

we note the rather remarkable linear dependence of  $k_{et}$  and  $k_{ips}$  upon the concentration of salt ranging from 0 to 0.5 M for  $\text{LiClO}_4$ .

### Conclusions

The ground-state charge-transfer complex of *trans*-stilbene with electron-poor olefins is a chemical system that has yielded new information regarding the decay dynamics of the contact ion pair. For the decay via back-electron transfer there is a linear dependence of  $\ln k_{et}$  upon the solvent polarity parameter  $E_T$ . The rate of ion-pair separation is highly solvent dependent but could not be related to any particular solvent parameter. Finally both the rate of electron transfer and ion-pair separation are linear functions of ionic strength for the salts  $\text{LiClO}_4$  and  $(n\text{-Bu})_4\text{NClO}_4$  over the concentration range of 0–0.3 M salt.

Further studies will entail an examination of these processes as a function of temperature in order to obtain the thermodynamic activation parameters for ion-pair separation, quantities heretofore unknown.

**Acknowledgment.** This work was supported by a grant from the National Science Foundation (CHE 8418611). K.S.P. acknowledges support from the Alfred P. Sloan Foundation and Henry Camille Dreyfus Foundation for a teacher-scholar grant. J.L.G. acknowledges generous support from a NIH postdoctoral fellowship.

**Registry No.** *trans*-Stilbene–fumarionitrile, 70152-65-7; *trans*-stilbene–dimethyl fumarate, 98481-62-0; *trans*-stilbene–maleic anhydride, 63255-27-6.

## Electron-Donating Ability of Aliphatic and Aromatic Rings

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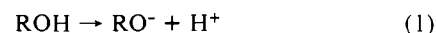
**Abstract:** Core-ionization energies and Auger kinetic energies of the halogens in halobenzenes and cyclohexyl halides and sulfur in thiophene, thiophenol, tetrahydrothiophene, and thiocyclohexanol have been used to determine the factors that affect the ability of the ring to accommodate a change in charge at the heteroatom in the ring or at a substituent position. This ability depends on the initial charge distribution in the molecule and on the rearrangement of this distribution when charge is added near the substituent. The results show that the aromatic ring is more electron withdrawing than the aliphatic ring. The effect of charge rearrangement is, however, nearly the same for both systems. Semiempirical calculations provide understanding of these results. The difference in initial-state charge distribution arises from the delocalization of  $\pi$ -electrons from the substituent to the ring. The lack of difference in charge rearrangement results from a cancellation of the effect of polarizability of the  $\pi$ -system in the aromatic ring by the effect of the greater number of electrons in the aliphatic system.

The ability of a molecule to accept charge at a particular site is a fundamental chemical property to which many other properties are closely related. Among these are acidity, basicity, ionization energy, rate of acid- and base-catalyzed reactions, and hydrogen bonding. This ability is closely related to the familiar concepts of electronegativity.

Organic chemists have devoted considerable effort to understanding this property in terms of field and resonance effects through the use of various  $\sigma$  parameters.<sup>2</sup> A somewhat different approach has been taken by physical and theoretical chemists, who have considered hydrogen-bond energies,<sup>3</sup> proton affinities,<sup>4–6</sup> gas-phase acidities,<sup>5,7,8</sup> and core-ionization energies<sup>9,10</sup> in terms of the effects of the charge distribution of the molecule before

reaction and the rearrangement of molecular charge as the reaction goes to completion.

We take acidity as an example to illustrate these ideas. We define  $A$  (for acidity) to be  $\Delta E$  for the reaction



and  $\Delta A$  to be the difference between the value of  $A$  for the compound of interest and that for some reference compound. We can divide  $\Delta A$  into two components, one  $\Delta V_A$ , an initial-state potential at the site of the acidic hydrogen due to the charge distribution in the unionized acids, and the other  $\Delta R_A$ , a final-state relaxation energy due to the rearrangement of charge on ionization. It can be seen that

$$\Delta A = -\Delta V_A - \Delta R_A \quad (2)$$

(The signs in eq 2 are easily understood. The more negative  $\Delta A$ , the stronger is the acid relative to the reference compound. A relatively positive potential at the hydrogen tends to force the hydrogen off; the negative of the potential is, therefore, a measure of acidity. The relaxation, or polarization effect, always favors the charge change, regardless of direction, and is, therefore, negative.) Similar expressions have been developed<sup>8,9,11,12</sup> for basicities,  $B$  (equal to the proton affinity), core-ionization energies,  $I$ , and Auger kinetic energies,  $K$

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(12) Expressions equivalent to eq 2, 3, and 4 have been presented in ref 8 and 9 and used in ref 5. The sign convention used here is different from that of the earlier references but is in keeping with the conventions now in use and is, in our opinion, easier to understand than the earlier convention.

$$\Delta B = -\Delta V_B + \Delta R_B \quad (3)$$

$$\Delta I = \Delta V_I - \Delta R_I \quad (4)$$

$$\Delta K = -\Delta V_K + 3\Delta R_K \quad (5)$$

(the factor of 3 appears in eq 5 for consistency with other treatments of this problem<sup>10,11</sup> and so that the various  $\Delta R$ 's are all of about the same magnitude). If the relationships between the various  $\Delta V$ 's and between the  $\Delta R$ 's are known, then measurement of appropriate pairs of experimental quantities, on the left, would suffice to give the derived quantities on the right. Theoretical analysis<sup>11</sup> shows that  $\Delta V_I \approx \Delta V_K$  and  $\Delta R_I \approx \Delta R_K$ . Linear correlations between core-ionization energies and proton affinities establish relationships between  $\Delta V_B$  and  $\Delta V_I$  and between  $\Delta R_B$  and  $\Delta R_I$ .<sup>4,5,13,16</sup> Linear correlation between gas-phase acidities and core-ionization energies for selected molecules indicates that  $\Delta V_I \approx \Delta V_A$ .<sup>5</sup>

Ab initio theoretical calculations support the view that  $\Delta V_I \approx \Delta V_A$  and that  $\Delta R_I \approx \Delta R_A$ .<sup>14</sup> There, therefore, seems to be a reasonable basis for using these equations to determine values of  $\Delta V$  and  $\Delta R$ .

Smith and Thomas<sup>5</sup> have used combined gas-phase acidities and core-ionization energies to determine the values of  $\Delta V$  and  $\Delta R$  for a number of aliphatic carboxylic acids. Their results are chemically reasonable and agree well with theoretical calculations of the same quantities. With the use of chlorine core-ionization and Auger kinetic energies, Aitken et al.<sup>10</sup> have determined  $\Delta V$  and  $\Delta R$  in a number of simple organic molecules. Their results are also in agreement with theoretical calculations. More recently, Saethre et al.<sup>15</sup> have used the same technique in a study of charge distribution in diatomic halides. Their derived values for  $\Delta V$  and  $\Delta R$  agree well with those obtained from ab initio theory.<sup>15</sup> With the use of gas-phase acidities and core-ionization energies, Siggel and Thomas<sup>14</sup> have determined  $\Delta V$  and  $\Delta R$  for phenol and cyclohexanol. Their results are in agreement with those from ab initio theory.

Most of the applications described above have focused on molecules without double bonds. It is of interest to extend these investigations to molecules containing  $\pi$ -electrons to see what effect the  $\pi$ -system has on  $\Delta V$  and  $\Delta R$ . We present here the results of such a study.

The specific experiments were measurements of core-ionization and Auger kinetic energies in  $C_6H_5X$  and  $C_6H_{11}X$  ( $X = F, Cl, Br, \text{ and } I$ ) and in the sulfur-containing species  $C_4H_4S, C_4H_8S, C_6H_5SH, \text{ and } C_6H_{11}SH$ . The aliphatic compounds were chosen for reference in order to provide a molecule of about the same size as the corresponding aromatic compound. The differences in polarizability should then be due principally to resonance in the  $\pi$ -system. The initial-state potentials at the halogen site were also obtained relative to the elemental halogens in order to give a more direct estimate of charge density at the halogen atom.

For this analysis we have assumed that  $\Delta V_I = \Delta V_K$  and that  $\Delta R_I = \Delta R_K$ , in keeping with the theoretical derivation of eq 4 and 5<sup>11</sup>. As noted above, there is good agreement between experimental values of  $\Delta V$  and  $\Delta R$  derived by using these assumptions and those calculated theoretically.<sup>10,15</sup> In the following discussion, we will, therefore, drop the subscripts I and K.

## Experimental Section

X-ray photoelectron and Auger electron spectra were measured with the Oregon State University cylindrical mirror analyzer.<sup>17</sup> All samples

**Table I.** Core-ionization Energies ( $I$ ), Auger-Kinetic Energies ( $K$ ), Relative Initial-State Potentials ( $\Delta V$ ), and Relative Final-State Relaxation Energies ( $\Delta R$ ) [Energies are in eV]

compound	$I^a$	$K^b$	$\Delta I^c$	$\Delta K^c$	$\Delta V^c$	$\Delta R^c$
fluorobenzene	692.88	600.4 (2)	1.10	-1.20	1.05	-0.05
fluorocyclohexane	691.78	601.6 (2)				
chlorobenzene	206.14	2375.95	0.65	-0.91	0.52	-0.13
chlorocyclohexane	205.49	2376.86				
bromobenzene	189.67 <sup>d</sup>	1378.82	0.67	-0.75	0.63	-0.04
bromocyclohexane	189.00 <sup>d</sup>	1379.57				
iodobenzene	626.52	507.22	0.52	-0.64	0.46	-0.06
iodocyclohexane	626.00	507.86				
thiophenol	169.48	2101.73	0.48	-0.55	0.44	-0.04
thiocyclohexanol	169.00	2102.28				
thiophene	169.95	2101.44	1.23	-1.32	1.18	-0.05
tetrahydrothiophene	168.72	2102.76				

<sup>a</sup> Fluorine 1s, chlorine 2p<sub>3/2</sub>, bromine 3p<sub>3/2</sub>, iodine 3d<sub>5/2</sub>, sulfur 2p<sub>3/2</sub>.  
<sup>b</sup> Fluorine KL<sub>1</sub>L<sub>1</sub>, chlorine KL<sub>2,3</sub>L<sub>2,3</sub><sup>1</sup>D, bromine L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub><sup>1</sup>G, iodine M<sub>4</sub>N<sub>4,5</sub>N<sub>4,5</sub><sup>1</sup>G, sulfur KL<sub>2,3</sub>L<sub>2,3</sub><sup>1</sup>D. <sup>c</sup> Relative to corresponding aliphatic molecule. <sup>d</sup> The corresponding 3d<sub>5/2</sub> energies are 76.15 and 75.47, respectively.

were obtained from commercial sources and used without further purification. The samples were mixed with approximately equal amounts of neon gas at pressures of about 20 mtorr in the gas cell. The spectra were calibrated by recording simultaneously the sample and the neon calibration lines. Samples excited with aluminum and magnesium K $\alpha$  X-rays were calibrated by using the Ne 1s and 2s lines. For samples excited with silver L $\alpha_1$  radiation, calibration was based on the Ne KLL(<sup>1</sup>D) and 1s lines. The Ne 1s and Ne KLL energies have recently been re-examined,<sup>18</sup> and all energies are based on these new calibration standards.

The peak positions of the recorded spectra were determined from least-squares fits of Gaussian or Voigt functions to the data. Deconvolution of spin-orbit components was accomplished assuming identical width parameters for the two components. Small corrections were made for the recoil energy of the residual ion and for relativistic effects in the analyzer. The final core-ionization and Auger kinetic energies are the average of at least two measurements. On the basis of estimated standard deviations and reproducibility of consecutive runs, we estimate an overall uncertainty of about 0.05 eV. However, the fluorine KL<sub>1</sub>L<sub>1</sub> line is exceptionally weak and broad, and we estimate an uncertainty of 0.2 eV for this line.

## Results and Discussion

Table I shows the experimental core-ionization and Auger kinetic energies for the aromatic and aliphatic ring compounds as well as the shifts in these energies,  $\Delta I$  and  $\Delta K$ , for the aromatic compounds relative to the aliphatic compounds. We see that for all cases the values of  $\Delta I$  are positive; those of  $\Delta K$  are negative and of approximately the same magnitude as the  $\Delta I$ 's. It follows from eq 4 and 5 that the relative relaxation energy,  $\Delta R = (\Delta I + \Delta K)/2$ , is close to zero, as can be seen from the last column of Table I. Since  $\Delta R$  is approximately zero,  $\Delta V$  is very nearly equal to  $\Delta I$  (eq 4), and is, therefore, positive for all unsaturated compounds.<sup>19</sup>

That  $\Delta R$  is approximately zero is unexpected. We had anticipated that the  $\pi$ -electrons of the aromatic rings would lead to more polarizable molecules and higher relaxation energies for these compounds compared to the aliphatic compounds. This is not the case.

The positive values of  $\Delta V$  indicate that the aromatic ring is more electron withdrawing (or less electron donating) than the corresponding aliphatic ring. Delocalization of  $\pi$ -electrons from the substituent to the  $\pi$ -system of the ring compensates for part of

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(19) Because  $\Delta R$  is nearly zero,  $\Delta V$  equals  $\Delta I$  and the charge distribution could be estimated on the basis of  $\Delta I$  values alone, as is often done. However, the assumption of constant relaxation energy may lead to erroneous results, as has been demonstrated in ref 15.

**Table II.** Comparison of Calculated and Experimental Ground-State Properties for  $i = \text{F, Cl, Br, and S}$  (Shifts Are Relative to Those in the Corresponding Aliphatic Compounds, Values of  $\Delta V$  in eV)

compound	$\Delta q_i^a$	$q_\pi^b$	$\Delta V^c$ (atom)	$\Delta V^d$ (mol)	$\Delta V^e$ (tot)	$\Delta V^f$ (exptl)
fluorobenzene	0.03	0.04	0.94	0.02	0.96	1.05
chlorobenzene	0.03	0.03	0.71	-0.32	0.39	0.52
bromobenzene	0.04	0.03	0.68	-0.19	0.49	0.63
thiophenol	0.03	0.03	0.61	-0.16	0.45	0.44
thiophene	0.08	0.18	1.49	-0.66	0.83	1.18

<sup>a</sup>Relative atomic charge on  $i$ . <sup>b</sup> $\pi$ -charge on atom  $i$ . <sup>c</sup>Shift due to the difference in atomic charge  $\Delta V(\text{atom}) = k_i \Delta q_i$ . <sup>d</sup>Shift due to difference in molecular charge distribution  $\Delta V(\text{mol}) = \Delta \sum_{j \neq i} q_j e^2 / r_{ij}$ . <sup>e</sup>Total shift  $\Delta V(\text{tot}) = \Delta V(\text{atom}) + \Delta V(\text{mol})$ .

the charge withdrawn from the ring through the  $\sigma$ -bond to the electronegative substituent. This delocalization is not possible in the aliphatic rings. The effect is particularly pronounced in thiophene, where the sulfur is actually part of the aromatic system. For thiophene  $\Delta V$  is twice as great as for thiophenol, where the sulfur is merely attached to the ring.

Semiempirical calculations support these conclusions and help us to understand them. In addition, a simplified point-charge model can be used to analyze the charge distributions in these molecules. These are discussed in the following section.

**Ground-State Properties.** The initial-state potentials  $V$  and other ground-state properties for these molecules have been calculated with use of the CNDO/2 semiempirical method.<sup>20</sup> The calculations were performed without d-orbitals on the heavy atoms. Values of  $\Delta V$ , relative charge, and  $\pi$ -charges based on these calculations are summarized in Table II.

In Table II, the column headed  $\Delta q$  gives the calculated charge on the halogen or sulfur atom in the aromatic compound relative to that in the aliphatic compound. In every case these are positive, supporting the qualitative conclusion drawn from the  $\Delta V$  values, that the aromatic rings are poorer electron donors than are the aliphatic rings. The next column, which gives the  $\pi$ -charge on these atoms, shows that this difference arises largely because of delocalization of charge from the substituent  $\pi$ -orbitals into the  $\pi$ -orbitals of the aromatic ring. The effect is particularly pronounced for thiophene, in keeping with the experimental result mentioned above.

The ground-state potential shifts may be related to the molecular charge distribution by the familiar point-charge model<sup>21</sup> (or ground-state potential model<sup>9</sup>):

$$\Delta V = k_i \Delta q_i + \Delta \sum_{j \neq i} q_j e^2 / r_{ij} \quad (6)$$

Here  $\Delta q_i$  is the difference in atomic charge for the  $i$ 'th atom,  $k_i$  is a constant often equated to the expectation value,  $\langle 1/r_i \rangle$ , for the reciprocal valence radius, and  $r_{ij}$  is the distance between atom  $i$  and atom  $j$ . The shift thus consists of a local atomic term, which depends on the difference in atomic charge, and a nonlocal molecular (Madelung) term, which depends on the difference in charge distribution for the rest of the molecule. Equation 6 may then be written as

$$\Delta V(\text{tot}) = \Delta V(\text{atom}) + \Delta V(\text{mol}) \quad (7)$$

The calculated shifts for the two terms on the right, as well as their sum, are given in Table II. The shifts have been calculated with use of the CNDO/2 charge distributions and  $k_i$  values from Carlson's compilation of  $\langle 1/r \rangle$  values.<sup>22</sup> Table II shows that in

**Table III.** Experimental Ground-State Potential,  $\Delta V$  (eV), for Halogen Relative to the Corresponding Homonuclear Dihalide, Halogen Charge,  $q_i$ , and Relative Amount of Charge,  $\Delta q_i$ , Withdrawn from the Halogen

compound	$\Delta V^a$	$q_i^b$	$\Delta q_i^b$	$q_i^c$	$\Delta q_i^c$
fluorobenzene	-4.98	-0.20	0.03	-0.16	0.03
fluorocyclohexane	-6.03	-0.23		-0.19	
chlorobenzene	-1.42	-0.11	0.04	-0.09	0.03
chlorocyclohexane	-1.93	-0.15		-0.12	
bromobenzene	-0.73 <sup>d</sup>	-0.07	0.06	-0.05	0.05
bromocyclohexane	-1.37 <sup>d</sup>	-0.13		-0.10	
iodobenzene	-0.97	-0.12	0.05	-0.09	0.04
iodocyclohexane	-1.43	-0.17		-0.13	

<sup>a</sup>Shift relative to the homonuclear dihalide, see ref 15. <sup>b</sup>Countercharge located at closest carbon. <sup>c</sup>Countercharge located in the middle of carbon ring. <sup>d</sup>Br 3d<sub>5/2</sub> energy shift, since Br 3p<sub>3/2</sub> energies are not available for Br<sub>2</sub>.

each case the atomic term dominates the total sum, with the result that the relative charge on atom  $i$  determines the sign of  $\Delta V$ . This observation justifies our inference on the basis of the experimental  $\Delta V$  values that the aromatic rings are more electron withdrawing than the aliphatic rings. It is seen from the table that the calculated total shift always is less than the experimental. However, the trend is well reproduced, including the nonmonotonic variation from fluorine to bromine.

#### Halogen Charge Density in Aromatic and Aliphatic Compounds.

If the ground-state potential shifts for the halogen compounds are taken relative to the elemental (uncharged) halogens,  $\Delta q_i$  in eq 6 simply represents the halogen atomic charge,  $q_i$ . However, for a polyatomic molecule the countercharge  $q_j$  is distributed over the remaining atoms, and in order to apply eq 6 some simplification has to be introduced. If one assumes that the countercharge,  $q_j = -q_i$ , is located at some average position in the molecule, eq 6 gives

$$q_i = \Delta V / (k_i - e^2 / r_{ij}) \quad (8)$$

where  $r_{ij}$  is the distance to that position. Equation 8 shows that  $q_i$  is directly proportional to  $\Delta V$ . We have calculated  $q_i$  for two different locations of the countercharge. In the first model the charge is located at the closest carbon, and in the second model the charge is located in the middle of the carbon ring. In either case the halogen is in equatorial position for the aliphatic compounds. These models probably represent two extreme possibilities. As above, the  $k_i$  values are taken from the compilation by Carlson.<sup>22</sup>

Table III shows the experimental ground-state potentials,  $\Delta V$ , relative to the elemental halogens and the charges derived with use of these experimental values in conjunction with eq 8. The absolute value of the charge increases with decreasing  $r_{ij}$ , and for halogens in axial positions the charges are about 0.01e more negative than for halogens in equatorial positions. Table III shows that all halogens are negatively charged as expected from their electronegativities but that the substituent connected to the benzene ring has a smaller negative charge than the corresponding cyclohexyl halogen. The relative amount of charge,  $\Delta q_i$ , withdrawn from the halogen by the aromatic ring is fairly constant with a slight maximum for Br and remains about the same for both models. The atomic charges for the Br compounds are also slightly lower than expected from electronegativities alone and may indicate a particularly strong interaction between Br and the ring systems. Presumably the charges observed are determined by several factors, such as electronegativity, matching of orbital energy and spatial overlap between the carbon ring and the halogen, and the halogen-carbon bond distance. The last two factors probably work in opposite directions going down the periodic table.

In order to verify the validity of our models for locating the countercharge, we used the halogen charge from the CNDO/2 calculation to calculate the molecular potential if the charge was located as in our models. Table IV compares the results with the

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**Table IV.** Halogen Charge,  $q_i$ , Relative Amount of Charge Transferred to the Aromatic Ring,  $\Delta q_i$ , and the Molecular Potential Calculated in Different Approximations. The Values Are Based on CNDO/2 Calculations (The Potentials Are in Volts)

molecule	$q_i$	$\Delta q_i$	molecular potential		
			a	b	c
fluorobenzene	-0.20	0.03	2.3	2.3	1.1
fluorocyclohexane	-0.23		2.2	2.4	1.2
chlorobenzene	-0.16	0.03	1.2	1.4	0.7
chlorocyclohexane	-0.19		1.5	1.6	0.9
bromobenzene	-0.11	0.04	0.8	0.8	0.6
bromocyclohexane	-0.15		1.0	1.1	0.8

<sup>a</sup> Molecular potential calculated from the CNDO/2 charge distribution. <sup>b</sup> Molecular potential assuming countercharge on nearest bonded carbon. <sup>c</sup> Molecular potential assuming countercharge in the middle of the carbon ring.

molecular potential as calculated from the CNDO/2 charge distribution. In all cases the agreement with exact calculation (column a) is good if we assume that the countercharge is on the closest bonded atom. Inspection of the calculated CNDO/2 charge distribution shows that the charge on that atom has a larger positive value than the negative halogen charge. A charge of the same size as that on the halogen placed at the carbon position therefore represents an average value for the molecular potential. We may therefore conclude that the experimental charges derived in Table III using the countercharge on the closest atom give the best estimate of the correct charges. Table IV also shows the charges as obtained from the CNDO/2 calculations. The absolute values as well as the relative amount of charge transferred to the aromatic system are in agreement with the charges based on the experimental data and given in Table III.

**Relaxation Energies and Charge Rearrangement.** The most striking feature of the experimental results in Table I is that the relaxation energy is nearly the same in aromatic and aliphatic compounds. The factors that determine the relaxation energy are the atomic relaxation, which arises from shrinkage of the atomic orbitals on the ionized atom toward the core hole, transfer of electrons from the surroundings to the core-ionized atom, and polarization of the surroundings. The chemically interesting information is contained in the second and third since these same factors influence the energies for proton addition, proton removal, and valence ionization.

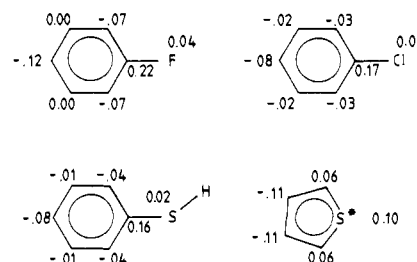
Following a procedure outlined in the appendix we estimate that the atomic contributions to  $\Delta R$  range from -0.07 eV to about -0.02 eV. Subtracting these numbers from the values for  $\Delta R$  given in Table I (-0.04 to -0.13 eV) gives extra-atomic relaxation even closer to zero than those values shown in Table I.

Relative extra-atomic relaxation energies of zero for these pairs of compounds are surprising, since one would intuitively assume that the more mobile  $\pi$ -electrons of the aromatic compounds would have a higher relaxation energy due to higher polarizability and ability to transfer electrons to the ionized atom. We see, however, that this is not the case.

In order to better understand these results we have performed CNDO/2 calculations both for the ground-state and for the core-ionized state by using the equivalent-cores approximation.<sup>23</sup> Table V shows the electron transfer and the difference in electron transfer for the aromatic and aliphatic molecules upon ionization of F, Cl, and S. It is seen that in each case more electrons are transferred away from the carbon atoms in aromatic compounds than in aliphatic. This we attribute to the higher polarizability of the aromatic compounds. However, Table V also shows that the electrons transferred from carbon in aromatic compounds are more than balanced by those transferred away from hydrogen in the aliphatic compounds. The result is a large transfer of electrons to the ionized site which is almost the same for the aromatic

**Table V.** Calculated Electron Transfer,  $\Delta p$ , and Relative Electron Transfer,  $\Delta(\Delta p)$ , from the Carbon and Hydrogen Atoms upon Core-Ionization of  $i = F, Cl, \text{ and } S$ 

molecule	carbon		hydrogen		ionized atom	
	$\Delta p_C$	$\Delta(\Delta p_C)$	$\Delta p_H$	$\Delta(\Delta p_H)$	$\Delta p_i$	$\Delta(\Delta p_i)$
fluorobenzene	-0.25	-0.27	-0.32	0.28	0.57	-0.01
fluorocyclohexane	0.02		-0.60		0.58	
chlorobenzene	-0.10	-0.18	-0.20	0.19	0.30	-0.01
chlorocyclohexane	0.08		-0.39		0.31	
thiophenol	-0.19	-0.14	-0.47	0.15	0.66	-0.01
thiocyclohexanol	-0.05		-0.62		0.67	
thiophene	-0.27	-0.16	-0.40	0.20	0.67	-0.04
tetrahydrothiophene	-0.11		-0.60		0.71	

**Figure 1.** Change in  $\pi$ -electron population upon core-ionization of F, Cl, and S.

and aliphatic molecule. It appears therefore that the effect of larger polarizability of the  $\pi$ -system is cancelled by the effect of the greater number of electrons (hydrogens) in the aliphatic system. In fact, inspection of the table shows that the number of transferred electrons per hydrogen atom is almost constant within each pair of molecules.

Although polarization of the  $\pi$ -system appears to be an important part of the relaxation in aromatic systems, the actual  $\pi$ -electron transfer to the ionized atom is very modest. Figure 1 shows the change in  $\pi$ -electron population upon core-ionization. There is a large redistribution of charge in the  $\pi$ -system, but very little is transferred out of the ring or to sulfur within the thiophene ring. As much as 90% of the electrons are transferred through the  $\sigma$ -system. It is, however, interesting to note that the polarization removes  $\pi$ -electrons most strongly from the ortho and para positions, in agreement with the resonance forms known from organic chemistry.

## Conclusions

Our investigations compare the electron withdrawing or donating power and polarizability of aromatic and aliphatic rings. For substituents attached to the rings, the aromatic rings are less electron donating than the corresponding aliphatic rings. This behavior results from the delocalization of  $\pi$ -electrons from the substituent to the  $\pi$ -orbitals of the aromatic ring. The polarizability of the two types of rings is approximately the same. There is a near cancellation of the higher polarizability of the  $\pi$ -electrons in the aromatic systems by the extra polarizability arising from the greater number of electrons in the aliphatic systems. Relaxation results from transfer of electrons to the ionized atom through the  $\sigma$ -bond and through rearrangement of the charge on the ring. There is little transfer of  $\pi$ -electrons from the ring to the core-ionized atom. Thiophene is similar to the substituted benzenes, even though the sulfur is part of the ring and the aromatic system.

Similar measurements comparing aliphatic saturated and unsaturated compounds show the same behavior.<sup>24</sup> The unsaturated compounds are less electron donating than the aliphatic ones; the relaxation energies for the two kinds of compounds are nearly the same. Comparison of core-ionization energies with gas-phase

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acidities, as well as ab initio calculations, for phenol and related aliphatic compounds lead to the same conclusion.<sup>14</sup>

**Acknowledgment.** This work was supported by the U.S. National Science Foundation and the Norwegian Council for Science and the Humanities. A NATO grant (RG 103/84) is gratefully acknowledged.

#### Appendix

**Estimation of Differential Atomic Relaxation.** The atomic portion of the relaxation energy arises because of the shrinkage of the atomic orbitals on the ionized atom toward the core hole. In comparisons of the same type of atom in different environments, contributions from identically occupied orbitals will cancel. We will be concerned only with the differentially occupied valence orbitals. For an atom with a valence occupancy of  $n$  electrons there will be a potential at the core equal to  $kn$ . After core ionization, this will change to  $k^F n$  and, according to the relaxation potential model,<sup>9</sup> the contribution to the relaxation energy from this source will be  $n(k^F - k)/2$ . The differential atomic relaxation in two different environments will be  $\Delta n(k^F - k)/2$ .

The value of  $k$  can be readily estimated by using  $\langle 1/r \rangle$  expectation values from Hartree-Fock calculations or from Slater

orbitals and Slater's screening rules.<sup>20</sup> For  $k^F$ , the same procedures can be used, but we must take into account that  $\langle 1/r \rangle$  is affected not only by the removal of the core electron but also by the additional valence electrons that are attracted to the atom in response to the newly created core-hole. Using Slater's rules we estimate  $(k^F - k)$  to be 5.8 eV for  $F(1s2s^22p^5)^+$  and 3.4 eV for  $F(1s2s^22p^6)$ . The average value of 4.6 eV agrees reasonably well with the equivalent-cores quantity  $k_{Ne} - k_F$  (4.4 eV from Slater's rules and Slater orbitals and 4.5 from Desclaux's values of  $\langle 1/r \rangle$ ).<sup>25</sup> Similarly we estimate 2 eV for sulfur and chlorine, 1.2 eV for bromine, and 0.9 eV for iodine.

Combining these values with either the theoretical or experimental values for  $\Delta q = -\Delta n$  (Tables II and III, respectively) gives differential atomic relaxation energies between -0.02 and -0.07 eV, as noted in the text.

**Registry No.** C<sub>6</sub>H<sub>5</sub>F, 462-06-6; C<sub>6</sub>H<sub>11</sub>F, 372-46-3; C<sub>6</sub>H<sub>5</sub>Cl, 108-90-7; C<sub>6</sub>H<sub>11</sub>Cl, 542-18-7; C<sub>6</sub>H<sub>5</sub>Br, 108-86-1; C<sub>6</sub>H<sub>11</sub>Br, 108-85-0; C<sub>6</sub>H<sub>5</sub>I, 591-50-4; C<sub>6</sub>H<sub>11</sub>I, 626-62-0; C<sub>6</sub>H<sub>5</sub>SH, 108-98-5; C<sub>6</sub>H<sub>11</sub>SH, 1569-69-3; C<sub>4</sub>H<sub>4</sub>S, 110-02-1; C<sub>4</sub>H<sub>8</sub>S, 110-01-0.

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## Electron Spin Resonance and Electron Spin Echo Modulation Studies of *N,N,N',N'*-Tetramethylbenzidine Photoionization in Frozen Micellar Solutions: Structural Effect of 1-Butanol Addition to Sodium and Tetramethylammonium Dodecylsulfate and Dodecyltrimethylammonium Chloride Micelles

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**Abstract:** The electron spin echo modulation (ESEM) and electron spin resonance (ESR) spectra of the photogenerated *N,N,N',N'*-tetramethylbenzidine cation radical (TMB<sup>+</sup>) in frozen micellar solutions of sodium and tetramethylammonium dodecylsulfate (SDS and TMADS, respectively) as well as dodecyltrimethylammonium chloride (DTAC) have been studied as a function of 1-butanol (1-BuOH) concentration from 0 to 200 mM. A 5-doxylstearic acid spin probe has also been used in the ESEM experiments. The efficiency of TMB photoionization has been determined from ESR data, while ESEM analysis has given information about micelle hydration and aqueous interactions of TMB<sup>+</sup>. The variations observed with 1-BuOH addition depend on the micellar charge and the nature of the counterion in dodecylsulfate micelles. The main findings are that (1) hydration of TMADS micelles decreases from 0 to 200 mM 1-BuOH, while hydration of SDS and DTAC micelles increases somewhat from 0 to 100 mM and remains constant from 100 to 200 mM 1-BuOH, and (2) the efficiency of charge separation upon photoionization of TMB can be increased by alcohol addition in SDS micelles but not in TMADS and DTAC micelles. The results are interpreted primarily in terms of the effect of added alcohol on the surfactant headgroup density.

Recent work from this laboratory<sup>1-5</sup> has been directed toward elucidation of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies such as micelles and vesicles. Electron spin resonance (ESR) studies of the photoproducted *N,N,N',N'*-tetramethylbenzidine cation radical (TMB<sup>+</sup>) in frozen micellar solutions have indicated that the photoionization efficiency depends on such factors as micelle size and charge, the nature of the counterion, and the ionic strength

of the solution. Electron spin echo modulation (ESEM) analysis has shown that the photoionization efficiency in anionic micelles is greater for stronger TMB<sup>+</sup> interactions with water nominally outside the micelle.<sup>3-5</sup>

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