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Electronegativities from Core-Ionization Energies: Electronegativities of SF_5 and CF_3

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Core-ionization energies have been measured for SF_6 (S 2p), SF_5SF_5 (S 2p), SF_5Br (S 2p and Br 3d), and SF_5CF_3 (S 2p and C 1s). These results, together with others that establish correlations between core-ionization energies and Pauling electronegativities, make it possible to assign group electronegativities to SF_5 and CF_3. This method gives electronegativities for these groups comparable to that of bromine, whereas analysis of the effect of these groups on acidity indicates electronegativities comparable to that of fluorine. Other methods of estimating electronegativity fall between these extremes. These disparities can be understood in part as reflecting the effects of polarizibility of the substituent, which tends to lower both the core-ionization energy and the deprotonation energy, making the electronegativity appear to be less in one case and more in the other. In addition, and possibly more important, the core-ionization energies presented here reflect the effect of the group on an adjacent atom, whereas the acidity reflects the effect on a remote atom. It appears that fluorine has a large effect on an adjacent atom but a relatively small effect on a remote atom. By contrast SF_5 and CF_3 have a relatively small effect on an adjacent atom, but this effect falls off only slowly with distance from the substituent. Thus, the effective electronegativities of CF_3 and SF_5 relative to those of the halogens depend on the site at which the molecule is probed as well as on the process that is under consideration.

Introduction

Electronegativity is a concept that is widely known and widely used by chemists. Tables of elemental electronegativities are to be found in both introductory and advanced chemical texts, and although many prescriptions have been used to calculate elemental electronegativity, they are all in essential agreement.[1] A limitation of elemental electronegativities is, however, that there is only a single electronegativity for each element, even though, for example, the electronegative effect of oxygen as $=$O is quite different from that of oxygen as $-$OH or the effect of SH is quite different from that of SF_5. Thus, in addition to elemental electronegativities, it is useful to have group electronegativities, and considerable effort has been directed toward this goal.[2−4] Here we explore the use of inner-shell photoelectron spectroscopy (ESCA) to establish such information, with the particular immediate goal of determining the electronegativities of SF_5 and CF_3.

A number of studies have indicated a high electronegativity for both SF_5 and CF_3. For instance, for the pairs of acids XYH (X $=$ F, CF_3; Y $=$ COO, C_6H_4O, C_6H_4COO), CF_3 gives a stronger acid than F.[5] In studies of solution acidities, Sheppard[6] has shown that SF_5 has an even greater influence on acidity than does CF_3, with an effect comparable to that of NO_2. Using a variety of chemical evidence, Wells has concluded that the electronegativity of CF_3 is approximately midway between that of chlorine and that of fluorine. A similar result is given by Bergmann and Hinze for CF_3. Their method indicates that the electronegativity of SF_5 is greater than that of CF_3 but less than that of fluorine. From triple-bond stretching frequencies, Canich et al.[7] concluded that the electronegativity of CF_3 is greater than that of SF_5 and that both lie between that of fluorine and that of chlorine.

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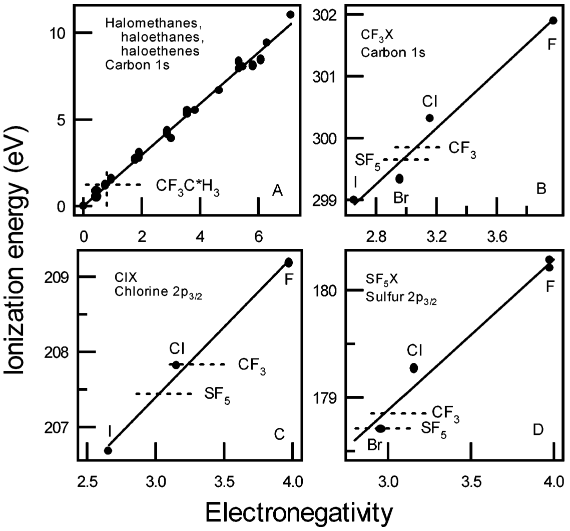

Figure 1. Correlations between core-ionization energies and electronegativities. For (A), the ionization energies are relative to that of the parent hydrocarbon—methane, ethane, or ethene—and the electronegativity scale is the sum of the ligand electronegativities (relative to that of hydrogen). For (B)−(D), the absolute ionization energy is given and is plotted against the electronegativity of X. Pauling electronegativities from Allred are used here.[13]

On the other hand, other evidence suggests significantly lower electronegativities for CF_3 and SF_5 than are indicated above. For instance, on the basis of ultraviolet spectroscopy, Gard and Woolf[8] concluded that the electronegativity of SF_5 is comparable to that of chlorine. Using the results of NMR measurements, Canselier[9] et al. also found that the electronegativity of SF_5 is about the same as that of chlorine. The bromine quadrupole-coupling constants in SF_5Br indicate that the sulfur−bromine bond is nearly covalent[10] and, therefore, that SF_5 and bromine have similar electronegativities. Carbon 1s photoelectron spectroscopy, discussed in more detail below, suggests that the electronegativity of CF_3 is comparable to that of bromine. Thermochemical determinations of electronegativity, quoted by Wells,[3] give electronegativities for CF_3 that are between that of bromine and that of chlorine.

In view of this discordant information on the electronegativities of CF_3 and SF_5, it is useful to investigate this question in more detail. For this purpose, we use the correlation between carbon 1s ionization energies and atomic electronegativities to obtain group electronegativities for SF_5 and CF_3. In 1970, Thomas showed that there was an excellent linear correlation between the Pauling electronegativity of the halogens and the carbon 1s core ionization energies of eight halomethanes.[11] Specifically, the correlation was with the quantity $\Sigma(\chi_X - \chi_H)$, where χ_X is the electronegativity of a ligand, χ_H is the electronegativity of hydrogen, and the sum is taken over the four ligands. An example of such a correlation is shown in Figure 1A, where we have plotted the carbon 1s ionization energies[12] of halomethane against the electronegativity sum indicated above.[13] Also shown in Figure 1A are similar data for ethane and ethene halogenated at the site of core ionization. The ionization energies are given relative to that of the parent compound: methane for halomethanes; ethane for haloethanes; ethene for haloethenes.

The line in Figure 1A shows the results of a linear regression ($R^2 = 0.99$) which fits the data with a root-mean-square deviation of 0.25 eV. The slope of the line is 1.48 eV/Pauling electronegativity unit. Turning this relationship around, we see that a measurement of the carbon 1s ionization energy in CH_3R could be used to establish the group electronegativity of R with an accuracy of about 0.2 units. As an example, this approach gives electronegativities of 2.12, 2.67, and 3.58 for CH_3, NH_2, and OH, respectively. These are essentially in agreement with theoretical values proposed by Bergmann and Hinze (2.30, 2.74, and 3.58) and by Huheey (2.27, 2.61, and 3.51), although the value for CH_3 is somewhat lower than that given by theory. This approach appears to give results that are consistent with expectations, and we now consider its application to determining the electronegativities of SF_5 and CF_3.

Experimental and Computational Procedures

Sulfur 2p, bromine 3d, and carbon 1s ionization energies were measured for SF_6, SF_5SF_5, SF_5Br, and CF_3SF_5. SF_5SF_5 was synthesized using the procedure described by Winter, Nixon, and Gard,[14] and SF_5Br, by that described by Winter, Terjeson, and Gard.[15] SF_6 and SF_5CF_3 were obtained from commercial sources.

The gas-phase X-ray photoelectron spectra were measured in the Oregon State University cylindrical mirror electrostatic analyzer, described elsewhere.[16] Core ionization was achieved with aluminum X-rays, $h\nu = 1486.553$ eV.[17] The gas pressure in the sample cell of 80 mTorr, measured with a capacitance manometer, was divided about equally between the sample gas and neon. Neon was included so that the neon 1s and 2s lines could be used for calibration.[18] The resolution of the spectrometer was approximately 1 eV. All spectra were fit with Voigt functions using a nonlinear least-squares program. Peak positions were converted to ionization energies using a program that includes a relativistic correction for the kinetic energy of the photoelectron and corrects for the recoil energy of the ion. Generally two spectra were run for each compound, with 1000 counts at the peak channel for the peak of interest. Our experience is that the precision of a single measurement is about 0.03 eV and that the overall accuracy of a set of measurements is about 0.05 eV.

Ab initio calculations for molecules of interest were carried out using the Gaussian 98 package.[19] For core-orbital energies and

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Table 1. Core-ionization Energies (eV)

compd	level	ionization energy	ref
BrX			
CF_3Br	Br $3d_{5/2}$	77.00	12
Br_2	Br $3d_{5/2}$	77.40	12
SF_5Br	Br $3d_{5/2}$	77.37	a
SF_5X			
SF_5Br	S $2p_{3/2}$	178.87	a
SF_5SF_5	S $2p_{3/2}$	178.71	a
SF_5Cl	S $2p_{3/2}$	179.27	12
SF_6	S $2p_{3/2}$	180.21, 180.28	*a*, 21
SF_5CF_3	S $2p_{3/2}$	178.85	a
CF_3X			
SF_5CF_3	C 1s	299.65	a
CF_3CF_3	C 1s	299.85	12
CF_3Br	C 1s	299.33	12
CF_3Cl	C 1s	300.31	12
CF_4	C 1s	301.96	22
ClX			
ICl	Cl $2p_{3/2}$	206.68	12
SF_5Cl	Cl $2p_{3/2}$	207.44	12
Cl_2	Cl $2p_{3/2}$	207.82	23
CF_3Cl	Cl $2p_{3/2}$	207.83	23
ClF	Cl $2p_{3/2}$	209.18	23

[a] This work.

atomic charges restricted Hartree−Fock calculations were done with the 6-31G** basis set. Atomic charges have been calculated using the FitCharge option of Gaussian98, which fits atomic charges to the potential at the van der Waals surface. For calculations related to the acidities of FCOOH and CF_3COOH the B3LYP method with the 6-31*G^{++} basis set was used. This approach has been found to reproduce experimental acidities reasonably well.[20] Geometry optimization was done for each molecule. However, for $C_6H_5CF_3$ and $C_6H_5SF_5$ the CCC and HCC bond angles in the benzene ring were assumed to be 120°.

Results and Discussion

The results of our measurements are summarized in Table 1, where we have included several values from the literature[12,21−23] for use in the discussion that follows. Our measurement for the sulfur 2p ionization energy in SF_6 agrees with that reported by Asplund et al.[21]

Electronegativities from Core-Ionization Energies. From the correlation between core-ionization energies and electronegativities of the halogens shown in Figure 1A, we can obtain the electronegativity for CF_3 using the measurement for the ionization energy of the methyl group in CH_3CF_3. This is illustrated by the dashed lines in Figure 1A—the horizontal line indicates the ionization energy of this carbon, and the vertical line indicates the corresponding electronegativity for the substituent, CF_3. The electronegativity of CF_3 obtained in this way is 0.79 plus that of hydrogen, or 2.99 (on the Pauling scale). Figure 1B shows a similar correlation for the carbon 1s ionization energy in CF_3X plotted against the electronegativity of X. The ionization energies for CF_3CF_3 and CF_3SF_5 are indicated by the horizontal lines, and these provide electronegativity values for CF_3 and SF_5 of 2.97 and 2.88, respectively. These results are surprising, in that the values are about the same as that for bromine, 2.96. As noted above, most other approaches have led to electronegativities for CF_3 and SF_5 that are either between those of chlorine (3.16) and fluorine (3.98), or greater than that of fluorine.

A third set of values comes from compounds of the type ClX, using the chlorine 2p ionization energies. The correlation between ionization energy and halogen electronegativity is shown in Figure 1C for X = F, Cl, and I. The line shows a linear fit to the points. From the measurements for CF_3Cl and SF_5Cl, indicated by the horizontal dashed lines, we obtain electronegativities for CF_3 of 3.23 and for SF_5 of 3.03. These are somewhat higher than those given above but still lead to electronegativities for CF_3 and SF_5 that are significantly less than that of fluorine.

A fourth correlation, Figure 1D, is that for SF_5X (X = F, Cl, Br), where we use the sulfur 2p ionization energies of SF_5SF_5 and SF_5CF_3 to obtain the electronegativity values. These are 2.98 for CF_3 and 2.88 for SF_5, in excellent agreement with those obtained from the carbon 1s measurements.

Finally, we consider the bromine 3d ionization energies. Here there are not enough measurements to provide a correlation. However, it is apparent that the 3d ionization energy in SF_5Br is about the same as in Br_2, suggesting that SF_5 and Br have comparable electronegativities, in agreement with the qudruople-coupling results. For CF_3Br the ionization energy of bromine is slightly less than for Br_2, indicating that the electronegativity of CF_3 is less than that of bromine.

With the exception of the chlorine measurements these approaches to determining the electronegativity, all agree in assigning electronegativities to CF_3 and SF_5 that are comparable to that of bromine. The chlorine measurements show somewhat higher values but still give electronegativities less that of fluorine. Since these values are rather lower than those obtained by most other methods, it is necessary to ask if this approach does indeed correctly reflect the group electronegativity. In particular, we need to take into account that core-ionization energies are influenced not only by the charge distribution in the molecule but by relaxation of this charge distribution to screen the core hole that is formed on ionization. This screening is expected to be greater for large, polarizible groups than for small atoms, and we might, therefore, expect that the ionization energies for the mol-

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ecules with CF_3 and SF_5 as substituents might be abnormally lowered by this effect. In this case, the method we have used would assign electronegativities to these species that would be too low.

We can estimate the effect of this screening (or, relaxation) by comparing Koopmans theorem ionization energies with the actual ionization energies. The former, equal to the negative of the orbital energies from a Hartree–Fock calculation, represent the energy to remove an electron leaving the rest of the charge distribution frozen. The actual energies, obtained either from experiment or from theory, differ from the Koopmans theorem energies by approximately the relaxation energies. The results of such a comparison show that the relaxation energy/substituent attached to a central carbon decreases in the order $Br > SF_5 > Cl > CF_3 \approx F = H$. Moreover, the effects of multiple substituents are approximately additive, so that the relaxation energies associated with such molecules as CBr_4 and CCl_4 are several electronvolts and are much larger than the relaxation associated with either SF_5 or CF_3. We see, however, from Figure 1A, which includes points for CBr_4 and CCl_4, that all points fall close to the same correlation line. There is no systematic deviation associated with the molecules that have highly polarizible groups. It appears that the polarizibility of the ligand is to some extent already built into the definition of electronegativity, at least for the halogens. If we assume that this is also the case for CF_3 and SF_5, then polarizibility is not the source of the apparently low electronegativities that this approach assigns to these groups.

This is, however, not the complete story. Although the points for methane, ethane, and ethene fall on the correlation line in Figure 1A, the corresponding points for CF_3H and HCl fall significantly above the correlation lines in Figure 1B,C. This discrepancy presumably reflects the low polarizibility of hydrogen and hence a low relaxation energy associated with hydrogen as a substituent. We can gain further insight into this question by looking at the hardness[24] of the various substituents, which is inversely proportional to the polarizibility.[25] From the results given by Bergmann and Hinze, we find three groups of substituents. These are hydrogen, which has low electronegativity but high hardness (6.4 V/e), the halogens, which have a range of electronegativities and hardness between 4.6 and 8.7 (approximately correlated with the electronegativity), and a variety of functional groups, including CF_3 and SF_5, with hardness between 2 and 3, uncorrelated with the electronegativity. Thus, it is possible that there is a relaxation/polarizibility effect that must be included in assessing the group electronegativities. If this is the case, the electron spectroscopic technique will give electronegativities that are lower than those obtained by other methods.

Reconciling the Electronegativity Scales. At one extreme, we have the data on acidities, giving electronegativities for CF_3 and SF_5 greater than that of fluorine. At the other, the inner-shell ionization energies point to electronegativities comparable to that of bromine. Between are a number of measurements and calculations pointing to electronegativities for these substituents somewhere between those of chlorine and fluorine. How do we reconcile these results? There are two different factors to consider. First, is the relaxation effect, already mentioned. Second is that CF_3 and SF_5 appear to produce their substituent effects in a way different from the manner in which fluorine produces its effects. These two points are amplified below.

Although most of the estimates of group electronegativity depend on properties of a neutral molecule, core ionization and acidity depend on the energy to form an ion—positively charged in the case of core ionization and negatively charged in the case of proton removal. In simplest approximation, these energies can be written as $\Delta I = \Delta V_I - \Delta R_I$ and $\Delta A = -\Delta V_A - \Delta R_A$, where Δ implies a measurement relative to a reference compound, I indicates the core-ionization energy, A indicates the acidity (deprotonation energy), V represents the effect of the charge distribution of the neutral molecule on the energy of the process, and R represents the effect of charge relaxation/polarization that accompanies the change in charge. For core ionization, V_I can be approximately equated to the potential energy of a unit positive charge at the center of the atom that is to be ionized or, alternatively, ΔV_I can be equated to $-\Delta\epsilon$, where ϵ is the orbital energy of the orbital in question.[26] For acidity, V_A can be shown to be equal to the electrostatic potential energy of the acidic proton.[27] The effect of a substituent that leads to positive ΔV is to increase the core-ionization energy and to decrease the deprotonation energy (that is, to make the acid stronger). If the substituent has high polarizibility and, therefore, produces a positive value of ΔR, then the overall effect on the ionization energy is less than expected from ΔV, whereas the effect on the acidity is greater. This appears to be what is seen with CF_3 and SF_5. The effect on ionization energy is less than would be expected from other estimates of the electronegativity, whereas the effect on the acidity is greater. This point has made elsewhere with regard to the acidities of propyne, trifluoropropyne, and ethynylsulfur pentafluoride[28] and may account, at least in part, for the observation that estimates of the electronegativities for CF_3 and SF_5 based on ionization energies are on the low side and estimates based on acidities are on the high side.

A second difference between core-ionization measurements and acidity measurements is that the ionization energies discussed so far reflect the effect of a substituent directly attached to the core-ionized atom, whereas the acidic proton is always somewhat removed from the substituent. For ionization energies, the effect of a single fluorine substituent falls off rapidly with distance from the fluorine.

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For instance, in fluoroethane, the carbon 1s ionization energy of the carbon to which the fluorine is attached is shifted by 2.3 eV relative to ethane, while the ionization energy of the other carbon is shifted by only 0.42 eV.[29] A nearly identical situation is seen for fluorobenzene, where the ionization energy for the *ipso* carbon is shifted by 2.4 eV from benzene but the ionization energies for the other ring carbons are shifted by only 0.39 eV.[30] By contrast, in (trifluoromethyl)-benzene, the *ipso* and other ring carbons have experimentally undistinguishable carbon 1s ionization energies, shifted by 0.64 eV from benzene.[31] Thus, although the effect of CF_3 on the *ipso* carbon is less than that of fluorine, the effect of the CF_3 group in the rest of the ring is greater than the effect of fluorine; the effect of CF_3 falls off with distance more slowly than that of fluorine. Less information has been published on electron spectroscopy involving the SF_5 group, but such information suggests very similar behavior for SF_5 and CF_3. For instance, the carbon 1s spectra for trifluoropropyne and ethynylsulfur pentafluoride are nearly identical, showing only a small shift between the ionization energies of the two carbons in the ethynyl group. The spectra of 1,1,1-trifluoropropane and ethylsulfur pentafluoride show similar behavior,[32] and as in trifluoromethylbenzene, the carbon 1s ionization energy of the carbon in the 2 position is greater than in fluoroethane.

These ideas can be given quantitative expression with the help of theoretical calculations. As an example, we consider the acids FCOOH, and CF_3COOH. Taking FCOOH for reference, the experimental value of ΔA for CF_3COOH is -0.26 ± 0.33 eV. In agreement with this, the theoretically calculated deprotonation energy, ΔA, of CF_3COOH (relative to FCOOH) is -0.238 eV. ΔV_A, however, is only -0.012 eV, or essentially 0. The principal reason for the higher acidity of CF_3COOH relative to FCOOH is, therefore, larger ΔR_A in CF_3COOH, resulting from the higher polarizibility of the CF_3 group. On the other hand, if we consider V_I for the carbon to which the substituent is attached, this is more positive in FCOOH than in CF_3COOH by 1.43 eV. Thus, our view of the relative electronegativities of F and CF_3 depends on where in the molecule we probe. From the point of view of acidity, we conclude that the electronegativity of CF_3 is equal to or greater than that of F, whereas from the point of view of the electrostatic potential at the carbon (and, hence, the carbon 1s ionization energy) we conclude that the electronegativity of CF_3 is considerably less than that of F.

How do we account for the differences in how F, on one hand, and CF_3 and SF_5, on the other, exert their influence. It is instructive to look at the charge on the substituent in various molecules. This can be done either by considering Mulliken charges or the charges derived by fitting point charges in such a way as to give the correct potential at the van der Waals surface (the FitCharge option of Gaussian98). For the comparison of CF_3 and F the conclusions from the two approaches are essentially the same. If we consider the molecules ClF, BrF, CF_4, FCOOH, C_6H_5F, CH_3F, and HF, the charge on fluorine as derived from the potential ranges from -0.145 for ClF to -0.455 for HF. The Mulliken charges are all about -0.4. The two methods agree that fluorine in all of these molecules carries a significant negative charge, in keeping with its high electronegativity. By contrast, for the same series with F replaced by CF_3, the potential-derived charges for the CF_3 group are close to zero—the average charge is 0.01, with a spread of 0.03. Thus, the CF_3 group is essentially neutral. This same conclusion was reached in the 1970s by Holmes and Thomas[31] on the basis of carbon 1s photoelectron spectroscopy of the (trifluoromethyl)benzenes and by Brownlee and Taft[33] on the basis of CNDO calculations. For SF_5 replacing F, the Mulliken charges on the SF_5 group are also close to 0. Thus, it appears that the effect of fluorine is to withdraw charge strongly from the adjacent atom, but this effect is only weakly transmitted to the rest of the molecule. CF_3 and SF_5, by contrast, have a weaker electron-withdrawing effect on the adjacent atom, but this effect is felt over a longer range than is found with fluorine. It is possible that this result arises from the large dipole moments of these highly polarized groups.

Summary and Conclusions

The group electronegativities assigned to CF_3 and SF_5 depend strongly on the method used to make the assignment. They range from values greater than that of fluorine if the electronegativity is based on the effect of the substituent on acidity to approximately that of bromine if they are based on core-ionization energies. Part of this discrepancy can be resolved by considering the polarizibility of the substituents, which increases the effect of the substituent on acidity and decreases the effect on ionization energy (relative to the effects of less polarizible substituents). In addition, it is to be recognized that most of the core-ionization energies discussed here reflect the effect of a substituent attached directly to the core-ionized atom, whereas acidity reflects the effect of a more remote substituent. If, instead, we consider the influence of a substituent on the core-ionization energy of a more remote atom, then the effects of CF_3 and SF_5 are, indeed, greater than that of fluorine.

That substituent effects depend on the process studied and on the location of the substituent is not surprising. Physical organic chemists have long recognized that such effects cannot be described by a single parameter and that it is necessary to include the influence of inductive effects, polarizibility, and resonance.

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