

Disproportionation of *cis*-Stilbene Radical Anions

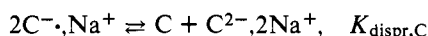
F. Jachimowicz, G. Levin, and M. Szwarc*

Contribution from the Department of Chemistry, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210. Received July 26, 1977

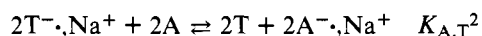
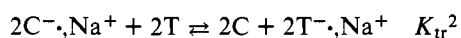
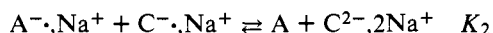
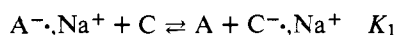
Abstract: Radical anions derived from *cis*-stilbene ($C^{\cdot-}, Na^+$) readily disproportionate in THF, $K_{\text{dispr},C} > 2$, whereas $K_{\text{dispr},T} = 0.03$. The latter constant refers to the radical anions derived from *trans*-stilbene ($T^{\cdot-}, Na^+$). The largeness of $K_{\text{dispr},C}$ compared to $K_{\text{dispr},T}$ implies that the geometry of this radical anion resembles that of *cis*-stilbene and the resulting strain is released on the formation of its dianion. This suggestion was tested by studying disproportionation of radical anions of hydrocarbon I having a CH_2 bridge linking the two ortho carbons of stilbene. Conversion to dianion cannot release the strain in this species, and indeed the respective disproportionation constant was found to be 0.1. Proton and ^{13}C NMR spectra of I are reported as well as the optical spectra of $I^{\cdot-}, Na^+$ and $I^{2-}, 2Na^+$.

Contrary to the past belief¹⁻³ reduction of the isomeric stilbenes yields distinct isomeric radical anions referred to later as *cis*- and *trans*-stilbenides.⁴⁻⁷ This nomenclature does not necessarily imply the conventional geometric distinction, but it is used in an operational meaning. Attachment of an electron to *cis*-stilbene yields the *cis*-stilbenide ($C^{\cdot-}$) which is converted into the *cis* hydrocarbon on removal of the extra electron. Similar definition applies to the term *trans*-stilbenide ($T^{\cdot-}$). Nevertheless, we wish to inquire what is the geometry of these species.

Spontaneous isomerization of the free *cis*-stilbenide into *trans* isomer is slow^{5,7} and proceeds with a unimolecular rate constant of about 10^{-3} s^{-1} , although the equilibrium constant $C^{\cdot-} \rightleftharpoons T^{\cdot-}$ is greater than the equilibrium constant of the hydrocarbon isomerization, $C \rightleftharpoons T$. The process $C^{\cdot-}, Na^+ \rightleftharpoons T^{\cdot-}, Na^+$ is presumably even slower. However, $C^{\cdot-}, Na^+$ readily disproportionates into its parent hydrocarbon, C, and the dianion $C^{2-}, 2Na^+$, viz.



and the pertinent equilibrium constant in tetrahydrofuran may be calculated from the following cycle:

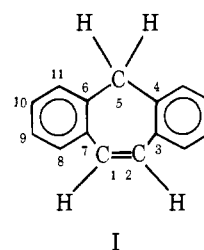


where A denotes anthracene and $A^{\cdot-}, Na^+$ its radical anion. Thus $K_{\text{dispr},C} = K_1 K_2 K_{\text{tr}}^2 K_{A,T}^2$. The lower limit for the product $K_1 K_2$ was found from kinetics of electron transfer induced *cis*-*trans* isomerization,⁴ K_{tr} was found from flash-photolytic studies,⁶ and $K_{A,T}$ has been recently determined by an electrochemical method.⁸ We find therefore $K_{\text{dispr},C} \geq 2$.

The disproportionation constant of sodium *trans*-stilbenide in tetrahydrofuran was first determined by Garst⁹ and later by our group.¹⁰ Our results lead to $K_{\text{dispr},T} = 0.03$, about 100 times smaller than $K_{\text{dispr},C}$. This large ratio $K_{\text{dispr},C}/K_{\text{dispr},T}$ is significant and may shed light on the geometry of $C^{\cdot-}, Na^+$.

It seems that the geometry of $C^{\cdot-}, Na^+$ resembles that of *cis*-stilbene and leads to a substantial steric strain, even larger than that operating in the unreduced hydrocarbon. The rigidity of the $C=C$ double bond is not yet relaxed in the radical anion but it is greatly reduced in the dianion. Consequently, the disproportionation releases much of the steric strain and this favors the equilibrium constant of that reaction. Such a gain is not expected in the disproportionation of the sodium *trans*-stilbenide, the geometry of which presumably resembles that of *trans*-stilbene.

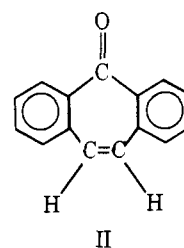
To confirm the proposed explanation, we investigated the disproportionation of radical anions of I, i.e., $I^{\cdot-}, Na^+$ in THF.



The strain operating in this hydrocarbon or its radical anion cannot be alleviated in its dianion, and hence one anticipates a low value for its disproportionation constant. The results reported in the Experimental Section confirmed this expectation; namely, the value of $K_{\text{dispr},I} = 0.1$ is comparable to $K_{\text{dispr},T} = 0.03$. In conclusion, the crowding encountered in *cis*-stilbene and its radical anion is at least partially alleviated in its dianion, and this factor is responsible for the high value of the pertinent disproportionation constant.

Experimental Section

Preparation of Compound I. Reduction of commercially acquired ketone II (Aldrich) with aluminum isopropoxide at 250 °C leads to



the formation of I from II.¹¹ The crude material was sublimed under high vacuum and then recrystallized from acetone-methanol mixture. The resulting colorless but slightly fluorescent platelets melt at 131 °C.

Its 1H NMR in CCl_3D shows two peaks at 3.76 and 7.05 ppm and a narrow multiplet centered at 7.3 ppm. The decoupled ^{13}C NMR shows a sharp line at δ 41.81 ppm attributed to carbon 5 and seven sharp lines at δ 138.4, 135.5, 131.8, 128.6, 128.4, 128.1, and 126.3 ppm. Analysis of the coupled and partially decoupled spectra demonstrates that the 138.4-ppm line is due to carbons 3 and 7 and the 135.5-ppm line to carbons 4 and 6. Further, the analysis assigns the 131.8-ppm line to the olefinic carbons and the remaining four lines arise from the aromatic CH groups. All the C-H couplings are in the range 161-164 Hz and the CH_1 coupling is 158 Hz. The mass spectrum reveals the molecular ion at m/e 192 with the appropriate isotope satellite.

Radical Anion and Dianion of I. Partial reduction of I by metallic sodium mirror in THF solution produces $I^{\cdot-}, Na^+$. The maximum of

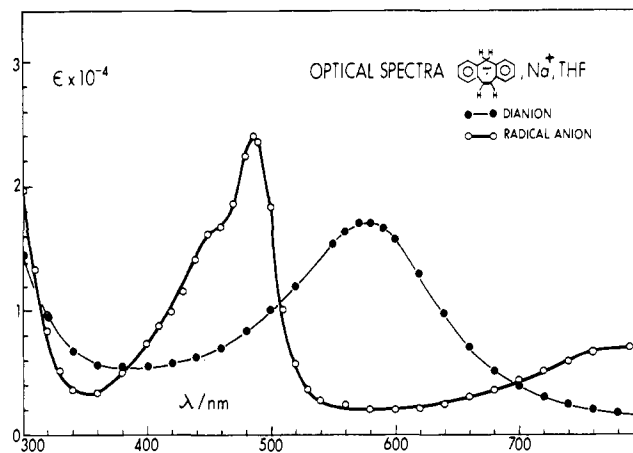
Table I. Disproportionation Equilibrium of $I^{\cdot-}, Na^+$ in THF

$10^4[I^{\cdot-}, Na^+]_e, M$	$10^4[I^{2-}, 2Na^+]_e, M$	$10^4[I]_e, M$	K_{disp}
6.9	3.4	1.7	0.12
4.9	6.8	0.3	0.08
2.9	9.0	0.1	0.11
3.7	1.7	1.0	0.12
3.7	2.2	0.4	0.08
3.2	2.8	0.4	0.11
$\bar{K}_{disp} = 0.10 \pm 0.02$			

its absorption appears at 487 nm (see Figure 1), and the respective extinction coefficient was determined by measuring the intensity of the overmodulated ESR signal of its solution and comparing it with a signal produced by a perylene solution of known concentration (both signals were measured in the same ESR tube). Alternatively, an excess of I was added to HMPA solution of sodium biphenylide of known concentration. Although λ_{max} shifted to 499 nm, the calculated molar absorbance agreed with that determined by the ESR technique, namely, $\epsilon = 2.4 \times 10^4$. The ESR spectrum of $I^{\cdot-}, Na^+$ was reported in the literature¹² and the results of its analysis have been confirmed recently by Professor Gerson.¹³

Exhaustive reduction of I leads to the formation of the dianion, $I^{2-}, 2Na^+$. It was established by the ESR technique that the concentration of $I^{\cdot-}, Na^+$ in that solution was lower than 0.2%. The λ_{max} of $I^{2-}, 2Na^+$ in THF appears at 577 nm (see again Figure 1). The molar absorbance was calculated from the known initial concentration of I and the result was confirmed by transferring the electrons to perylene and determining its absorption spectrum. Thus ϵ of $I^{2-}, 2Na^+$ at 577 nm was found to be 1.7×10^4 . From the absorption spectra the molar absorbance of $I^{\cdot-}, Na^+$ at 577 nm was calculated to be 0.23×10^4 and that of $I^{2-}, 2Na^+$ at 487 nm to be 0.9×10^4 . At 800 nm only radical anions absorb and the respective ϵ is 0.7×10^4 .

Equilibrium of Disproportionation $2I^{\cdot-}, Na^+ \rightleftharpoons I + I^{2-}, 2Na^+$. The equilibrium constant of the above disproportionation was determined in THF solutions at ambient temperatures. The optical and ESR spectra were recorded at successive degrees of reduction of I. Two solutions of I were investigated; their initial concentrations $[I]_0$ were 1.2×10^{-3} and 0.64×10^{-3} M, respectively. From their spectra the concentrations of $I^{\cdot-}, Na^+$ and $I^{2-}, 2Na^+$ were calculated, while the concentration of the unreduced I was obtained from the balance. The results collected in Table I give $K_{dispr} = 0.10 \pm 0.02$.

**Figure 1.** Optical spectra of sodium salts of radical anions (open circles) and dianions (full circles) of I in THF.

Acknowledgment. We wish to thank the National Science Foundation for their generous support of this investigation.

References and Notes

- (1) (a) G. J. Holjtnik and P. H. van der Meij, *Z. Phys. Chem. (Frankfurt am Main)*, **20**, 1 (1959); (b) M. A. Doran and R. Waack, *J. Organomet. Chem.*, **3**, 94 (1965).
- (2) (a) R. Chang and C. S. Johnson, *J. Chem. Phys.*, **46**, 2314 (1967); (b) C. S. Johnson and R. Chang, *ibid.*, **43**, 3183 (1965); (c) R. Chang and J. H. Markgraf, *Chem. Phys. Lett.*, **23**, 575 (1972).
- (3) C. Takahashi and S. Maeda, *Chem. Phys. Lett.*, **28**, 22 (1974).
- (4) T. A. Ward, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 258 (1975).
- (5) S. Sorensen, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 2341 (1975).
- (6) H. C. Wang, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, **99**, 2642 (1977).
- (7) F. Gerson, H. Ohya-Hishiguchi, M. Szwarc, and G. Levin, *Chem. Phys. Lett.*, **52**, 587 (1977).
- (8) F. Jachimowicz, H. C. Wang, G. Levin, and M. Szwarc, *J. Phys. Chem.*, **82**, 1371 (1978).
- (9) E. R. Zabolotny and J. F. Garst, *J. Am. Chem. Soc.*, **88**, 1645 (1964).
- (10) Unpublished potentiometric study from this laboratory.
- (11) R. D. Hoffsommer, D. Taub, and N. L. Wendler, *Chem. Ind. (London)*, 482 (1964).
- (12) B. J. Tabner and J. Zdzyslewicz, *J. Chem. Soc., Perkin Trans. 2*, 811 (1973).
- (13) F. Gerson, private communication.