vestigations confirms that the stoichiometry of one molecule of $O_2(^1\Delta_g)$ consumed per molecule of stable reactant must be correct. Whereas our TME results are somewhat higher than theirs, our DMF results are lower. If the stoichiometry of these reactions was not a one to one ratio, then the two sets of results would be systematically different. In addition, since we followed the reaction by the rate of $O_2(^1\Delta_g)$ removal, it shows that collisional deactivation of the excited O_2 by TME or DMF is negligibly slow compared to the chemical reactions.

A comparison of the temperature dependence of these two reactions is shown in Figure 2. The higher preexponential factor of the TME reaction compared to the DMF reaction will lead to an ultimate inversion of reactivity at sufficiently high temperatures. It is of interest to note that the lower preexponential factor observed in the DMF reaction is consistent with expectations based on entropy changes in forming the activated complex. The formation of a cyclo addition product in this reaction would be expected to lead to an unusually large entropy decrease. From the thermodynamic formulation of reaction rates it is easy to show that for a bimolecular reaction the Arrhenius preexponential factor can be equated to the term (ekT/h) $\exp(\Delta S_c^{\ddagger}/R)$, where $\Delta S_c^{\ddagger}$ is the entropy change, in units of molarity, in going from reactants to activated complex. Thus the observation of the much lower preexponential factor obtained in the DMF reaction implies that the cyclization is essentially complete in the activated complex.

We also investigated a number of reactions of $O_2(^1\Delta_g)$ with various straight-chain olefins. In each case the reaction was too slow to be measured using the esr method. From a knowledge of flow velocities employed in experiments with propylene we calculate that the $O_2(^1\Delta_g)$ + propylene reaction must be slower than 5×10^7 cm^3 mol^{-1} sec^{-1} at 298°K. These results confirm the findings of Herron and Huie.[2] Actually in these experiments we observed no measurable decrease in the $O_2(^1\Delta_g)$ concentration. This again demonstrates that collisional deactivation of $O_2(^1\Delta_g)$ by low molecular weight olefins must be a relatively slow process.

X-Ray Photoelectron Spectroscopy of Halomethanes[1a]

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Abstract: Carbon 1s ionization potentials, relative to that of methane (290.8 eV), have been measured for CH_3F (2.8 eV), CHF_3 (8.3 eV), CF_4 (11.0 eV), CH_3Cl (1.6 eV), CH_2Cl_2 (3.1 eV), $CHCl_3$ (4.3 eV), CCl_4 (5.5 eV), and CH_3Br (1.0 eV), together with fluorine 1s ionization potentials for CH_3F (692.4 eV), CHF_3 (694.1 eV), and CF_4 (695.0 eV), and chlorine 2s ionization potentials for CH_3Cl (277.2 eV), CH_2Cl_2 (277.6 eV), $CHCl_3$ (277.7 eV), and CCl_4 (278.0 eV). The carbon and halogen binding energies increase linearly with the number of halogens. Comparison of the fluorocarbon results with binding energies based on use of Koopmans' theorem indicates that there is a substantial absolute error between experiment and theory, but that the Koopmans'-theorem results account fairly well for the relative ionization potentials in this series of compounds. The measured binding energies are found to vary linearly with the sum of differences between the electronegativities of the ligands and that of hydrogen. A plausible reason is developed for this linear relationship.

Inner-electron binding energies for extensive series of nitrogen, sulfur, and chlorine compounds have been determined by X-ray photoelectron spectroscopy.[2-4] These and other measurements show that the binding energies of the inner electrons increase with oxidation number, with formal charge on the atom, and with increasing electronegativity of the ligands attached to the atom. Some success has been obtained in correlating the measured shifts with charges assigned to atoms in various ways. The technique shows some promise of providing information on charge distributions in molecules and quantitative information on the electronegativity of different ligands.

Some information has been published on the carbon 1s electron binding energies in different compounds and the results are generally in agreement with expectations.[5,6] However, no systematic study of carbon compounds has yet appeared. As part of such a study, we report here the carbon 1s binding energies for the compounds CH_4, CH_3F, CHF_3, CF_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, and CH_3Br. In addition, we report the fluorine 1s and chlorine 2s binding energies. These compounds provide a series in which the electro-

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(1) Supported in part by the U. S. Atomic Energy Commission. (b) Address correspondence to author at this address.

(2) (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindbreg, "ESCA Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksell, Uppsala, 1967, pp 97–137; (b) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1967).

(3) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968); *Inorg. Chem.*, **8**, 2642 (1969).

(4) K. Hamrin, G. Johansson, A. Fahlman, C. Nordling, and K. Siegbahn, *Chem. Phys. Lett.*, **1**, 557 (1968).

(5) T. D. Thomas, *J. Chem. Phys.*, **52**, 1373 (1970).

(6) Reference 2a, pp 78–79, 137–3.

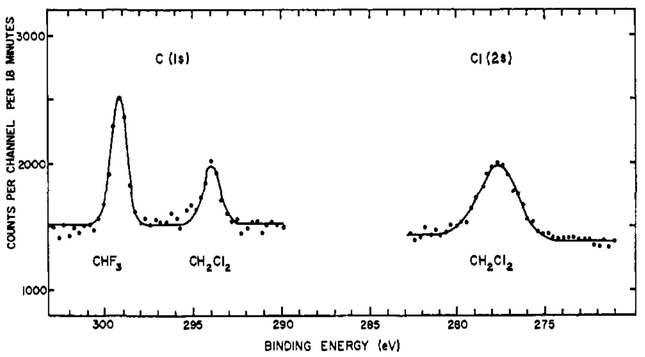

Figure 1. Spectrum of carbon 1s and chlorine 2s electrons in fluoroform and methylene chloride. The solid line represents a least-squares fit to the data. Exciting radiation is magnesium Kα X-rays.

negativity of the ligands and the number of electronegative ligands attached to the central atom can be easily varied without changing the type of bonding or the molecular geometry (other than the bond length). In addition, since fluorine is the most electronegative element, the shift of the carbon 1s binding energy between methane and carbon tetrafluoride gives the maximum range of shifts to be expected for organic compounds. Finally, there are Hartree–Fock calculations[7–12] of the carbon 1s binding energies for methane and the fluoromethanes. These measurements provide a useful test of whether this kind of calculation can correctly predict these shifts.

Experimental Method and Results

The binding energies of the various compounds were determined by irradiating gaseous samples with magnesium Kα X-rays (1253.6 eV).[13] The kinetic energies of the photoelectrons were measured in an iron-free, double-focusing spectrometer of 50-cm radius.[14] The kinetic energy E_K of an electron is related to its binding energy E_b by conservation of energy.

$$E_b = 1253.6 - E_K$$

In order to measure the shifts accurately, we ran two samples together, one the sample of interest, the other either fluoroform, methane, or benzene taken as a standard. The carbon 1s and fluorine 1s binding energies for these compounds are known from other measurements.[5] By this technique any effects of instrumental drift or gas pressure on line position are the same for both lines. The pressures in the gas cell ranged from 0.01 to 0.05 Torr. Over the range 0.005–0.15 Torr we have found that the position of the fluorine 1s line from fluoroform does not vary by more than 0.2 eV.[15] Presumably any differential pressure dependence of two compounds run together is substantially less than this. The chlorine 2s binding energy is very close to the carbon 1s binding energy in fluoroform and was measured relative to it. A spectrum showing the carbon 1s line from fluoroform together with the carbon 1s and chlorine 2s lines of dichloromethane is given in Figure 1. A spectrum of the fluorine 1s lines in tetrafluoromethane and fluoromethane is shown in Figure 2. In these figures the solid curves represent least-squares fits to the data assuming gaussian peak shapes and a constant background. The difference in width between the two fluorine peaks is striking.

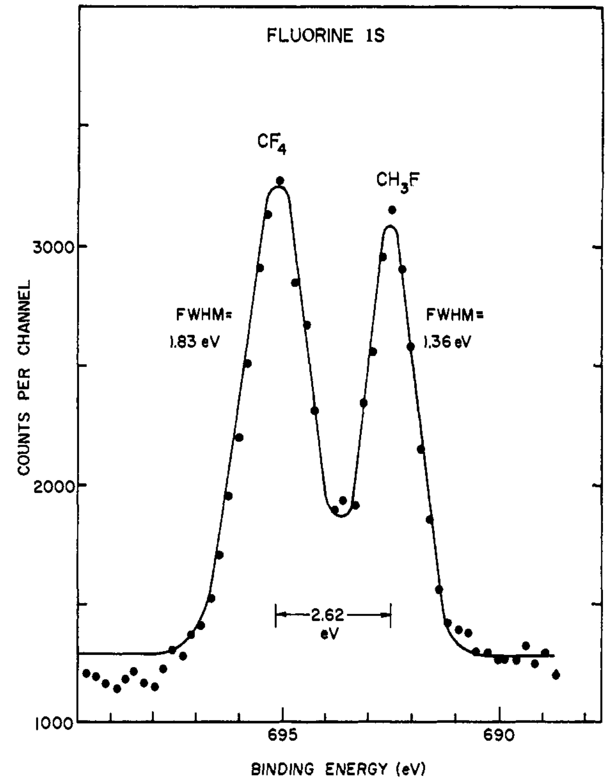

Figure 2. Spectrum of fluorine 1s electrons in carbon tetrafluoride and methyl fluoride. The solid line represents a least-squares fit to the data. The splitting and line widths indicated were determined by this least-squares procedure. The exciting radiation is magnesium Kα X-rays.

Table I. Binding Energies for Inner Electrons in Halomethanes

	Carbon 1s binding energy, eV		
Compound	Rel to methane (290.8 eV)	Absolute	Halogen binding energy, eV Absolute
CH_3Br	1.0	291.8	
CH_3Cl	1.6	292.4	277.2[a]
CH_2Cl_2	3.1	293.9	277.6[a]
$CHCl_3$	4.3	295.1	277.7[a]
CCl_4	5.5	296.3	278.0[a]
CH_3F	2.8	293.6	692.4[b]
CHF_3	8.3	299.1	694.1[b]
CF_4	11.0	301.8	695.0[b]

[a] Chlorine 2s. [b] Fluorine 1s.

The measured binding energies for carbon 1s electrons are given relative to that for methane (290.8 eV)[5] in Table I, together with the absolute values for the fluorine 1s electrons and chlorine 2s electrons.

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(7) T. K. Ha and L. C. Allen, *Int. J. Quantum Chem. Symp.*, 1, 199 (1967).

(8) H. Basch and L. C. Snyder, *Chem. Phys. Lett.*, 3, 333 (1969).

(9) H. Basch, C. R. Brundle, and M. B. Robin, unpublished work.

(10) W. J. Hehre and J. Pople, private communication.

(11) M. E. Schwartz, *Chem. Phys. Lett.*, in press.

(12) M. E. Schwartz, *J. Amer. Chem. Soc.*, in press.

(13) Reference 2a, Appendix, 6.

(14) J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, *Ark. Fys.*, **28**, 375 (1965); T. Yamazaki and J. M. Hollander, *Nucl. Phys.*, **84**, 505 (1966).

(15) D. A. Shirley and T. D. Thomas, unpublished work.

Discussion

Qualitative Trends. The carbon 1s binding energies show an obvious and expected increase with increasing electronegativity of the ligands and with increasing number of electronegative ligands. The fluorine 1s and chlorine 2s binding energies increase slowly with the number of halogens. These results are easily explained. The replacement of a hydrogen by a halogen results in withdrawal of valence electrons from the central atom with a resulting increase in the binding energy of the inner electrons. When additional hydrogens are replaced by halogens the positive charge and the carbon 1s binding energy increase even further. Because there is some electron transfer from the carbon to the halogen, the fluorine 1s and chlorine 2s binding energies for the monohalomethanes are presumably substantially less than for the isolated atom. As the positive charge on the central atom increases with the addition of halogens, there is an increase in positive potential at each ligand and a resulting increase in binding energy for the electrons on that atom, as is observed. (A similar discussion has been given by Schwartz, Coulson, and Allen[16] in interpreting the results of their theoretical calculations on fluoromethanes.)

It would be interesting to know whether each additional halogen withdraws the same amount of charge as does the first one. The linear increase of binding energies with number of fluorines tempts one to conclude that this is the case. However, there is probably not a linear relationship between charge withdrawn and the change in binding energy; theoretical calculations indicate that the binding energy increases somewhat faster than linearly with increasing charge.[17] The fluorocarbon data thus suggest that the additional fluorines are not so effective as the first in withdrawing charges from the carbon. Even more suggestive of this conclusion are the chlorocarbon data. Here we see that the first chlorine causes a shift in carbon 1s binding energy of 1.6 eV, the second 1.5 eV, and the third and fourth 1.2 eV each.

Comparison between Measured and Calculated Ionization Potentials. The measured ionization potentials are the differences between the total energy of the neutral molecule and the total energy of the ion that is missing the appropriate electron. The proper theoretical value with which to compare is the difference between these total energies as calculated by some method, for instance, the Hartree–Fock method. Very few such calculations are available and we must, instead, rely on Koopmans' theorem[18] to give us approximate theoretical values for the ionization potentials. According to this theorem, the Hartree–Fock one-electron (or orbital) energies are equal to the ionization potentials.

Richards[19] has reviewed for the benefit of experimentalists the assumptions of Koopmans' theorem and the dangers of using it. First, Koopmans' theorem is applicable only if the molecular orbitals of the ion are the same as those of the neutral molecule. This will not in general be the case, and because of failure of this assumption, the one-electron energies from the Hartree–Fock calculation will be greater than the correct values. The difference corresponds to a reorganization energy of the molecular orbitals to the ionic orbitals. Second, the use of Hartree–Fock results involves the assumption that the correlation energy for the ion is the same as that for the molecule. According to Richards this effect tends to make the Hartree–Fock energies less than the correct values. Finally, it is assumed that the relativistic corrections are the same for the ion as for the molecule.

Hartree–Fock calculations of the orbital energies for methane and the fluorinated methanes have been made by Ha and Allen,[7] by Hehre and Pople,[10] by Basch and coworkers,[8,9] and by Schwartz.[11,12] In addition, Basch, Brundle, and Robin[9] have calculated the carbon 1s ionization potentials for CH_4, CH_3F, CH_2F_2, and CHF_3 by taking the difference between the Hartree–Fock energy for the molecule and the Hartree–Fock energy for the ion with a 1s hole and Schwartz has used the same method for methane[11] and fluoromethane.[12] The calculated orbital energy (Koopmans'-theorem value) for the carbon 1s electron on methane is 305.0 eV, compared with a measured value (Table I and ref 5) of 290.8 eV and the more nearly correctly calculated values of 292.9 from Basch, *et al.*,[9] and 291.0 eV from Schwartz.[11] The 12–14-eV difference between the Koopmans'-theorem value and the other two represents the reorganization energy that is ignored by Koopmans' theorem.[20] The agreement between the measured value and the difference between the calculated total energies of molecule and ion is good.

For a series of compounds, such as have been studied here, it seems reasonable that the relativistic and correlation[7] corrections will be the same for all of the compounds. Then, if the relaxation energy is the same for all molecules of the series, the Hartree–Fock orbital energies should give the shifts in binding energy among the various compounds, even though they do not agree with the absolute binding energies. Figure 3 shows the experimental and theoretical carbon 1s binding energies (relative to methane) plotted against the number of fluorines. The experimental results are shown as open circles and the theoretical values as closed circles. The three sets of theoretical results connected by solid lines are based on Koopmans' theorem. Curve B, the one closest to the experimental curve is from Basch, Brundle, and Robin,[9] and was calculated with the largest basis set. The set of points connected by the dashed line represents values obtained by taking the difference between the calculated total energies for the molecule and the ion.[9] The difference between the shifts calculated this way and the shifts indicated by curve B, which is based on Koopmans' theorem, is slight. Schwartz has obtained theoretical results that are very similar to these.[12] His value for the CH_4–CH_3F shift is 2.4–3.2 eV using Koopmans' theorem and 3.2 eV using binding energies calculated by taking the difference between the total energies of molecule and ion. The experimental value (from Table I) is 2.8 eV. The differences between the Koopmans'-theorem values of curve B and the experimental values are small and are

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[16] M. E. Schwartz, C. A. Coulson, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 447 (1970).

[17] Reference 2a, p 82–85.

[18] T. Koopmans, *Physica*, 1, 104 (1933).

[19] W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, 2, 419 (1969).

[20] See reference 2a, pp 63–71, for a discussion of some of the discrepancies between binding energies calculated by use of Koopmans' theorem and those calculated by taking the difference between the total energies of molecule and ion.

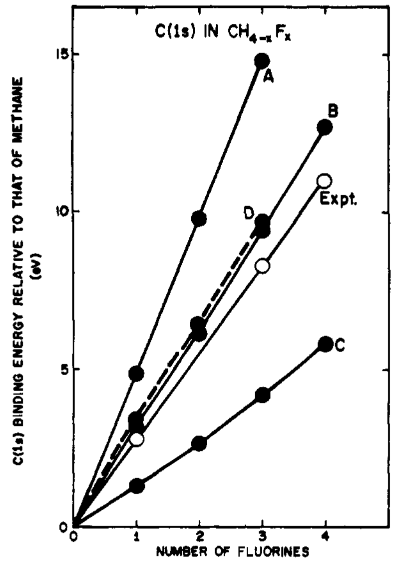

Figure 3. Experimental (○) and theoretical (●) variation of carbon 1s binding energies with number of fluorines attached to a single carbon. Both the experimental and theoretical values are plotted relative to that of methane. The theoretical values represented by the curves labeled A, B, and C were obtained from Hartree–Fock calculations by use of Koopmans' theorem and are from ref 7, 9, and 10, respectively. Those represented by curve D were obtained by taking the difference between the calculated total energies of the molecule and ion (ref 9).

of the same magnitude as those found for a variety of carbon-, nitrogen-, and oxygen-containing compounds.[21]

A comparison between the experimental and calculated shifts of the fluorine 1s binding energies is shown in Figure 4. The binding energies are plotted relative to that of CF_4. The calculated values are from Basch, Brundle, and Robin[9] and are based on Koopmans' theorem. The experimental value for CF_4 is 695.0 eV (see Table I); the Koopmans' theorem value is 718.1 eV. The error in the calculated value is in the same direction as is found for the carbon 1s energies. There is, however, only a small discrepancy between the experimental shifts and those calculated using Koopmans' theorem.

Correlation with Electronegativity. A number of attempts have been made to correlate the shifts of 1s binding energies with charges assigned to the atoms.[2–4,8–16] These charges are estimated from simple electronegativity considerations or from some kind of molecular orbital calculations. This sort of correlation is made in the same spirit that Koopmans' theorem is applied, namely, it is tacitly assumed that the energies are determined by the charge distributions in the molecule and that rearrangement energies can be ignored. In view of the substantial energies that appear to be associated with rearrangement, there might be some skepticism about the physical significance of these correlations.

It is possible, however, that the relaxation energies vary in some orderly way. If so, then these correlations may be of some value in determining the systematics of the binding energy shifts. The compounds we have studied, because they have essentially the same geometry and bonding, should provide a good test of the various methods of correlating the data.

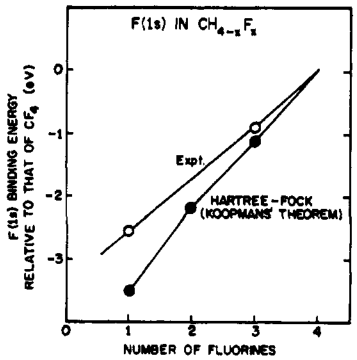

Figure 4. Experimental (○) and theoretical (●) variation of fluorine 1s binding energies with number of fluorines attached to a single carbon. Both the experimental and theoretical values are plotted relative to that of CF_4. The theoretical values were obtained from Hartree–Fock calculations by use of Koopmans' theorem (ref 9).

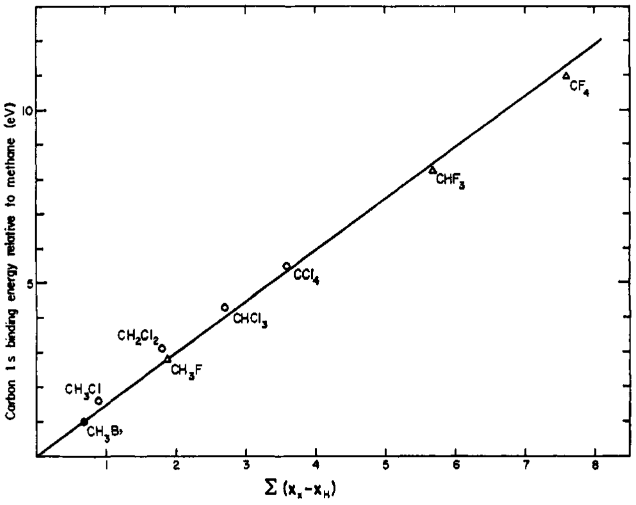

Figure 5. The carbon 1s binding energies (relative to that of methane) for halomethanes are plotted *vs.* the sum of electronegativity differences. The difference is taken between the electronegativity of the ligand and that of hydrogen. The sum is taken over all the ligands.

A very simple and satisfactory correlation of the data for halomethanes is shown in Figure 5. Here we have plotted the binding energy shifts *vs.* the quantity $\Sigma(X_x - X_H)$. The symbol X_x stands for the electronegativity of the halogen, and X_H is the electronegativity of hydrogen.[22] The summation is taken over all the atoms attached to the carbon (or, effectively, over the halogens, since $X_H - X_H = 0$). Since the various compounds are related to one another by replacement of hydrogens by halogens, it is reasonable that the shifts should be somehow dependent on the electronegativity difference between hydrogen and the halogen. In addition it is reasonable that the shift should increase with the number of halogens. That the data should follow a linear relationship is not obvious. We have made an attempt to justify this linearity in the paragraphs that follow.

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(21) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **52**, 3295 (1970).

(22) Pauling's electronegativities were used here. They were taken from C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Oxford University Press, London, 1965, p 176.

In the simple electrostatic model discussed by Siegbahn and coworkers,[23] the shift ΔE in the inner electron binding energy due to the removal of a charge qe from the atom of interest to a ligand atom is given as

$$\Delta E = qe^2(1/r - 1/R)$$

where r is the radius of a shell around the atom from which q is removed and R is the distance to a ligand atom to which q is removed. In a more sophisticated treatment qe^2/r is replaced by the results of a quantum mechanical calculation, but even in this case the first term remains approximately proportional to q. If there are several ligands then the expression becomes

$$\Delta E = qe^2/r + e^2\sum_i q_i/R_i$$

where q_i is the charge on the ith ligand.

We now make the questionable assumption that R_i, the distance to the ith ligand, is independent of what the ligand is (or, that $1/R_i$ can be replaced by some average value $1/R$). Then

$$\Delta E = qe^2/r + (\sum q_i)e^2/R$$

Since the molecule is neutral $q = -\Sigma q_i$ and

$$\Delta E = qe^2(1/r - 1/R)$$

as for the case of only one ligand. The important point is that under this assumption the shift is approximately proportional to the charge on the central atom and approximately independent of how the balancing charge is distributed among the several ligands.

The above paragraph represents the argument for seeking some correlation between the measured shifts and atomic charges. Satisfactory correlations have been found for nitrogen 1s, sulfur 1s and 2p, and chlorine 2p binding energies.[2-4] To obtain atomic charges for nitrogen and sulfur, Nordberg and coworkers[2b] have taken the charge on an atom to be equal to the formal charge plus the sum of the ionic characters of the bonds attached to the atom. The ionic character I was obtained from an empirical relationship given by Pauling[24]

$$I = 1 - \exp[0.25(X_A - X_B)^2]$$

where X_A and X_B are the electronegativities of the atom of interest and of the atom joined to it. This relationship is based on the dipole moments of HI, HCl, and HBr and probably underestimates I. In spite of this Nordberg, *et al.*,[2b] and Hamrin, *et al.*,[4] have found good correlations between measured shifts for nitrogen and sulfur compounds and the calculated charges.

If the halomethane data are treated in this way the results are unsatisfactory. Although all of the fluorine data fall on a straight line and the chlorine and bromine data fall approximately on a straight line when plotted against such charges, these lines differ in slope from one another by a factor of about 2.

The problem seems to lie with the use of Pauling's relationship for the ionic character. Gordy[25] has made a more critical analysis of the dipole moment data and has combined this with results of nuclear quadrupole resonance experiments to conclude that

$$I = (X_A - X_B)/2 \quad \text{for } |X_A - X_B| < 2$$
$$I = 1 \quad \text{for } |X_A - X_B| > 2$$

For all systems considered here, the first of these expressions applies.

For all of the halomethanes, the formal charge on the carbon is zero. Then combining the assumption made by Nordberg, *et al.*,[2b] with Gordy's expression we conclude that the charge on the central carbon atom is given as

$$q = \sum_i (X_i - X_C)/2$$

where X_i is the electronegativity of the ith ligand and the sum is over all the ligands. Combining this result with the idea expressed above that the shift in energy (relative to atomic carbon) is proportional to q we have

$$\Delta E \propto \sum_{i=1}^{4} (X_i - X_C)$$

or for methane

$$\Delta E_{CH_4} \propto \sum_{i=1}^{4} (X_H - X_C)$$

Then the shift between methane and any of the halomethanes will be

$$\Delta E_X - \Delta E_{CH_4} \propto \sum_{i=1}^{4} (X_i - X_H)$$

which is what is plotted in Figure 5.

We can examine this relationship more quantitatively. The proportionality constant relating the energy shift to the electronegativity difference (as determined from the straight line of Figure 5) is 1.48 eV per electronegativity unit. From Gordy's relationship between electronegativity and partial ionic character this corresponds to about 3 eV for a change in charge of one electronic charge. Let us compare this value with what we might obtain from the simple electrostatic model discussed above. According to this model

$$\Delta E = qe^2(1/r - 1/R)$$

The Hartree–Fock calculations of Siegbahn and coworkers[17] indicate that removal of an sp^3 hybrid electron from carbon causes a shift of the carbon 1s electrons by 17.1 eV. We may thus replace e^2/r with this quantity. The radius R to which the electron is removed is not less than about 1 Å (CH distance) and no more than 2 Å (CBr distance); as an average we might take 1.5 Å. Then $\Delta E \approx 7.5q$ eV. This is considerably larger than the value of 3 eV per charge determined from the experimental data. The agreement could be improved by assuming either a smaller average value of R (1.2 Å) or that the ionic character is less than $(X_A - X_B)/2$.

There are at least two reasons why we should be hesitant about taking the above model very seriously. First, the charges that are assigned by this procedure to the various atoms in the molecule are higher than seems reasonable. Second, the model does not take into account the changing electronegativity of the central atom as the ligands change (as pointed out by Nordberg, *et al.*[2b]).

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(23) Reference 2a, pp 79–82.

(24) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 98.

(25) W. Gordy, *Discuss. Faraday Soc.*, **19**, 14 (1955).

Let us look at the first of these. Taking the electronegativity of carbon as 2.5 and that of chlorine as 3.0, we conclude that the charge on the carbon atom in carbon tetrachloride is $+1.0\ e$. As opposed to this, Gordy[25] has estimated from quadrupole coupling data that the charge is only $+0.48$. Similarly, using 4.0 as the electronegativity of fluorine and 2.1 for hydrogen we obtain $+2.05$ as the carbon charge in fluoroform. Schwartz, Coulson, and Allen,[16] using empirically corrected Hartree–Fock results, find a charge of only 0.53 on this atom. Furthermore, if the charge of the carbon is as high as 2+, the assumption that the shift in energy varies linearly with charge is almost certainly wrong.[17] Gordy's formula, however, applies only to the ionic character of the σ part of the bond. In carbon tetrachloride there is a partial cancellation of the charge transferred from carbon to chlorine in the σ bond by a back-donation of electrons in the π bond. Thus the effective ionic character of the bond is substantially less than would be predicted by the formula $(X_A - X_B)/2$.

Looking now at the second point mentioned above, we note that the electronegativity[25] of a methyl group is 2.33 while that of a CCl_3 group is 2.58. Using Gordy's rule, then, the ionic character of a bond between one of these groups and a chlorine would be 0.34 for the methyl and 0.21 for CCl_3. The corresponding charges on the chlorines are -0.34 for CH_3Cl and -0.21 for CCl_4. Because of the changing electronegativity of the central atom the charge removed by the chlorines is not proportional to the number of chlorines. (In carbon tetrachloride, the charges are even less than indicated here, because of the π bonding.) Similar conclusions are drawn from the theoretical calculations of Schwartz, Coulson, and Allen. They show that for the fluorinated methanes the charge on the fluorines drops from -0.212 for CH_3F to -0.208 for CHF_3. In the binding energy shifts there is some compensation for this effect. Although the charge increases less than in direct proportion to the number of fluorines, the binding energy probably increases more than in direct proportion to the charge.

Summarizing this section, we have seen that there is a linear correlation between the binding energy shifts and the electronegativity of the ligands. We have seen a plausible argument that there should be such a linear correlation. However, to obtain a satisfactory agreement between the experimental values and theoretical estimates we must use ionic characters that are rather smaller than those obtained from Gordy's formula. This formula applies only to the σ bonds and we must reduce the ionic character from the predicted value to account for back-bonding in the π bond.

Acknowledgments. I would like to thank David A. Shirley and Charles S. Fadley for many thoughtful discussions and J. M. Hollander for making the electron spectrometer available to me. I am indebted to Charles Butler for assistance in constructing various pieces of apparatus needed in these experiments. I am pleased to acknowledge fellowship support from the John Simon Guggenheim Memorial Foundation. I would also like to thank Drs. Pople, Basch, and Schwartz for providing me with results of their calculations prior to publication.

Nonaqueous Silver Nitrate Solutions. Raman Spectral Studies in Acetonitrile

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Abstract: The Raman spectra of $AgNO_3$–CH_3CN solutions (0.01 to 9 mol/l.) have been investigated with He–Ne and Ar^+ ion lasers as excitation sources. In the symmetrical NO_3^- stretching frequency region, two frequencies, 1036 and 1041 cm^{-1}, are observed. The concentration dependence of the relative intensities of these two frequencies is examined from the viewpoint of ion–ion interactions. The band contours of C≡N and C—C stretching frequencies of CH_3CN have also been examined. As $AgNO_3$ is added, these bands resolve into two components and the variations of their relative intensities with concentration are understood, largely, through marked solvation interaction in the solute–solvent system.

Studies of Raman and infrared spectra of nitrates in aqueous solutions have been extensively used to explore the types of interactions arising in electrolyte systems. Recently, the splitting and the intensity of the NO_3^- bands in 1200–1500- and 750-cm^{-1} regions have been reviewed[1] to define spectroscopic guidelines to the disposition of the solvent molecules around the ions, and ion–ion association interactions in aqueous nitrates. The present paper reports the results of a Raman spectral investigation of $AgNO_3$ in an aprotic solvent, CH_3CN, to evaluate these criteria for nonaqueous electrolytes.

Experimental Section

Reagent grade $AgNO_3$ and CH_3CN were purified by the recrystallization, drying, and distillation techniques previously used in this laboratory and described elsewhere.[2,3] The preparation of the

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(1) D. E. Irish, A. R. Davis, and R. A. Plane, *J. Chem. Phys.*, **50**, (1969).

(2) G. J. Janz, M. J. Tait, and C. B. Baddiel, *J. Phys. Chem.*, **69**, 3634 (1965).

(3) R. P. T. Tomkins, E. Andalaft, and G. J. Janz, *Trans. Faraday Soc.*, **65**, 1906 (1969).