Electron Distribution in Trifluoromethylbenzenes. Electron Donation by the Trifluoromethyl Group

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Abstract: The core-electron ionization potentials for mono- and di(trifluoromethyl)benzene have been measured in order to give information on the electron distribution in these molecules and to investigate differences between the inductive effect of fluorine and that of CF_3. For trifluoromethylbenzene the measured ionization potentials in eV are: F(1s), 693.88; C(1s, ring), 291.02; C(1s, CF_3), 298.24. For 1,3-di(trifluoromethyl)benzene: F(1s), 694.14; C(1s, ring), 291.48; C(1s, CF_3), 298.64. For 1,4-di(trifluoromethyl)benzene: F(1s), 694.17; C(1s, ring), 291.48; C(1s, CF_3), 298.58. In no case was it possible to resolve the ring carbon to which the CF_3 group was attached from the other ring carbons. Comparison of our gas-phase measurements with those made in condensed phases shows that most of the difference between the two kinds of measurements is accounted for by a work function correction. However, the ionization potentials for different atoms in the same molecule shift by different amounts between condensed and gas phase. A point-charge analysis of the core binding energy shifts shows that the carbon adjacent to the CF_3 group is negative, in agreement with theoretical predictions and with the results of similar experiments on aliphatic compounds. More surprising is the conclusion that the CF_3 group donates electrons to the ring. The well-known inductive effect of CF_3 results not because CF_3 withdraws electrons from its neighbors but because the positive dipole of CF_3 creates a positive potential on the adjacent atoms. It is noted that the chemical properties of these molecules correlate well with the core binding energy shifts, which are a measure of the potential at a given atom.

Both fluorine and trifluoromethyl are considered to be strongly electron-withdrawing groups. Their effects when attached to a benzene ring are, however, somewhat different.[1] Both tend to deactivate the ring, but fluorine less so than CF_3. Fluorine is ortho–para directing and CF_3 is meta directing. Various explanations involving induction, resonance, and hyperconjugation have been proposed to explain these effects.

The measurement of core-electron binding energies by X-ray photoelectron spectroscopy (ESCA) is an effective probe for studying the distribution of charge within molecules. A previous study on fluorinated benzenes,[2] combined with a point-charge model, has given results that are in agreement with chemical experience and with the predictions of CNDO calculations. According to these experiments, fluorine induces a positive charge on the carbon to which it is attached and a negative charge on the ortho carbon; the net charge on the ring is positive.

We have extended these earlier measurements to the compounds trifluoromethylbenzene, 1,3-di(trifluoromethyl)benzene, and 1,4-di(trifluoromethyl)benzene. Our goal has been to investigate the charge distributions within these molecules, to correlate the binding energy shifts with the chemical properties, and to study the reasons for the different chemical effects of CF_3 and fluorine as substituents.

CNDO/2 calculations[3] for trifluoromethylbenzene provide predictions of charges on the various atoms in this molecule. These can be compared with the results of a point-charge analysis of the core binding energy shifts. Such analysis for other molecules has given results in excellent agreement with the predictions of CNDO.[2] For this molecule, and others, the calculations indicate the carbon adjacent to the CF_3 group to be negatively charged. If, however, the CF_3 group is electron-withdrawing, as is generally believed, we would expect this carbon to be positively charged. The measured core binding energies provide a test of these predictions.

Experimental Procedures

Carbon and fluorine 1s electron binding energies were measured in the Oregon State University cylindrical-mirror electrostatic spectrometer.[4] Al $K\alpha_{1,2}$ X-rays were used as the source radiation; in addition, Mg $K\alpha_{1,2}$ X-rays were used in an unsuccessful attempt to resolve the lines due to different ring carbons. The 1,3- and 1,4-di(trifluoromethyl)benzene were obtained from PCR, Inc. with 97 to 99% purity, and practical grade trifluoromethylbenzene was obtained from Eastman Kodak. No evidence was seen for additional peaks or peak broadening due to impurities. The line widths for the ring carbons were nearly as narrow and symmetric as those for benzene (99–100% purified). The compounds had sufficient vapor pressure to be run in the gas phase at room temperature at pressures from 0.04 to 0.1 Torr. A carbon 1s background was eliminated by preventing X-rays from striking the exit window of the sample cell. Peak to background ratios were typically 10:1 for ring carbons and 4:1 for trifluoromethyl carbons.

Each sample was run with a reference standard in order to compensate for any variations in line position during the 3 to 4 hr of the run. The carbon 1s line from CF_4 (at a binding energy of 301.96 (5) eV[5]) provided a convenient reference for the carbon 1s measurements; the neon $^1D_2$ Auger line (at a kinetic energy of 804.57 (2) eV[5]) provided a similar reference for the fluorine 1s measurements. The various spectra were fit with gaussian shapes and linear backgrounds by least-squares techniques.

Results

Only two well-resolved carbon 1s peaks appear in each spectrum; the CF_3 carbons appear as an isolated peak but the ring carbons are an unresolvable envelope of six lines. Taking 1,4-di(trifluoromethyl)benzene as an example, we can estimate the maximum separation of lines within this envelope. There are two inequivalent carbons in the ring in a ratio of 2:1. We observe a full width at half maximum (FWHM) for this compound of 1.5 eV compared to 1.2 eV for benzene. We assume that the actual spectrum is the superposition of two lines in the ratio of 2:1, each with a FWHM of 1.2 eV. The shapes of such double lines for various separations have been calculated by Siegbahn and coworkers;[6] from a comparison of our measured spectra with their results, we conclude that the difference in binding energies for ring carbons attached to CF_3 and those attached to H is less than 0.6 eV.

The measured core-electron ionization potentials are given in Table I. We note first that these are all larger by 3.1 to 5.5 eV than those given by Clark, Kilcast, and Musgrave,[7] the major part of the difference arising because their measurements were made in the condensed phase and are relative to the Fermi level of gold. Correcting for a gold work function of 4.8 eV reduces the discrepancy to between

Table I. Core-Electron Ionization Potentials in Trifluoromethylbenzenes (eV)

Compd	Ring carbons	CF_3 carbons	Fluorines
C_6H_6	290.38 (7)		
$C_6H_5CF_3$	291.02 (7)	298.24 (8)	693.88 (3)
1,3-$C_6H_4(CF_3)_2$	291.48 (6)	298.64 (7)	694.14 (3)
1,4-$C_6H_4(CF_3)_2$	291.48 (8)	298.58 (8)	694.17 (3)

Table II. Atomic Charges for Atoms in Trifluoromethylbenzenes

Compd	Atom	Charge, q/e	CNDO charge
Mono	F	−0.223	
	C_F[a]	0.728	
	C_1[b]	−0.130	−0.051
	$C_{2,6}$	0.027	0.028
	$C_{3,5}$	0.018	0.005
	C_4	0.018	0.022
	H	−0.007	0.005
1,3-Di	F	−0.238	
	C_F[a]	0.772	
	$C_{1,3}$[b]	−0.128	
	C_2	0.043	
	$C_{4,6}$	0.033	
	C_5	0.023	
	H	0.001	
1,4-Di	F	−0.220	
	C_F[a]	0.735	
	$C_{1,4}$[b]	−0.124	
	$C_{2,3,5,6}$	0.043	
	H	−0.019	

[a] C_F refers to the carbon in the CF_3 group. [b] The number 1 carbon is one to which a CF_3 group is attached.

−1.7 and 0.7 eV, presumably due to extramolecular relaxation energies. Our relative measurements (in the gas phase) disagree in some details with theirs. For instance the shift between carbon 1s in benzene and carbon 1s of the CF_3 group in trifluoromethylbenzene is 7.86 ± 0.09 eV in our measurements and 8.9 ± 0.3 in theirs. This difference is well outside the experimental error and suggests the problems of comparing two different samples in the solid phase are more difficult than has been indicated by Clark et al. For differences within the molecule we have 7.22 ± 0.08 eV as the difference between the ring carbons and the CF_3 carbon in trifluoromethylbenzene; Clark et al. give 7.6 ± 0.2. The difference is small, but it is outside experimental error.

It is to be noted that the electrons from the ring carbons are shifted to higher binding energies than in benzene. The environment for these electrons is more positive than in benzene. It is also to be noted that the average binding energies of ring carbons in the compounds discussed here are very close to those for the corresponding fluorinated benzenes, even though the spectra for the latter compounds are resolved into two well-separated peaks, whereas those for the present compounds show only one peak. The average environment of the ring carbons is nearly the same in both cases.

The ring carbon, trifluoromethyl carbon, and fluorine ionization potentials are all shifted to higher values by the addition of the second CF_3 group (in either position). The additional shift is largest for the ring carbons (0.46 eV), intermediate for the trifluoromethyl carbon (0.37 eV), and smallest for the fluorines (0.27 eV); the effect falls off with distance from the substituent. A similar effect is seen for the fluorinated benzenes; each additional fluorine causes the average ring carbon to shift by 0.6 eV and the average fluorine binding energy by 0.3 eV. Addition of either a fluorine or a trifluoromethyl group causes the rest of the molecule to have a more positive potential.

Discussion

Point-Charge Analysis. The binding energy shifts can be analyzed to give the charge distribution within the molecule using a point-charge model that is described in detail elsewhere.[2,8-10] The principal assumptions of this model are that relaxation energies are the same for a given atom in different environments, that the core-electron binding energy varies linearly with atomic charge, that all charges are spherically distributed about their atomic centers, that each atom lies outside the sphere of charge around the other atoms, and that effects of overlap population can be ignored. At this time it seems that the most questionable of these assumptions is the first, concerning relaxation energies; we take the others to be valid and discuss this one in detail below.

The expression that arises from these assumptions is

$$\Delta E_i = q_i k_i + \sum_{j \neq i} (q_j e^2)/r_{ij}$$

Here ΔE_i is the core-electron binding energy of atom i in the molecule relative to the same atom when neutral. The hypothetical neutral carbon atom is taken as the carbon in benzene and that of the fluorine atom as in F_2 (696.70 (5) eV[10]). The charge on atom i is signified by q_i. The constant k is the change in core-electron binding energy when one electron is removed from the atom. Values for k are k_C = 22.0 eV/e and k_F = 32.5 eV/e given by Davis, Shirley, and Thomas[2] for the fluorobenzene series. The term r_{ij} refers to the distance between nucleus i and nucleus j; values for these distances were the same as those used by Brownlee and Taft[3] for their CNDO/2 calculations. Various orientations of the CF_3 groups with respect to the ring and each other had little effect on the derived charges. Therefore, we report results only for the trans conformations.

For each atom on the molecule there is, in principle, one such equation, one measured binding energy, and one unknown charge. As has been noted by Davis et al.,[2] however, it is impossible to measure a complete set of core-level shifts, because hydrogen has no core levels. In order to solve this problem we have used the same simplifications as they. All hydrogens in each molecule are constrained to have the same charge. This assumption together with the equation of electrical neutrality for the molecule, $\Sigma q_i = 0$, gives us as many equations as unknown charges. Within each molecule the binding energies of all the inequivalent ring carbons have been taken to be the same and equal to the measured average value. The effects of this assumption are discussed below. The fluorines are treated as equivalent to one another. Table II gives the atomic charges calculated according to this procedure.

In the simplification of the equations of the point-charge model, we have assumed all binding energies for ring carbons to be the same. In the presentation of experimental results, we showed that for the 1,4 compound these energies could differ by no more than 0.6 eV. We have repeated the point-charge analysis for this compound assuming peaks with a 2:1 intensity ratio, split by 0.6 eV, but with the observed average binding energy. The results of these calculations are compared in Table III with those of the regular point-charge analysis. Qualitatively the conclusions are the same in each case: the carbon to which the substituent is attached has a negative charge, the ortho carbon has a positive charge, and the ring as a whole has a negative charge of about −0.08 e.

A similar question must be raised with regard to relaxation energies. The calculations of Davis and Shirley[11] and those of Cavell[12] show that the relaxation energy of a carbon atom may increase by about 0.8 eV when a hydrogen

Table III. Atomic Charges in 1,4-Di(trifluoromethyl)benzene for Different Assumptions about Energy of Splittings

Atom	Calculated charges, q/e			
	a	b	c	d
F	−0.220	−0.220	−0.219	−0.220
C_F	0.735	0.745	0.725	0.720
$C_{1,4}$	−0.124	−0.164	−0.084	−0.050
$C_{2,3,5,6}$	0.043	0.064	0.021	0.026
H	−0.019	−0.025	−0.013	−0.031
Ring	−0.075	−0.085	−0.068	−0.06

[a] No core binding energy shift between $C_{1,4}$ and $C_{2,3,5,6}$. [b] $C_{1,4}$ core binding energy 0.6 eV lower than $C_{2,3,5,6}$. [c] $C_{1,4}$ core binding energy 0.6 eV higher than $C_{2,3,5,6}$. [d] Relaxation energy of 1 eV on $C_{1,4}$.

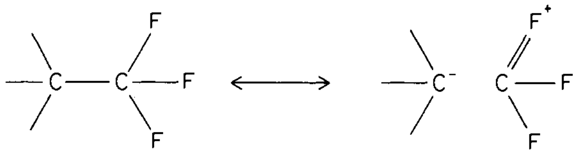
attached to it is replaced by a CF_3 group. Adding 1 eV to the core binding energies we have assigned to the 1 carbon in these compounds shifts the total ring charge from −0.06 to −0.04 e in the monosubstituted compound and from −0.075 to −0.06 e in the 1,4-disubstituted compound. (More detailed results are given in Table III.) The conclusion that the ring is slightly negative and the CF_3 group slightly positive is independent of any reasonable assumptions we might make about either relaxation effects or unresolved lines.[18]

Several features of the derived charges deserve notice. As expected the fluorines have negative charges and the carbon to which they are attached has a positive charge. In agreement with the predictions of theoretical calculations[3] the carbon adjacent to the CF_3 group has a negative charge; this conclusion is independent of corrections for relaxation effects and for unresolved lines. In the monosubstituted compound the ortho carbon is slightly more positive than the meta and para carbons; because the various ring carbons were not resolved in the spectra, this conclusion is not a strong one. In each case the ring charge is slightly negative (−0.06 e for $PhCF_3$) and is approximately twice as great for the disubstituted compounds as for the monosubstituted compound.

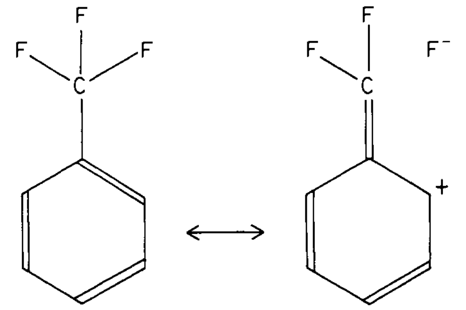
That the ring charge in these compounds is negative deserves special emphasis, since it implies that the CF_3 group is electron donating (even though the chemical effect of CF_3 is that expected for electron withdrawal). This conclusion is not unique to the molecules studied here. Similar measurements and analysis by Davis, Banna, and Shirley[13] on $CF_{3-n}H_nCH_3$ ($n = 0 \rightarrow 3$) and $CF_{2-n}H_nCH_2$ ($n = 0 \rightarrow 2$) indicate that the group containing the fluorine donates negative charge to the rest of the molecule. Ab initio calculations by Hehre and Pople[14] for $CF_{4-n}H_n$ ($n = 0 \rightarrow 4$), for CF_3CH_3, and for CF_3CCH lead to the same conclusion. CNDO/2 calculations by Brownlee and Taft[3] are mixed, sometimes predicting the CF_3 to be electron withdrawing, sometimes electron donating. Experimentally the amount of charge donated by the CF_3 group is −0.04 to −0.06 e. The theoretical values for this quantity range from +0.06 to −0.133 e. Some possible reasons for this effect are discussed below.

It is interesting to compare the results of the point-charge analysis with the charges predicted by the CNDO/2 method. In general, such comparisons have shown excellent agreement between the experimentally derived and theoretically predicted numbers. It should, however, be noted that the assumptions of the point-charge model and those of CNDO are quite similar. Table II gives a comparison between the charges we have derived and those calculated by Brownlee and Taft.[3] Qualitatively the agreement is good. The 1 carbon is negative, though substantially more so in the experimental number than in the theoretical one. The other ring carbons are all slightly positive, with the carbon ortho to the substituent slightly more so than the others. The most striking disagreement between experiment and calculation is that the ring charge is determined from experiment to be negative and from theory to be positive. As noted above, we have tested a number of the assumptions made in our analysis and find this conclusion to be relatively independent of these assumptions.

A number of mechanisms have been proposed to account for the effect of trifluoromethyl substituents on the charge distribution of the molecule to which they are attached.[1] First, we might expect a direct withdrawal of electrons from adjacent atoms by the CF_3 group. Our experimental results, those of Davis et al.,[13] and most theoretical calculations indicate, however, that the net charge transfer is in the opposite direction. There is direct polarization of the rest of the molecule by the strong dipole of the CF_3 group, causing electrons to flow toward the substituent but without actual charge transfer to the CF_3 group. Hyperconjugation allows negative charge to move from the fluorines to the atom to which the CF_3 group is attached, and, in aromatic systems, to move from the ortho and para positions of the ring to the fluorine. Resonance structures A and B show how electrons can be donated from the fluorine to the β carbon; this mechanism has been suggested by Pople and Gordon.[15] Structures C and D show the removal of electrons from the ortho position to the fluorine. A similar structure can be drawn with positive charge at the para position. Other mechanisms, such as the π inductive effect and p–π interaction, have been proposed for aromatic systems, but are thought to be of secondary importance.[16]



A B



C D

The charges we have derived are readily explained in terms of these mechanisms. The addition of a CF_3 group causes electrons to flow toward the group, making one end of the ring negative and the other end positive. Hyperconjugation, using structures A and B, causes negative charge to move from the fluorines to the 1 carbon, which thus becomes still more negative. Hyperconjugation, using structures C and D, causes the 2 and 6 carbons to become positive. The first hyperconjugative mechanism must be sufficiently strong to inject more negative charge into the ring than is withdrawn by the other two mechanisms, so that the net charge on the ring is slightly negative and the CF_3 group slightly positive. (The same hyperconjugative mechanism must be equally important for aliphatic systems as well. Point-charge analyses of binding energy shifts[13] and a variety of theoretical calculations[13,14] indicate that CF_3, CHF_2, CH_2F, $=CFH$, and $=CF_2$ are all electron donating not only to the adjacent atom but to the entire molecule to which they are attached.)

In view of the strong effects of such substituent groups as CF_3, CHF_2, and CH_2F on acid strengths and other chemical properties, it seems contradictory, at first, to suggest that these are electron-donating groups. The chemical and physical data are reconciled when we realize that the acidity depends on the ease of changing the charge at some point in the molecule, and, hence, on the potential (rather than on the existing charge) at that point. This potential arises not only from charges at that site, but also from those on all the other atoms in the molecule. The CF_3 group presents the positive end of a strong dipole to the molecule; it is the direct Coulomb interaction of this dipole with the proton rather than net electron withdrawal that gives rise to the high acidities of compounds conaining CF_3 groups. The inductive effect of CF_3 is "through space" rather than "through the bonds".

Martin and Shirley[17] have pointed out that it is often the core-electron binding energy itself rather than the atomic charge that should correlate with chemical properties. This is presumably the case for CF_3-substituted compounds. The charge on the atom adjacent to the CF_3 group is negative; because of the nearby strong positive charge, however, the overall potential is somewhat positive, with the result that core-electron binding energies are increased (as is observed) and the compound becomes more acidic (as is observed).

It may also appear contradictory to chemical evidence to propose that CF_3 donates negative charge to the benzene ring. In general, increased negative charge in the ring is associated with increased reactivity toward substitution at the ortho and para position. The CF_3 group, however, has the effect of deactivating the ring and is meta directing. The charges we have assigned are, however, consistent with these observations: the increased negative charge is localized at the 1 position, which is not susceptible to attack; the ortho position is found to be more positive than the meta and is hence deactivated.

Comparison of Trifluoromethylbenzene with Fluorobenzene. As noted above, the photoelectron spectra for fluorobenzene and trifluorobenzene are strikingly different from one another. In the former case the carbon to which the fluorine is attached is clearly resolved from the other ring carbons; in the latter, all the ring carbons are unresolved. The average shift (and, hence, average potential) over all of the ring carbons is, however, about the same for the two molecules.

From the point of view of chemical reactivity we are interested not in the shift averaged over all the carbons, but the shift averaged over those available for further reaction. For fluorobenzene this shift is +0.39 eV (relative to benzene). Because these carbons are not resolved in trifluoromethylbenzene from the carbon to which the substituent is attached, we cannot give an accurate number for this average shift in this compound. Unless, however, the number 1 carbon is shifted by more than 1.5 eV from the other carbons in the ring, this average is greater for trifluoromethylbenzene than for fluorobenzene, in keeping with the relative reactivities of these substances. A separation this large would have been apparent in our spectra as a shoulder on the high-binding-energy side of the main peak of the monosubstituted compound and would have been quite clear in the disubstituted compound. No such features were seen in the spectra. We conclude therefore that the binding energy of the ring carbons in these compounds correlates well with the reactivity of the ring, becoming more positive as the ring becomes less reactive.

The mechanism by which the positive potential is developed in the ring is quite different in the two cases. In fluorobenzene, the fluorine withdraws electrons from the adjacent carbon through the σ bond and redonates a small amount of charge to the ortho (and, presumably, para) position. The ring as a whole has a positive charge and the net potential at any point in the ring is positive. There is a slight negative charge at the ortho position, helping to make this site slightly more susceptible to electrophilic attack. In trifluoromethylbenzene, on the other hand, there is apparently electron donation to, rather than electron withdrawal from, the ring. The lowering of reactivity due to the CF_3 arises because of the large positive dipole of the CF_3 group in the neighborhood of the ring. There is some evidence for resonance leading to positive charge at the ortho position.

An unusual feature is apparent in both the fluorobenzene data and the trifluoromethylbenzene data. In spite of the presence of strongly polarizing groups attached to the rings at specific locations, the actual binding energies of the carbons to which only hydrogens are attached are largely independent of their position in the ring. It is as if charge flows in the ring so as to create a nearly uniform potential at every point in the ring, just as charge will flow in a conductor to maintain a uniform potential throughout. Presumably it is the π electrons that are sufficiently mobile to provide this equalization.

Alternating Charges. It has been suggested by Pople and Gordon[15] that charges alternate along a carbon chain that has a fluorine at one end. Evidence for this effect has been seen in the work of Davis, Banna, and Shirley,[13] who have reported data on fluorinated ethanes. The point-charge analysis on the fluorobenzene and the trifluoromethylbenzene gives further support to this idea. In each case, the derived charges alternate through chains of about 4 atoms, with the magnitude of the oscillation becoming less with distance from the fluorines. Thus in fluorobenzene the derived charges (starting from the fluorine) are −0.19, +0.23, −0.04, +0.01, and 0. For trifluoromethylbenzene the series is −0.22, +0.73, −0.13, +0.03, +0.02, and +0.02.

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(18) NOTE ADDED IN PROOF. From a point-charge analysis of the core ionization potentials of the chlorofluoromethanes, we have found that it may be necessary to allow the quantity k_C in the above equation to vary linearly with charge. Including this effect in the analysis of the trifluoromethyl compounds does not, however, change the essential conclusions. Assuming k_C to be equal to $19 + 6.94q_C$ gives a ring charge of -0.038 and a charge on the 1 carbon of -0.171.

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.

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

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

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

followed by

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

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., $\mathrm{Li^+,A\cdot^-}$, $\mathrm{Na^+,A\cdot^-}$, $\mathrm{K^+,A\cdot^-}$, and $\mathrm{Cs^+,A\cdot^-}$, 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 $\mathrm{C\cdot^-,Cat^+}$ pairs present in THF are too stable to contribute significantly to the isomerization and the reaction proceeds through step 3, because the

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

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 $\mathrm{C\cdot^-,Cat^+}$,$\mathrm{C^{2-},2Cat^+}$, 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 ($\mathrm{Na^+,B\cdot^-}$). 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 $\mathrm{CaH_2}$ 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 ($\mathrm{Na^+,B\cdot^-}$) was prepared in the conventional way in THF, the solvent distilled off in vacuum, and the residue redissolved in HMPA. The concentration of $\mathrm{Na^+,B\cdot^-}$ was determined spectrophotometrically.

Two ampoules, one containing *cis*-stilbene solution and the other the solution of $\mathrm{Na^+,B\cdot^-}$, 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.