 nm is observed in every kinetic run (see, e.g., Figure 3), the final absorbance reaching the value expected for $\mathrm{T}\cdot^-$ formed by a quantitative conversion of the initially added $\mathrm{Na}^+,\mathrm{B}\cdot^-$ into the *trans*-stilbenide.

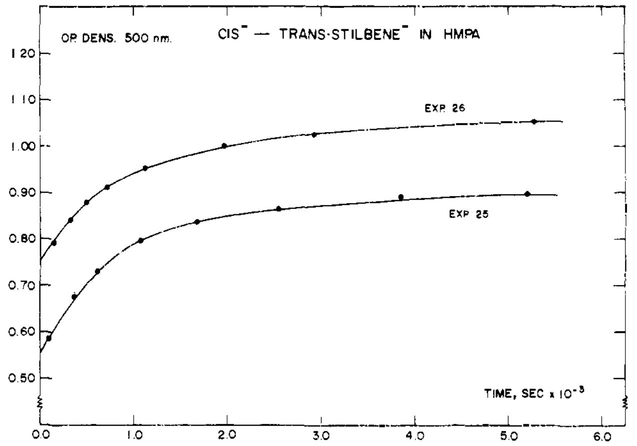

Figure 3. Plot of optical density at 500 nm ($\lambda_{\max}$ of $\mathrm{T}\cdot^-$) versus time. Note the time scale. The OD scale of experiment 26 was shifted up by 0.2 unit.

Alternatively, the fate of $\mathrm{T}\cdot^-$ radical ions could be studied by monitoring the overmodulated ESR signal which measures the total concentration of all the radicals present in the system. In contrast to the behavior of the absorbance at 500 nm that decreases on the addition of C to a solution of $\mathrm{T}\cdot^-$ and then slowly recovers, the overmodulated ESR signal seems to be constant throughout the run.

These two observations imply that on the addition of C, $\mathrm{T}\cdot^-$ is converted into another *radical* and the new radical eventually yields back $\mathrm{T}\cdot^-$. The conversion of $\mathrm{T}\cdot^-$ into $\mathrm{C}\cdot^-$ appears to be the only plausible reaction that accounts for these facts. One has then to conclude that the optical spectrum of $\mathrm{C}\cdot^-$ is closely similar to that of $\mathrm{T}\cdot^-$, although the extinction of $\mathrm{C}\cdot^-$ appears to be smaller than that of $\mathrm{T}\cdot^-$. This conclusion may not be surprising, because the spectra of *cis*- and *trans*-stilbene are alike; again the latter absorbs stronger than the former.

Mechanism of Isomerization and Its Kinetics. Only two steps seem to be involved in the isomerization of *cis*-stilbene induced by the stilbenide radical anions, viz.,

$$\mathrm{T}\cdot^- + \mathrm{C} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{T} + \mathrm{C}\cdot^- \qquad K_1 = k_1/k_{-1} \tag{1}$$

and

$$\mathrm{C}\cdot^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{T}\cdot^- \qquad K_2 = k_2/k_{-2} \tag{2}$$

The product $K_1K_2 = K$, where K is the equilibrium constant of the reaction

$$\mathrm{C} \rightleftharpoons \mathrm{T}, \quad K$$

This mechanism leads to the following differential equations

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_1[\mathrm{T}\cdot^-][\mathrm{C}] - k_{-1}[\mathrm{T}][\mathrm{C}\cdot^-]$$

$$-\mathrm{d}[\mathrm{C}\cdot^-]/\mathrm{d}t = -k_1[\mathrm{T}\cdot^-][\mathrm{C}] + k_{-1}[\mathrm{T}][\mathrm{C}\cdot^-] + k_2[\mathrm{C}\cdot^-] - k_{-2}[\mathrm{T}\cdot^-]$$

Let us denote the equilibrium concentration of the reagents by $[\mathrm{C}]_e$, $[\mathrm{T}]_e$, $[\mathrm{C}\cdot^-]_e$, and $[\mathrm{T}\cdot^-]_e$, the total concentration of the stilbenes by b, i.e.,

$$[\mathrm{C}]_t + [\mathrm{T}]_t = [\mathrm{C}]_e + [\mathrm{T}]_e = b$$

Table I

Expt no.	$10^4 a$, M	$10^4 b$, M	$10^4 x_0$, M	a/b	10^5 × slope	$10^5(b/a)$ slope	I	Ib/x_0
12	0.19	9.1	7.5	0.021	2.2	105	0.36	0.44
27	5.8	114.0	101.0	0.051	5.9	115	0.27	0.30
1	0.50	8.9	7.6	0.057	8.0(?)	140(?)	0.34	0.40
2	0.70	11.3	9.6	0.062	7.25	116	0.37	0.44
16	9.8	136.0	116.0	0.072	6.1	85	0.55	0.65
11	0.25	3.2	2.6	0.077	5.2	67.5	0.40	0.49
28	5.6	73.6	65.4	0.076	8.0	105	0.33	0.37
30	6.4	79.6	69.1	0.080	8.3	103	0.32	0.37
18	9.2	96.7	82.4	0.095	7.6	81	0.38	0.45
19	2.1	19.5	15.8	0.106	6.5	61	0.40	0.49
24	8.0	59.8	52.6	0.133	14.5	109	0.28	0.32
25	24.2	128.0	110.0	0.189	19.0	101	0.31	0.36
26	24.1	122.0	102.0	0.198	17.5	88	0.29	0.35
22	25.8	87.4	70.8	0.295	22.8	77	0.31	0.38
23	23.8	77.2	62.2	0.308	28.8	93	0.26	0.32
21	23.6	76.4	66.0	0.309	25.9	83	0.29	0.34
13	10.9	9.1	7.1	1.200	87.4	73	0.34	0.44
						Average $(91.4 \pm 17) \times 10^{-5}$		0.41 ± 0.09

and of the radical ions by a, viz.,

$$[\mathrm{C}\cdot^-]_t + [\mathrm{T}\cdot^-]_t = [\mathrm{C}\cdot^-]_e + [\mathrm{T}\cdot^-]_e = [\mathrm{Na}^+, \mathrm{B}\cdot^-]_0 = a$$

The progress of isomerization is determined by $[\mathrm{C}]_t - [\mathrm{C}]_\infty = [\mathrm{T}]_\infty - [\mathrm{T}]_t = x$, while $[\mathrm{C}\cdot^-]_t - [\mathrm{C}\cdot^-]_\infty = [\mathrm{T}\cdot^-]_\infty - [\mathrm{T}\cdot^-]_t$ is denoted by y. In this notation

$$-\mathrm{d}x/\mathrm{d}t = \{k_1[\mathrm{T}\cdot^-]_e + k_{-1}[\mathrm{C}\cdot^-]_e + (k_{-1} - k_1)y\}x - \{k_1[\mathrm{C}]_e + k_{-1}[\mathrm{T}]_e\}y$$

$$-\mathrm{d}y/\mathrm{d}t = \{(k_2 + k_{-2}) + (k_1[\mathrm{C}]_e + k_{-1}[\mathrm{T}]_e) - (k_{-1} - k_1)x\}y - \{k_1[\mathrm{T}\cdot^-]_e + k_{-1}[\mathrm{C}\cdot^-]_e\}x$$

For the sake of brevity, we denote $k_2 + k_{-2} = \alpha$, $k_1[\mathrm{C}]_e + k_{-1}[\mathrm{T}]_e = \beta b$, $k_{-1} - k_1 = \gamma$, and $k_1[\mathrm{T}\cdot^-]_e + k_{-1}[\mathrm{C}\cdot^-]_e = \delta a$. Thus

$$-\mathrm{d}x/\mathrm{d}t = \{\delta a + \gamma y\}x - \beta b y$$

and

$$-\mathrm{d}y/\mathrm{d}t = \{\alpha + \beta b - \gamma x\}y - \delta a x$$

The kinetic conditions require $-\mathrm{d}x/\mathrm{d}t$ and $-\mathrm{d}y/\mathrm{d}t$ to be positive and the former has to be much larger than the latter because in our experiments $x \gg y$. Therefore, it is permissible to apply the stationary state approximation (see the Appendix for alternative treatment of these differential equations), namely, $\mathrm{d}y/\mathrm{d}t = 0$. This assumption leads then to

$$-\mathrm{d}x/\mathrm{d}t = \alpha\delta a x/(\alpha + \beta b - \gamma x)$$

and on integration one obtains

$$\{1 + (\beta/\alpha)b\} \ln (x_0/x_t) - (\gamma/\alpha)(x_0 - x_t) = \delta a t \quad \text{(I)}$$

Therefore, plots of $\ln (x_0/x_t) = \ln (\mathrm{OD}_0(325) - \mathrm{OD}_\infty(325))/(\mathrm{OD}_t(325) - \mathrm{OD}_\infty(325))$ versus time approach asymptotes having slopes $\delta a/[1 + (\beta/\alpha)b]$ and intercepts equal to $(\gamma/\alpha)x_0/[1 + (\beta/\alpha)b]$. Our definition of β and δ leads to the relations $\beta = k_1(1 + K_2)/(1 + K)$ and $\delta = k_{-1}(1 + K)/(1 + K_2)$. Literature data,[6] as well as our own analysis, show $K > 100$ at ambient temperature and, as will be shown soon, $K_2 > K$. Therefore, the expressions for the coefficients β and δ are reduced to $\beta \approx k_{-1}$ and $\delta \approx k_1$. We shall prove also that $k_{-1}b \gg k_2 + k_{-2}$, i.e., $\beta b \gg \alpha$, and thence eq I is reduced to eq II. Therefore, the slopes of the asymptotes are $\alpha K_1(a/b)$ and their intercepts $(1 - K_1)(x_0/b)$.

$$\ln (x_0/x_t) = \alpha K_1(a/b)t + (1 - K_1)(x_0 - x_t)/b \quad \text{(II)}$$

The results of 17 experiments are collected in Table I which contains the values of a, b, and x_0, as well as of the slopes and the intercepts of the corresponding asymptotes. Its inspection shows that the ratios (slope)/(a/b) and (intercept)/(x_0/b) are fairly constant, implying that $\alpha K_1 = (91.4 \pm 17) \times 10^{-5}$ sec^{-1}, and $1 - K_1 = 0.41 \pm 0.09$. Therefore, $K_1 \approx 0.6$ and $\alpha = k_2 + k_{-2} = 1/\tau_2 = 1.5 \times 10^{-3}$ where τ_2 denotes the relaxation time of the spontaneous isomerization $\mathrm{C}\cdot^- \rightleftarrows \mathrm{T}\cdot^-$. Our assumption, $K_2 > K$, is thus justified.

General knowledge of electron-transfer processes resembling reaction 1[7,8] suggests that in HMPA k_{-1} is at least 10^8 M^{-1} sec^{-1}. Therefore, the isomerization 2, $\mathrm{C}\cdot^- \rightleftarrows \mathrm{T}\cdot^-$, and not the electron transfer 1, $\mathrm{T}\cdot^- + \mathrm{C} \rightleftarrows \mathrm{T} + \mathrm{C}\cdot^-$, is the rate-determining step of the overall process. The slowness of the spontaneous isomerization 2 is demanded also by the observation that the absorbance at 500 nm, that measures the approach of the $\mathrm{T}\cdot^- + \mathrm{C}\cdot^-$ mixture to its equilibrium composition, reaches its limiting value in time of the order of 1000 sec.

The values of k_{-1} and $k_2 + k_{-2}$ deduced from our kinetic studies justify the validity of the previously assumed inequality, $k_{-1}b \gg k_2 + k_{-2}$. Thus, all the approximations introduced in our treatment of this kinetics are permissible.

Discussion

The proposed kinetic scheme postulates the existence of *two distinct* radical ions, namely $\mathrm{C}\cdot^-$ and $\mathrm{T}\cdot^-$, and implies that on loss of an electron one is converted into C while the other is converted into T. Alternatively, we could consider a scheme involving one kind of radical ion, $\mathrm{Z}\cdot^-$, and attribute the isomerization to the reaction

$$\mathrm{C} + \mathrm{Z}\cdot^- \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \mathrm{Z}\cdot^- + \mathrm{T} \quad (4)$$

Such a scheme leads to the kinetic equation

$$-\mathrm{d}x/\mathrm{d}t = (k_4 + k_{-4})[\mathrm{Z}\cdot^-]x = (k_4 + k_{-4})ax$$

where the symbols x and a have the previous meaning. This equation is at variance with our findings; it predicts a linear plot of $\ln (x_0/x)$ versus time with slope proportional to a and not to a/b. Hence, our results provide an indirect evidence for the existence of two distinct stilbenide radical ions.

Further evidence for the existence of *cis*-stilbenide, as distinct from the trans radical, is provided by the elegant work of Chang and Markgraf.[9] Their kinetic study demonstrated the first-order dependence of $\mathrm{d}[\mathrm{C}]/\mathrm{d}t$ on [C] but, unfortunately, no information was obtained on the dependence of the pseudo-first-order constant k_1 on the concentration of radical ions. In contrast with our mechanism, Chang and Markgraf propose the scheme involving a slow reaction

Table II. ESR Coupling Constants of the Stilbenide Radical Anions in G

	Position							
	2	6	3	5	4	α	Solvent	T, °C
Ref 10[a]	1.90	2.96	0.30	0.81	3.89	4.37[e]	DME	-60
Ref 13[b]	1.94	3.03	0.30	0.83	4.00[e]	4.51	DME	-100 to +100
Our work[c]	1.84	2.93	0.29	0.82	3.93	4.15	HMPA	20
Ref 14[d]	1.84	2.93	0.29	0.84	3.85	4.27	HMPA	20

[a] Reference 10: alkali metal reduction or electrolytic reduction of cis or trans isomer. [b] Reference 13: alkali metal reduction of *trans*-stilbene. [c] Our work: reduction of cis or trans isomer in HMPA by sodium biphenylide. [d] Reference 14: electrolytic reduction of *cis*-stilbene in the cavity of the ESR spectrometer. [e] Assigned by deuteration of the relevant protons.

$$\mathrm{T}\cdot^- + \mathrm{C} \longrightarrow \mathrm{T} + \mathrm{C}\cdot^- \qquad k_1 \sim 10^3 M^{-1}\ \mathrm{sec}^{-1}$$

followed by a rapid isomerization

$$\mathrm{C}\cdot^- \longrightarrow \mathrm{T}\cdot^-$$

The value of the overall k_1 obtained from their data is too large to be accounted for in terms of our mechanism which involves a fast reaction and a slow reaction. However, under their experimental conditions (DME, K^+) the $C^{2-},2K^+$ may be formed (see ref 3 and 4) and the rapid isomerization could arise then from the reaction

$$\mathrm{C}^{2-}, 2\mathrm{K}^+ \longrightarrow \mathrm{T}^{2-}, 2\mathrm{K}^+$$

The dianion could be formed also during electrolytic reduction, provided the concentration of the supporting electrolyte is high. For example, in the experiments of Johnson and Chang[10] where $[\mathrm{Bu_4N^+,ClO_4^-}] = 0.5\ M$, the isomerization of *cis*-stilbenide into the trans radical could proceed through the dianions.

Is there any justification for a slow isomerization 2? Kistiakowsky and Smith[6] found that the thermal isomerization of *cis*-stilbene requires 42.8 kcal/mol of activation energy and corresponds to the temperature-independent factor of $6 \times 10^{12}\ \mathrm{sec}^{-1}$ while a somewhat lower value of 36.7 kcal/mol was reported by Taylor and Murray.[11] A very approximate treatment[10] suggests that weakening of the C=C bond by the addition of one antibonding electron may reduce the barrier for the isomerization by one-third of its original value. One expects, therefore, an activation energy of about 24 kcal/mol for the spontaneous isomerization of *cis*-stilbenide into the trans isomer, and accepting a value of $\sim 10^{13}\ \mathrm{sec}^{-1}$ for the temperature independent factor, we calculate $k_2 \approx 2 \times 10^{-5}\ \mathrm{sec}^{-1}$, a value even smaller than that obtained from our kinetic results.

Additional supporting evidence favoring our mechanism is derived from the polarographic studies of Dietz and Peover[12] who reported a difference of ~0.03 V between the reduction potentials of *trans*- and *cis*-stilbene measured in dimethylformamide at mercury electrode. This difference in the reduction potentials was confirmed by our potentiometric titration of the stilbenes with $\mathrm{B}\cdot^-$ in HMPA solution. Our value of $K_1 = 0.6$ leads to the difference of 0.013 V, in fair agreement with the other findings.

Our results are self-consistent and supported by other evidence reported in the literature. However, there are observations which seem to imply that the isomerization 2 is much faster than claimed by us.

The addition of either *cis*- or *trans*-stilbene to an *equivalent* amount of biphenylide in HMPA yields *the same* radical species, whichever isomer is reduced. Its ESR spectrum, recorded immediately after mixing the reagents, was very sharp (line width ~70 mG), its pattern virtually identical with that reported by Johnson and Chang[10] and by Atherton et al.[13] (see Table II). A similar observation was reported earlier by Johnson and Chang.[10] They also found that only one radical species is formed when either *cis*- or *trans*-stilbene has been reduced electrochemically or by alkali metal. The same species is also formed when the electrochemical reduction is performed in the cavity of the ESR spectrometer,[14] and at no stage of the electrolysis has an alternative radical been seen.

The observed ESR spectrum is attributed to *trans*-stilbenide on the basis of the argument outlined in ref 8 and 9 invoking the relation between the rate of exchange and Frank-Condon principle.[15] It follows also from the analysis of the ESR spectrum and its temperature independence that the resulting solution is not a mixture of two radicals.

When HMPA solution of *cis*-stilbene was mixed with an equivalent amount of sodium biphenylide, the absorbence at 500 nm reached its ultimate value in a time shorter than the mixing time, i.e., the absorbance recorded in a flow system about 2 msec after mixing the reagents was the same as that expected for the equivalent concentration of $\mathrm{T}\cdot^-$. Thus, $\mathrm{T}\cdot^-$ is formed from $\mathrm{C} + \mathrm{B}\cdot^-$ in a time shorter than 2 msec in contrast with the observations made in the presence of an excess of C (see Figure 3).

The results of this experiment and the inability to demonstrate directly, e.g., by ESR spectroscopy, the presence of *cis*-stilbenide call for further investigation. We hope to clarify these puzzling features of the stilbene system in the course of future work. It seems that the dianions of stilbene play some role in the process when the ratio a/b is very large, e.g., in the experiments described in the preceeding paragraph but not when it is small.

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Appendix

The kinetic relation presented in this paper was derived by assuming stationary concentration of y. As the system approaches its equilibrium state, the values of x and y become small and the higher terms such as xy, etc., may then be neglected. The previously derived differential equations then become linear, namely

$$-\mathrm{d}x/\mathrm{d}t = \delta a x - \beta b y$$

$$-\mathrm{d}y/\mathrm{d}t = \delta a x + (\alpha + \beta b) y$$

with α, β, and δ having the earlier meaning. This approach to equilibrium is determined therefore by two relaxation times, their reciprocals denoted by λ_1 and λ_2. Since

$$\begin{vmatrix} \delta a - \lambda & -\beta b \\ -\delta a & \alpha + \beta b - \lambda \end{vmatrix} = 0$$

we find

$$\lambda_{1/2} = \frac{1}{2}(\alpha + \delta a + \beta b)\{1 + [1 - 4\alpha\delta a/(\alpha + \delta a + \beta b)^2]^{1/2}\}$$

This expression may be simplified provided that $4\alpha\delta a \ll (\alpha + \delta a + \beta b)^2$, an inequality fully justified under our experimental conditions. It follows that $\lambda_1 = \alpha + \delta a + \beta b \approx \beta b$ and $\lambda_2 = \alpha\delta a/(\alpha + \delta a + \beta b) \approx (\alpha\delta/\beta)(a/b)$, provided $\beta b \gg \alpha + \delta a$. Thus as the system approaches its state of equilibrium

$$[\mathrm{C}]_t - [\mathrm{C}]_e = M\exp(-\lambda_1 t) + N\exp(-\lambda_2 t)$$

the constants M and N being determined by the initial conditions. As is easily verified, $\lambda_1 \gg \lambda_2$, and therefore the first term could be neglected at later stages of the reaction and then

$$[\mathrm{C}]_t - [\mathrm{C}]_e = \text{constant}\ \exp(-\lambda_2 t)$$

i.e.

$$\ln\{([\mathrm{C}]_0 - [\mathrm{C}]_e)/([\mathrm{C}]_t - [\mathrm{C}]_e)\} = \text{constant} + (\alpha\delta/\beta)(a/b)t$$

This result is identical to that derived on the assumption of stationary concentration of radical anions. Hence, the slopes of the asymptotes shown in Figures 2 and 3 are given by $\alpha K_1(a/b)$ because $\delta \approx k_1$ and $\beta \approx k_{-1}$.

References and Notes

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Phase Transfer Catalysis. An Evaluation of Catalysts[1]

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Abstract: The catalytic effects of quaternary ammonium and phosphonium ions on the reaction of thiophenoxide ion with 1-bromooctane in a two-phase system have been determined. The kinetics are linearly dependent on catalyst concentration and independent of stirring rate. A wide variety of catalysts was examined with the larger and more symmetrical ions being more effective. An increase in the ionic strength of the aqueous phase or change to a more polar organic solvent also increased the rate. Correlations between rate constants and partition coefficients indicate that the major function of the catalyst is simply the solubilization of the nucleophile in the organic phase.

A variety of organic reactions have recently been reported to be catalyzed by tetraalkylammonium salts. The generation of dichlorocarbene,[3] the alkylation of carbonyl and related compounds,[4] nucleophilic substitutions,[5] and the benzoin condensation[6] are among the reactions which are facilitated by this approach.[7] Two common features of these seem essential: the system has two phases consisting of a water layer and an organic layer and involves an anion as a base or nucleophile. Several explanations have been proposed for the effectiveness of quaternary ammonium ions,[3a,5,6,8] but the phase transfer mechanism proposed by Starks accounts for the major features of the reactions.[5] An important factor which has heretofore received scant attention is the structure of the quaternary ammonium salt. We wish to report a comprehensive quantitative comparison of the efficacies of quaternary ammonium ions in catalyzing an SN2 reaction.[9] The kinetic parameters obtained also offer additional independent evidence for the phase transfer mechanism.

Results

The system chosen for study was the reaction of thiophenoxide ion ($C_6H_5S^-$) with 1-bromooctane (RBr). Despite the complexities of a two-phase system of water and an organic solvent, the reaction followed good second-order kinetics at any given concentration of quaternary ammonium ions. Plots of ln $[\mathrm{RBr}]/[C_6H_5S^-]$ vs. t were linear with correlation coefficients of 0.996 or better. Rates followed by disappearance of bromooctane and by appearance of product sulfide were in good agreement and were reproducible to ≤3%.

The stirring rate was found to have no effect on the reaction for stirring speeds of 200–2200 rpm. At lower speeds a slight induction period was noted and at very low speeds (<50 rpm), the reaction no longer followed second-order kinetics. Stirring speeds of 1000–1500 rpm were used in determination of other kinetic effects.

The rate of reaction was found to be linearly dependent on catalyst concentration. Figure 1 shows the effect of a 20-fold change in concentration of cetyltriethylammonium bromide. In subsequent work the catalyst concentration was usually fixed at 0.00137 mol, but for very slow or very rapid reactions, higher or lower concentrations were used and all the results were extrapolated to 0.00137 mol of catalyst.

The major portion of this study focused on the effects of catalyst structure on the rate. The rate constants collected in Table I show the influence of systematic variations in the structure of the quaternary ion. These data were obtained for a benzene–water system containing 2 N sodium hydroxide. Changes in the organic solvent or salt concentration in the aqueous phase had pronounced effects on the rates as indicated in Tables II and III.

In order to evaluate the origin of the relative catalytic efficiencies, information about the distribution of quaternary salts was also collected. The distribution of quaternary ammonium hydroxides between benzene and water was evaluated by titration of the organic layer; a comparison with the rate constants is given in Table IV. The influence of quater-