with aqueous NaCl, dried ($MgSO_4$), and concentrated (rotary evaporator). The residue was recrystallized from ethanol to obtain 4-α,α'-d_2 (1.85 g, 0.0083 mol, 55%, 94% D), mp 53-54 °C. ^1H NMR ($CDCl_3$/TMS): δ 4.10 (t, 2 H, J_{HD} = 1.8 Hz), 4.11 (small s, for 6% unlabeled benzyl group of 4-α-d_1), 7.35 (m, 10 H). ^{13}C NMR ($CDCl_3$/TMS): δ 54.0 (t, CHD, J_{CD} = 20 Hz), 128.6 (C_3, C_5), 134.4 (C_1), 128.6 (C_4), 128.9 (C_2, C_6).

Dibenzylamine (5) Isotopomers. Hydrolysis[17] of isotopomers of 4 proceeded with no loss of label to give the corresponding isotopomers of 5 following the method given here for the preparation of the sample enriched in (*S*,*S*)-5-α,α'-d_2. A mixture of 2 g of sulfuric acid (96%) in 12 mL of water and (*S*,*S*)-4-α,α'-d_2 (1.12 g, 0.0050 mol) was refluxed for 22 h. After initial cooling, 50% NaOH was added while the mixture was cooled to bring the pH to 11-12. The solution was extracted with ether, and the combined extracts were washed with saturated NaCl solution, dried (Na_2SO_4), and concentrated (rotary evaporator) to give a colorless oil of 5-α,α'-d_2 (0.95 g, 0.004 75 mol, 95%, 94% D). ^1H NMR ($CDCl_3$/TMS): δ 3.79 (t, 2 H, J_{HD} = 1.8 Hz), 3.81 (small s, for 6% 5-α-d_1), 7.33 (m, 10 H). ^{13}C NMR ($CDCl_3$/TMS): δ 52.7 (t, CHD, J_{CD} = 20.4 Hz), 126.9, 128.1, 128.4 (C_{2-6}), 140.2 (C_1).

Tribenzylamine (TBA) Isotopomers. Five different isotopomeric mixtures of TBA, plus unlabeled TBA, were prepared by the procedure described below for the sample enriched in (*S*,*S*,*S*)-TBA-d_3. The variations were introduced by the following combinations: 5 with racemic benzyl-α-d_1 bromide; *S*,*S*-enriched 5-α,α'-d_2 with benzyl bromide; racemic 5-α,α'-d_2 with benzyl bromide; racemic 5-α,α'-d_2 with racemic benzyl-α-d_1 bromide; and *S*,*S*-enriched 5-α,α-d_2 with (*R*)-benzyl-α-d_1 bromide.

To a flame-dried 50-mL 3-neck flask equipped with a stopper, condenser, nitrogen inlet, and magnetic stir bar were added 27 mL of dry THF and 2.56 mL (0.0041 mol, 1.6 M in hexane) of *n*-butyllithium. Then, *S*,*S*-enriched 5-α,α'-d_2 (0.808 g, 0.0041 mol) was added to this stirred solution, which became red. After the solution was stirred for 3 h, (*R*)-benzyl-α-d_1 bromide was added, and the mixture was refluxed for 4 h. After being cooled, the mixture was concentrated (rotary evaporator) and the residue was extracted with ether. The ether extracts were washed twice with saturated NaCl solution, dried (Na_2SO_4), and concentrated. The residue was recrystallized from ethanol to give TBA-d_3 as a white solid (0.77 g, 0.0027 mol, 65%), mp 93-95 °C, $[\alpha]^{25}_D$ + 0.64° (*c* 0.0188, ethanol, *l* = 1). ^1H NMR ($CDCl_3$/TMS): δ 3.4-3.6 (CHD signals, see text for analysis; unlabeled TBA signal at 3.55), 7.25 (t, 3 H, H_p), 7.34 (t, 6 H, H_m), 7.44 (d, 6 H, H_o). ^{13}C NMR ($CDCl_3$/TMS): δ 57.5 (t, CHD, J_{CD} = 19 Hz), 126.8, 128.2, 128.7 (C_{2-6}), 139.8 (C_1).

NMR Spectroscopy. Routine ^1H and ^{13}C NMR spectra were obtained at 299.9 and 75.4 MHz, respectively, on a Varian Model XL-300 spectrometer with a broad-band tunable probe. Isotope shift measurements in ^1H spectra were obtained under temperature control, for $CDCl_3$ solutions, and from resolution-enhanced spectra, on the Varian XL-300 and also at 399.9 MHz on a Varian Model VXR-400 spectrometer. Temperatures were read directly from the calibrated (CH_3OH) thermocouple monitor and varied less than 0.5 °C during each acquisition. Some additional measurements were carried out in $CFCl_3$ solution, with no significant change in results.

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On the Origin of Substituent Effects in Electrophilic Addition: Evidence from Core-Electron Spectroscopy

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The rate-determining step for electrophilic reactions involves the formation of a charged intermediate by addition of a positively charged species at a site in the molecule. Since core ionization involves the addition of a positive charge by removal of an electron, both processes are governed by the same factors: the initial-state charge distribution and the final-state charge rearrangement. Combining core-ionization energies with Auger energies provides direct experimental information on the relative importance of these factors. Core-electron energies have been measured for sulfur in a series of 2-substituted thiophenes. The substituents comprise CH_3, OCH_3, I, Br, Cl, CHO, CN, and NO_2 and possess a wide range of electron-donating and electron-withdrawing properties. The results show that the variation in substituent effect is predominantly determined by the initial-state charge distribution and that the final-state charge rearrangement is very little influenced by the nature of the substituent. These conclusions are supported by correlations of the core-electron energies with electronic substituent parameters, which show that resonance delocalization contributes significantly to the initial state but has virtually no effect on the final state. This result challenges the traditional view since resonance stabilization of the transition state (the final state of the charge addition) for electrophilic addition reactions is considered to be crucial to the understanding of both reactivity and orientation effects in aromatic rings. Ab initio calculations have been performed for all thiophene derivatives and support the experimental results. In addition they show that the conclusions are not limited to the sulfur atom, but are equally applicable to the ring carbons. Thus, the sulfur atom is a suitable probe for substituent effects in the aromatic thiophene ring.

Introduction

The effects of substituents on chemical properties such as equilibria, reaction energies, and reaction rates are of continuing interest. The rate-determining step for electrophilic reactions involves the formation of a charged intermediate by addition of a positively charged species at a site in the molecule. The rates for such reactions and the competition between different paths depends on the energy of these transition states.[2] Varying the substituents

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on the molecule can affect the energy of the transition state and, hence, the reaction rates and pathways. An example is the ability of a substituent to direct additional substitution or other reaction on an aromatic ring to positions ortho/para or meta to itself.[2a]

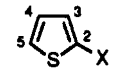
The standard view of these reaction mechanisms is that the energy of the intermediate is largely determined by its ability to delocalize the added charge—that is by final-state relaxation.[2] (Although the intermediate is not the final state of the overall chemical reaction, it is the final state of the charge addition in the rate-determining step of the reaction.) The role played by substituents is viewed as either increasing or decreasing the ability of the intermediate to delocalize charge, thus lowering or raising the activation energy for the reaction.

In this description, little attention is given to the charge distribution in the neutral molecule. This can, however, affect the potential at the site of electrophilic attack in such a way as to either favor or disfavor the formation of the carbocation. Our experience comparing single and double bonded systems shows that for these *structural* differences the initial-state charge distribution often plays a more important role than final-state relaxation in determining the ability of a molecule to accept charge.[3,4] It is therefore of interest to consider *substituent* effects from the same point of view, using core-electron spectroscopy.

Since core-ionization involves the addition of a positive charge by removal of an electron, there is close connection between core ionization and electrophilic addition, such as protonation. Indeed, it has been shown that for many systems there are linear correlations between core-ionization energies and proton affinities.[5] These correlations cover a wide variety of compounds including both aliphatic and cyclically conjugated compounds. Both protonation and core ionization are governed by the same factors: the initial-state charge distribution and the final-state relaxation. Combining core-ionization energies with either Auger energies or gas-phase acidities provides direct experimental information on the relative importance of these factors.[3,4,5g,6,7] Such information is not available through other experimental techniques. A comparison of core-ionization energies with gas-phase acidities has provided new understanding of the relative acidities of organic and inorganic molecules.[3]

Substituted thiophenes provide a unique opportunity to probe the effect of initial-state charge distribution versus final-state relaxation in an aromatic ring. From a chemical point of view, sulfur differs only slightly from carbon in its electronegativity and, therefore, replacing carbon with sulfur in the ring makes a minor perturbation. It has been found, for instance, that substituent effects are transmitted through a thiophene ring in the same way that they are transmitted through a benzene ring.[8] From the experimental point of view, however, sulfur is a heteroatom within the ring. As a result, it is straightforward to measure the effect of a substituent on the core-ionization and Auger energies at a site within the ring. Such measurements would not be possible if there were no heteroatom, since the core-ionization energies of carbon atoms within a ring are often indistinguishable. Heterocyclic systems containing first-row heteroatoms are not so useful as thiophene because there are no core-to-core Auger transitions in these compounds.

We report here on measurements of the effect that different substituents at the 2-position of thiophene have on the core-ionization energies and Auger kinetic energies of sulfur. The substituents explored (CH_3, OCH_3, I, Br, Cl, CHO, CN, and NO_2) span a wide range of character from strongly electron donating to strongly electron attracting. The experimental results show the effect of the substituent at the site of the sulfur atom. However, ab initio calculations indicate that the results are not restricted to the heteroatom, but are also valid for the carbon atoms of the thiophene ring.



The effects of substituents on chemical properties are frequently analyzed in terms of $\sigma\rho$ relationships of the Hammett type.[9] A major problem with this simple approach is that several different σ parameters are needed to describe the full range of substituent effects.[10-12] In this account, we have applied a triparametric relationship[11] to analyze initial- and final-state energies in terms of familiar substituent effects such as field, resonance, and polarizability. Core-ionization energies provide a unique opportunity to study these effects for a set of molecules since the final state is unaffected by additional effects such as dissociation or large geometrical rearrangement.

Experimental Section

Sulfur 2s and 2p core-ionization energies and KLL Auger kinetic energies were measured in the gas phase with the Oregon State University cylindrical mirror analyzer.[13] For the core-ionization energies, the excitation source was aluminum Kα X-rays (1483.553 eV[14]). Calibration was based on the positions of the 1s and 2s

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lines from neon that was mixed with the sample of interest.[15] All samples were obtained commercially and used without further purification. For the sulfur Auger energies, the excitation source was silver $L\alpha_1$ radiation (2984.34 eV[16]). In this case, calibration was based on the positions of the neon KLL(^{1}D) Auger line and the neon 1s line.[15] Appropriate relativistic corrections are included in the calibration scheme.[17]

Peak positions were determined from nonlinear least-squares fits of Voigt functions to the data. The spin–orbit components were deconvoluted assuming identical width parameters for the two components. 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 the results, we estimate the uncertainties in the reported numbers to be ~0.05 eV, except for the $2p_{1/2}$ ionization energies. For these, the uncertainties are larger because of the difficulties of resolving the $2p_{1/2}$ peak from the larger $2p_{3/2}$ peak.

Theoretical Calculations. Ab initio calculations were carried out for all molecules at the restricted Hartree-Fock level using the MOLECULE-ALCHEMY program package.[18] The atomic orbital basis sets for the non-hydrogen atoms were taken from a recent compilation by Huzinaga and co-workers.[19] These minimal basis sets were extended to split-valence quality. For C, O, and N the numbers of primitive functions in each contracted Gaussian-type orbital are (421/31), where the slash separates the s and p symmetries, respectively. These sets are identical with the MIDI-4 type of basis sets.[20] For S the expansion (4321/421) was used, and for Cl, Br, and I those recommended by Andzelm et al.[21] were used. For H the 4s basis given by Duijneveldt[22] was contracted to (31) and used without scaling.[23] For S, Cl, Br, and I the basis sets were augmented with a set of d functions for polarization.[19,21] The experimental geometry of the thiophene ring was used for all thiophene derivatives.[24] The geometries of the substituents were either taken from experimental values or adopted from corresponding benzene or ethene derivatives.[25]

Ab initio calculations at this level have been found to compare favorably with those using basis sets of the 44-31G[23] and 3-21G*[26] type and to give molecular results similar to those produced by extended SCF calculations.[20,21,23] Except for a recent study on 2-formylthiophene using 3-21G,[27] previous ab initio calculations on thiophene derivatives have been confined to minimal STO-3G basis.[28] The calculations presented here represent a compromise between quality and feasibility, especially for substituents like the heavy halogens.

Table I. Experimental Sulfur 2s and 2p Core-Ionization Energies and KLL Auger Kinetic Energies for Thiophene and 2-Substituted Thiophenes. Values for Substituted Thiophenes Are Given Relative to Thiophene[a]

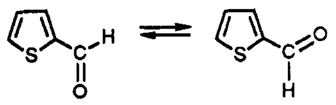
substituent	2s	$2p_{1/2}$	$2p_{3/2}$	$KL_{2,3}L_{2,3}(^1D)$
H	234.31	171.17	169.95	2101.42
CH_3	−0.22	−0.23	−0.23	0.50
OCH_3	−0.16	−0.15	−0.16	0.42
I	0.12	0.12	0.13	0.58
Br	0.20	0.18	0.20	0.30
Cl	0.29	0.27	0.28	0.01
CHO	0.28	0.23	0.27	0.00
CN	0.72	0.66	0.65	−0.37
NO_2	0.83	0.75	0.83	−0.53

[a] All values in eV.

The SCF hole-state calculations were performed within the restricted open-shell Hartree–Fock approximation using the maximum overlap criterion.[29] Calculated core-ionization energies were then obtained as the difference between the total energies of the final core-hole state and the initial closed-shell state. These so-called ΔSCF ionization energies take into account the redistribution of electrons after ionization. The potential at the nuclei in the initial state was taken as the negative of the orbital energy.[30,31] The relaxation energy was then obtained as the difference between the Koopmans' theorem energy and the calculated ionization energy.

The calculated S2p ionization energy for thiophene is 173.50 eV. This is more than 3 eV higher than the experimental value of 170.36 eV (weighted average of $2p_{1/2}$ and $2p_{3/2}$). The deviation is mainly due to the use of a relatively inflexible basis set, which describes the positive core-hole state less satisfactorily than the neutral ground state. A double-ζ basis set[4b,32] with polarization functions on all atoms gives a S2p ionization energy close to the experimental value.[33] This basis set, however, is too extensive for the substituted compounds considered here. Similar effects of the basis set on calculated ionization energies have been found earlier.[4b,34,35]

The 2-formyl compound can exist in two conformations with the oxygen atom either cis or trans to the sulfur atom. It has been found experimentally that the S,O-cis conformation dominates in the gas phase,[36] and the calculated values thus refer to this conformation. However, we have also calculated values of ΔI and ΔV for sulfur in the trans isomer, and found that both



S,O-*cis* S,O-*trans*

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Table II. Comparison of Shifts in Experimental and Calculated Core-Ionization Energies (ΔI), Initial-State Potential Energies (ΔV), and Relaxation Energies (ΔR) for 2-Substituted Thiophenes. Shifts Are Given Relative to the Parent Compound[a]

substituent	ΔI(exptl)[b]	ΔI(calcd)[c]	ΔV(exptl)	ΔV(calcd)[c]	ΔR(exptl)	ΔR(calcd)[c]
H	0.00	0.00	0.00	0.00	0.00	0.00
CH_3	−0.23	−0.37	−0.09	−0.19	0.14	0.18
OCH_3	−0.16	−0.19	−0.03	0.05	0.13	0.24
I	0.13	0.06	0.49	0.44	0.36	0.38
Br	0.20	0.21	0.45	0.47	0.25	0.25
Cl	0.28	0.35	0.43	0.47	0.14	0.22
CHO	0.27	0.32	0.41	0.54	0.15	0.12
CN	0.65	0.77	0.79	1.00	0.14	0.23
NO_2	0.83	1.12	0.98	1.33	0.15	0.21

[a] All values in eV. [b] $S2p_{3/2}$. [c] Average of $S2p_{x,y,z}$. The calculated values for thiophene are I = 173.50 eV, V = 181.78 eV, and R = 8.28 eV.

energies are 0.10 eV higher for the trans conformer than for cis.[37]

Experimental Results and Discussion

The experimental core-ionization and Auger kinetic energies for thiophene and 2-substituted thiophenes are listed in Table I. The $S2p_{3/2}$ value for thiophene agrees with earlier determinations.[38] The results for substituted compounds are given relative to thiophene in order to facilitate comparison. As expected, the shifts in core-ionization energy are very similar for S2s and S2p and increase with the electron-attracting ability of the substituents. An exception is 2-formylthiophene (thiophene-2-carbaldehyde), which shows a lower shift than is generally expected for this substituent. This is probably due to the close contact between sulfur and oxygen in the S,O-cis conformation, as mentioned previously.[37]

The relative importance of initial- and final-state effects can be obtained by comparison of core-ionization energies with the corresponding Auger kinetic energies.[39,40] The relationships are

$$\Delta I = \Delta V - \Delta R \tag{1}$$

for core-ionization energies, I, and

$$\Delta K = -\Delta V + 3\Delta R \tag{2}$$

for Auger kinetic energies, K. Here, Δ refers to the shift between two different compounds, V is the initial-state potential energy of a unit positive charge at the atom of interest, and R is the relaxation energy associated with the electron redistribution of the final state. These relationships have been used to investigate a variety of chemical systems and give results that are in agreement with theory[4,6] and other experimental methods of determining the same quantities.[41] Many of the results of these investigations are consistent with chemical expectations, but some have been unexpected and have led to new insights.[3,4]

Table II shows ΔI, ΔV, and ΔR for S2p. From our estimated uncertainties of 0.05 eV in the experimental quantities, we find an uncertainty of 0.05 eV in the value of ΔR for any compound relative to any other compound, and a corresponding uncertainty of 0.11 eV in the values of ΔV. These uncertainties come from eqs 1 and 2 and the usual rules for propagation of uncertainties. Since the shifts based on the 2s ionization energies are very close to those based on the 2p energies, the values of ΔV and ΔR would be essentially the same if we had used the 2s energies for the calculations.

The ΔR(exptl) column shows that substitution increases the relaxation energies for all molecules relative to the parent compound. We attribute this general increase to the higher polarizability of the substituents relative to H. However, except for the bromine and iodine substituents, this increase is relatively small (~0.14 eV) and remarkably constant for all molecules. The variation of experimental ΔI and ΔV values, on the other hand, is much larger, the range being 1.06 and 1.07 eV, respectively. The initial-state potential, in contrast to the final-state relaxation, is very much dependent on the nature of the substituent. Thus, the variation in ability of the thiophene ring to accept charge at the sulfur position is almost exclusively due to the charge distribution in the initial state. It is easily seen that electron-donating substituents like CH_3 and OCH_3 facilitate addition of a positive charge to the sulfur atom, whereas electron-attracting substituents such as CN and NO_2 largely oppose such addition. We believe that this result also applies to carbon atoms C(3) and C(5) of the thiophene ring. Evidence in support of this view comes from theoretical calculations, as will be shown in the following text.

The increase in relaxation energies as the halogen substituent is changed from Cl to I is to be expected from the relative polarizabilities of the halogen atoms. The ΔI and ΔV values for these substituents show that there is very little difference in their effects on the initial-state potentials. Thus, it is mainly the variation of relaxation energies that is responsible for the variation in ionization energies. A similar effect has been found both experimentally and theoretically for other halogenated compounds.[5g,6a,42]

Theoretical Results and Discussion

The foregoing discussion presents experimental evidence that substituent effects on sulfur in thiophene are governed primarily by initial-state charge distribution rather than by final-state charge rearrangement. Since addition reactions normally take place at a carbon atom, one may ask if the ring carbons and sulfur have similar behavior. To shed light on this question, we use theoretical calculations of the charge distribution and charge flow to show that the sulfur results are representative for the ring carbons.

We show first that the theoretical calculations accurately reproduce the experimental results. Experimental and theoretical core-electron energy shifts are compared in Table II and Figure 1. We note that despite the deviation

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(37) We expect ΔI and ΔV to be lower in the S,O-cis conformation because of the proximity of the negatively charged oxygen atom. The oxygen charge from the Mulliken population analysis is 0.41 e.

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Table III. Atomic Charge Distribution in 2-Substituted Thiophenes Relative to the Parent Molecule

substituent	S	C(2)	C(3)	C(4)	C(5)	H[a]	X[b]
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3	−0.01	−0.04	0.02	0.02	−0.01	−0.03	0.05
OCH_3	−0.05	0.48	0.00	0.02	−0.02	0.00	−0.43
I	0.03	0.02	0.05	0.01	0.01	0.03	−0.15
Br	0.02	0.15	0.04	0.01	0.01	0.03	−0.26
Cl	0.01	0.38	0.02	0.02	0.00	0.03	−0.45
CHO	0.04	−0.08	0.09	−0.01	0.04	0.02	−0.10
CN	0.05	0.06	0.12	−0.01	0.04	0.05	−0.30
NO_2	0.03	0.40	0.15	−0.01	0.05	0.08	−0.70
r[c]	1.00	−0.44	0.75	−0.73	0.86	0.65	−0.03

[a] Sum of H(3), H(4), and H(5). [b] Charge of substituent relative to H(2) in thiophene. [c] Correlation coefficient between the sulfur values and the other columns.

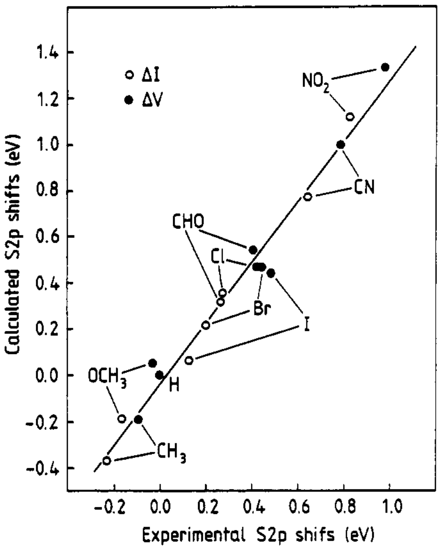

Figure 1. Shifts in calculated ionization energy (ΔI) and initial-state potential energy (ΔV) for 2-substituted thiophenes plotted against the corresponding experimental values. The shifts are given relative to the parent molecule. The line shows a linear least-squares fit to the data.

in absolute values, the calculated values of ΔI and ΔV reproduce the experimental trends quite well. Since the values of ΔR are small and relatively constant, it is less apparent that there is good agreement between experiment and theory for these. However, the calculations predict ΔR to be small and verify the higher relaxation energies for the Br and I substituents. Second, we see that the calculated shifts are systematically overestimated. The line in Figure 1 represents a linear least-squares fit to the data and has a slope of 1.30. Thus, the calculated shifts are overestimated by ~30%. The experimental and theoretical shifts are well correlated with a correlation coefficient $r = 0.990$. This good agreement gives confidence that predictions based on the theoretical calculations are reasonably accurate.

Initial-State Charge Distribution. Table III shows the atomic charges for the thiophene derivatives relative to those in the unsubstituted compound. The charges have been derived from the Mulliken populations. Whereas these probably do not accurately reflect atomic charges, they are useful in understanding the effects of the substituents on the atoms in the ring.[34,43] Except at C(2), where the substituent is attached, the charges deviate little from the charges in thiophene. Overall, however, the electron-attracting substituents make the charge on sulfur more positive, whereas electron-donating substituents make it more negative relative to its value in thiophene.

One of our interests is to determine the extent to which the substituent effects at S are the same as or different from those at the other positions in the ring. To a limited extent this can be seen from an item-by-item comparison of the entries in Table III with each other. For instance, it is apparent that there is a good correspondence between the entries for S and those for C(5). A more compact and efficient way to see these correlations is to consider the correlation coefficients between the values in the S column and the values in each of the other columns in Table III. These are given at the bottom of Table III. We see, as expected, that there is a positive correlation between the effects at sulfur and those for C(5). In addition, there is a positive correlation between sulfur and C(3) and a negative correlation between sulfur and C(4). Compared with monosubstituted benzenes, these are the expected results if S and C(3) behave as if ortho to the substituent, C(5) as if para, and C(4) as if meta.[44] There is little correlation between S and C(2), or between S and X, where the effects are dominated by direct electron withdrawal or donation by the substituent.

When the electron populations are analyzed in terms of atomic π-charge distribution, it is found that these follow the same trends as the net charges. The classical ortho/para-activating groups (CH_3 and OCH_3) are found to increase π-electron density on S, C(3), and C(5), whereas the meta-directing substituents (CN and NO_2) decrease the π-density at these positions and increase it at the C(4) position.

The initial-state atomic charge distribution in the thiophene ring is thus consistent with expected delocalization properties of the substituents.[45] In general, the results are in good agreement with the directing effects of substituents as observed experimentally.[2b,46] It is, however, more important to note that the effect of substituents on the sulfur atom generally is similar to that experienced by the C(3) and C(5) atom. This supports the idea that the sulfur atom can be used as a probe for events, such as electrophilic addition reactions, that usually take place at C(3) and C(5).

Correlation of S2p Shifts and C1s Shifts. In order to verify the use of sulfur as a probe for ring effects, we have calculated the initial-state potential energies for the ring carbons and correlated these with the corresponding

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Table IV. Change in Valence Electron Population following Sulfur Core-Ionization for 2-Substituted Thiophenes

substituent	S[a]	C(2)	C(3)	C(4)	C(5)	H[b]	X[c]
H	1.19	−0.31	−0.06	−0.06	−0.31	−0.33	−0.12
CH_3	1.21	−0.28	−0.07	−0.05	−0.30	−0.32	−0.19
OCH_3	1.20	−0.28	−0.09	−0.05	−0.30	−0.31	−0.16
I	1.22	−0.27	−0.04	−0.06	−0.30	−0.29	−0.26
Br	1.21	−0.27	−0.05	−0.06	−0.30	−0.30	−0.23
Cl	1.20	−0.31	−0.06	−0.06	−0.30	−0.31	−0.15
CHO	1.24	−0.30	−0.09	−0.04	−0.32	−0.31	−0.18
CN	1.23	−0.31	−0.09	−0.05	−0.32	−0.30	−0.17
NO_2	1.25	−0.35	−0.11	−0.05	−0.31	−0.30	−0.14

[a] Sulfur 2p core ionization. [b] Sum of H(3), H(4), and H(5). [c] Change in substituent population.

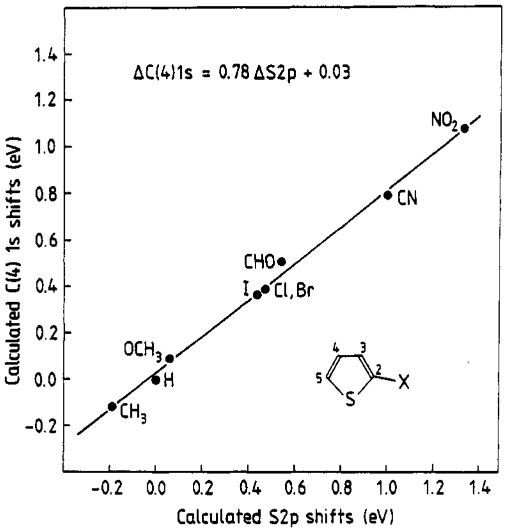

Figure 2. Calculated C(4)1s initial-state potential energy shifts in 2-substituted thiophenes plotted against the correpsonding S2p shifts. The values are given relative to the parent molecule. The linear least-squares correlation is shown.

energies for the sulfur atom. For shifts relative to the parent compound, we obtained the following results

$$\Delta C(3)1s = (1.28 \pm 0.12)\Delta S2p - 0.11 \qquad r = 0.97 \qquad s = 0.16$$

$$\Delta C(4)1s = (0.78 \pm 0.08)\Delta S2p + 0.03 \qquad r = 0.998 \qquad s = 0.03$$

$$\Delta C(5)1s = (1.08 \pm 0.09)\Delta S2p - 0.09 \qquad r = 0.98 \qquad s = 0.12$$

where r is the correlation coefficient and s the standard error of the regression.

The results show that there are indeed good correlations between the sulfur shifts and those for carbon. However, in view of the negative correlation of the charges on C(4) with those on S, we were surprised to find that not only is the correlation excellent between S and C(4), but also that the correlation is a positive one. Figure 2 shows the calculated initial-state C(4)1s shifts plotted against the corresponding S2p shifts. From the trends of atomic charge densities presented in Table III, one might expect a negative slope for the correlation. However, the potential is determined not only by the atomic charge but also by the charges on the surrounding atoms; evidently, the contribution from surrounding atoms dominates the initial-state shifts on C(4).

The slopes of these correlation lines are consistent with traditional views of substituent effects in aromatic systems. The greatest sensitivity to substituent effects is at the ortho and para positions and the greatest slope is for C(3) and C(5), which act as ortho and para carbons. At the meta position, the effect of substituents is in the same direction as the ortho and para position but lower in magnitude. This effect is reflected in the positive but smaller slope for C(4).

Charge Redistribution Due to Core Ionization. Table IV shows the change in gross electron population following core ionization at the sulfur atom. First, we note that about the same number of electrons are transferred to sulfur and that all the other atoms contribute to this flow of charge. The electrons are mainly taken from the nearest neighbors C(2) and C(5), but a substantial amount of charge is also supplied by the hydrogens and by the substituents. Second, compared to H(2) in thiophene there is a small increase of electrons taken from the substituents. This accounts for the small but relatively constant increase in relaxation energies relative to thiophene. The extra amount of electrons taken from Br and I is also consistent with the larger relaxation energy observed for these substituents.

Since it is generally assumed that the substituents primarily influence the π-system of aromatic rings, we have also calculated the change in valence π-electron population following sulfur core ionization. The results show that only about 0.3 π-electrons are transferred to sulfur and that these electrons are taken mainly from the ring carbons. The π-electron transfer from the substituents, however, is small and fairly constant for all substituents.

The conclusion from this analysis is that there is very little difference in the ability of the substituents to influence or modulate the transfer of electrons from the ring carbons to sulfur in response to an added positive charge. The loss of electrons from the substituents is essentially the same as for the parent compound. The results thus suggest that there is almost no difference between electron-donating and electron-attracting substituents in their ability to transfer electrons to the reaction site, in this case the sulfur atom. On the basis of the close relationship between calculated sulfur and carbon core-electron energies, we believe that the differential participation of the substituents in the final state is small also for reactions taking place at the carbon atoms.

Correlations of Core-Electron Energies with Electronic Substituent Parameters. The effects of substituents on chemical properties such as equilibria, reaction energies, and reaction rates are frequently analyzed in terms of a $\sigma\rho$ relationship of the Hammett type.[9,11] Since core-ionization energies are influenced by the same variables that affect reaction rates and other thermodynamic quantities, it is to be expected that there will be correlations between core-ionization energies and σ-parameters. Good correlations have been obtained for substituted benzene derivatives.[47]

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Table V. Results of Correlations of 2-Substituted Thiophenes Using Taft and Topsom's Equation[a]

$$\delta\Delta E = \sigma_F\rho_F + \sigma_R\rho_R + \sigma_\alpha\rho_\alpha + A_0$$

$\delta\Delta E$	ρ_F	ρ_R	ρ_α	A_0	r[b]	s[c]
ΔI	1.29 ± 0.10	0.80 ± 0.11	0.43 ± 0.15	−0.03	0.995	0.06
ΔV	1.36 ± 0.06	0.72 ± 0.10	0.20 ± 0.13	0.00	0.997	0.05
ΔR	0.06 ± 0.07	−0.07 ± 0.08	−0.23 ± 0.11	0.03	0.87	0.04
ΔK	−1.13 ± 0.20	−0.96 ± 0.22	−0.9 ± 0.3	0.08	0.98	0.18

[a] Parameters for Br and I substituents are not available. [b] Correlation coefficient. [c] Standard error of regression.

In this section, we analyze the core-electron energy shifts in terms of electronic substituent effects. However, a major difficulty with the simple Hammett approach is that no single parameter set can account for the full range of substituent effects encountered.[10–12] Recently Taft and Topsom[11] developed a more extensive parametrization to deal with this problem:

$$\delta\Delta E = \sigma_F\rho_F + \sigma_R\rho_R + \sigma_\alpha\rho_\alpha + A_0 \qquad (4)$$

The subscripts F, R, and α refer to the effects of field, resonance, and polarization, respectively. The data are thus analyzed in terms of a triparametric relationship where the constant A_0 represents the intercept, which should be close to zero.

Table V shows the correlations for ΔI, ΔV, ΔR, and ΔK. Unfortunately, parameters for Br and I are lacking, and with only seven data points the significance of the regression is reduced. However, a number of interesting features are found. We see from the magnitude of the ρ values that the major contribution to ΔV comes from the field effect and very little from polarizability. There is also significant contribution of resonance in the initial state. Resonance involving the substituents apparently leads to significant rearrangement of charge in the neutral molecule. This is in accordance with the calculated electron transfer due to substituents in the initial state.

The regression analysis for ΔR is hampered by the small sensitivity of this property to the substituent effects. Nevertheless, the result shows that there is virtually no influence from field and resonance effects on ΔR; the dominant contribution is the substituent polarizability. Although the bromo and iodo compounds have not been included in this correlation, the results for these compounds are consistent with this view; there is a relatively high relaxation energy associated with these polarizable substituents.

It is a striking conclusion from this analysis that resonance does not play a more pronounced part in the final-state relaxation process. However, the conclusion is fully consistent with the results of other investigations of relaxation processes in substituted benzenes[4a] and of the role of resonance delocalization in the acidity of organic and inorganic acids.[3] It is also in agreement with the calculations of charge flow following core ionization, which show very little difference between electron-donating and electron-attracting substituents in their ability to transfer electrons to the core-ionized sulfur atom.

Conclusions. Revision of the Standard Model

Core-ionization energies have been measured for sulfur in a series of 2-substituted thiophenes in order to determine how the substituents influence the ability of the ring to accommodate charge at the sulfur position. The core-ionization energies have been combined with Auger kinetic energies to provide information on how this ability is affected by the initial-state charge distribution and the final-state charge rearrangement. The results show that the variation in substituent effect is mainly determined by the initial state and that the final-state charge rearrangement is relatively unaffected by the nature of the substituent.

Calculations of the initial-state charge distribution show that the substituents transfer charge according to expected canonical forms with S and C(3) as classical ortho positions and C(4) and C(5) as the meta and para positions, respectively. Calculated values of ΔV for S2p correlate well with ΔV(C1s) values for the ring carbons and show that the sulfur atom is a useful probe for monitoring substituent effects in thiophene. The sensitivity to transmission of these effects varies as C(3) ≥ C(5) > C(4).

In contrast to the initial-state charge distribution, the calculated charge flow following core-ionization shows that the substituents are very similar in their ability to transfer electrons to the reaction site. This is in agreement with the small variation of relaxation energies observed experimentally.

Experimental values of ΔI, ΔV, ΔR, and ΔK have been correlated with electronic substituent parameters using trivariate regression analyses. The results show that the major contribution to ΔV comes from the field effect but that resonance delocalization involving the substituents also contributes significantly to the initial-state charge distribution. However, there is virtually no influence from resonance effects on the final-state charge rearrangement. This results challenges the traditional view since resonance stabilization of the final state has been considered to be an important contribution to chemical properties such as equilibria, reaction energies, and reaction rates. For example, the current theory of orientation in electrophilic aromatic substitution assumes that the positive Wheland intermediate[2d] (the final state of the charge addition), and hence the transition state, is stabilized by resonance.[2] Our results, on the other hand, show the greater importance of the initial-state charge distribution in determining the orientation effects of substituents.

In order to facilitate interpretation of these results, we now focus on the differences between our view of reactivity and the standard view that seems to be common among organic chemists. In either view, reactivity is controlled by the energy of the transition state relative to that of the reactants—the activation energy. Traditionally, electrophilic reactions have been discussed in terms of "stabilization (or destabilization) of the reactant" and "destabilization (or stabilization) of the transition state". Although these sound like perfectly plausible notions and have been in use for a long time, they are actually not helpful in a quantitative sense. For instance, one must ask what the reactant is stabilized with respect to. There is, however, no appropriate standard available.

As a specific example we consider the effect of a nitro substituent. Since nitro deactivates the ring, the activation energy for electrophilic attack in 2-nitrothiophene is higher than it is in unsubstituted thiophene. One cannot say, however, that 2-nitrothiophene is stabilized with respect to thiophene. The two molecules do not have the same composition, and therefore, there is no reaction that relates the energy of 2-nitrothiophene to that of thiophene.[48] We are in a similar quandary with respect to the transition state. In the end, what we know is that the nitro group increases the energy of activation over what it is in thiophene.

It is, however, meaningful to ask the question "Does this increase in activation energy arise because 2-nitrothiophene has a charge distribution that is different from that of thiophene, or does it arise because 2-nitrothiophene, is less able to delocalize the added charge than is thiophene?" This question can be given precise definition in both theory and experiment. It is simplest to think of these in terms of adding or removing a proton,[3a] but the ideas can be generalized to more complex systems.

The effect of the reactant charge distribution on the energy to add a proton is the potential energy of a proton at the site of addition. The nitro group at the 2-position makes the potential at sulfur and at C(5) more positive and, hence, less attractive to the proton; therefore, the activation energy is increased. This potential is well-defined quantum mechanically.[3a]

The effect of the charge delocalization, or relaxation, is to lower the energy of the transition state when the electrons rearrange from the reactant charge distribution to the distribution appropriate to the transition state. This relaxation energy is also well defined.[3a] It is conceivable that the nitro group, being electron withdrawing, inhibits the flow of electrons toward the electrophile. In the language of organic chemistry, the transition state would, in this case, be less stabilized[49] by delocalization for 2-nitrothiophene than it is for thiophene. However, both experiment and theory indicate that the degree of stabilization of the transition state due to delocalization is nearly the same for both molecules and is nearly the same for electron-withdrawing substituents as for electron-donating substituents.

One cannot say from a measurement of a shift in activation energy between 2-nitrothiophene and thiophene which of these effects is the more important. One needs either a theoretical calculation or a pair of measurements, such as we have presented, that are sensitive to these effects in different ways.

Traditionally, substituent effects have been explained by the ability of the substituent to delocalize charge in the transition state, whereas the initial-state effects have been largely ignored. Our results clearly indicate that the variation in substituent effect is predominantly determined by the ground-state charge distribution and that the charge rearrangement is very little influenced by the nature of the substituent. Our results thus challenge not only the current theory of electrophilic attack, but that of substituent effects as a whole.

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Supplementary Material Available: Calculated total energies of the initial closed-shell ground state and the sulfur 2p core-hole state for all of the molecules, cartesian coordinates for all of the molecules (3 pages). Ordering information is given on any current masthead page.

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[48] One might try to get around this problem by some construction of isodesmic reactions. These will, however, typically involve 4 species rather than 2, and it is still impossible to say what has been stabilized with respect to what. We have shown in ref 3e that consideration of isodesmic reactions does not provide a useful approach to these problems.

[49] Or, more loosely, "destabilized". However, since the charge rearrangement is always stabilizing, it is more accurate to speak of substituents being "less stabilizing" or "more stabilizing" in their effect on the transition state.

Effect of the Replacement of a Methyl by a Trifluoromethyl Group on the Acid–Base Properties of Pyrazoles

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Experimental determinations have been carried out of the thermodynamic basicities and acidities in the gas phase and in aqueous solution of pyrazoles substituted at positions 3 and 5 with methyl and trifluoromethyl groups. Corresponding theoretical calculations at the STO-3G level have also been done. The results are highly consistent both between relative gas-phase properties and theoretical calculations (including STO-3G calculations of anions) and between gas-phase and aqueous solution values. The trifluoromethyl group is found to considerably decrease the basicity (more in position 3 than in position 5) and increase the acidity (more in position 5 than in position 3).

Pyrazoles, due to the close proximity of an acid center (>N-H) and a basic center (⩾N:) in their structure and also due to the simplicity of the pentagonal aromatic ring, are very useful substrates for the study of acid–base properties in

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