of these reactions. The results are listed in Table II. For HCOH$^{\bullet+}$ and DCOD$^{\bullet+}$ the metastable peaks are composite, comprising a flat-topped component and a narrower Gaussian-type signal. These can be separated by isotopic substitution.[15] For example, DCOH$^{\bullet+}$ loses D$^{\bullet}$ to produce HCO^{+} (see above) with a small energy release and loses H$^{\bullet}$ to produce DCO^{+} with a large energy release (see Table II).

The kinetic energy release results are also consistent with the theoretical calculations. If we consider the possible fragmentation pathways for HCOH$^{\bullet+}$ that yield HCO^{+} + H$^{\bullet}$, these include direct bond cleavage of the hydroxyl hydrogen (via **7**) and the rearrangement–fragmentation process (via **4**). The first process may be expected to be straightforward and to lead to a considerable amount of energy being converted to translational energy of the fragments. The second process (rearrangement–fragmentation) could lead in the first place to loss of the hydroxyl hydrogen which, in view of the calculated transition structure (**4**), would be a process not dissimilar to the direct loss via **7**. Alternatively, to lose the carbon-bound hydrogen, reaction could proceed via a transient vibrationally excited formaldehyde radical cation.[29] The latter process would allow for more energy to be deposited in internal modes and hence would be expected to occur with a smaller amount of energy converted into translational energy of the fragments. The experimental kinetic energy releases[9,14,15] indeed follow this pattern (Table II): loss of the hydroxyl hydrogen is associated with a much larger kinetic energy release than is loss of the carbon-bound hydrogen. The experimental results for labeled species (HCOD$^{\bullet+}$, DCOH$^{\bullet+}$) demonstrate, in addition, that the rearrangement–fragmentation process may well be nonergodic: the loss of carbon-bound hydrogen (deuterium) with a small kinetic energy release greatly exceeds the same process involving oxygen-bound deuterium (hydrogen). The rearrangement–fragmentation processes for HCOH$^{\bullet+}$ thus bear a resemblance to the methyl loss from the enol form of the acetone molecular ion where there is already strong evidence for nonergodic behavior.[18,30]

Concluding Remarks

The theoretical calculations reported in this paper predict that only HCO^{+} ions are produced in metastable transitions involving H$^{\bullet}$ loss from HCOH$^{\bullet+}$. This prediction is confirmed conclusively through mass-spectrometry-based experiments which examine directly the mestastably generated ions. The measured kinetic energy release for the hydroxyl hydrogen is substantially greater than that for the originally carbon bound hydrogen and may arise from nonergodic behavior.

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[29] Note that although formaldehyde molecular ions do lose H$^{\bullet}$ close to the thermochemical threshold for HCO^{+} formation, it has been concluded[17] that in the metastable (μs) time frame, fragmentation takes place from the excited A $^{2}B_{1}$ state at an energy which lies ca. 310 kJ mol^{-1} above the ground X $^{2}B_{2}$ state of $H_2CO^{\bullet+}$. Formation of HOC^{+} from the excited state is thermochemically feasible in principle (see Figure 3) via an isomerization to HCOH$^{+\bullet}$. However, we could find no experimental evidence for production of HOC^{+} from ionized formaldehyde and so conclude that there may be an energy barrier for the rearrangement reaction.

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(31) **Note Added in Proof**: Since submission of this manuscript, a new experimental estimate of 152 kJ mol^{-1} has been reported (McMahon, T. B.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3919) for the energy difference between HOC^{+} and HCO^{+}. This is close to the theoretical value of 157 kJ mol^{-1} (Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1) and therefore provides additional support for the conclusions of the present paper.

A Simple Method for Calculating Atomic Charge in Molecules

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Abstract: Atomic charges are calculated by using a bond orbital electronegativity method which was developoed previously to estimate group electronegativity. For any molecule or radical containing *N* different bonds the method requires the solution of *N* simultaneous equations which are linear in orbital charge. Input data required are the following: an effective nuclear charge for each atom (from modified Slater's rules), an effective principal quantum number (also from Slater rules), percent *p* character of the atomic orbitals used in the bonds, an estimate of the bond order for each bond, and an estimate of the effective number of electrons in each bonded atomic orbital prior to bonding (between 0 and 2). The flexibility of the method allows the bonding information to be obtained from either classical or resonance theory. It also allows for the treatment and analysis of simple or complex bonding situations. Results from this method are compared to both ESCA data and theory (Mulliken and Politzer procedures). It is shown that the method reproduces results obtained from the more sophisticated theoretical methods as well as correlating very well with experiment. It is also shown that the method can be used to provide insights into details of the electronic charge distributions in molecules.

The concept of atomic charge is one that has continued to elude attempts at clear and unambiguous definition.[1,2] However it remains very useful to chemists.[1,3-10] As a result there have been various attempts made to obtain both calculated and measured values.[1,11-15] Lately significant efforts have been made in both

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the theoretical and experimental areas.[2,11-13,16]

Mulliken's definition of atomic charge is still the most popular of the theoretical approaches.[15] This can be written as

$$\delta_A = \sum_i n_i[\sum_m (c_{im}{}^2 + \sum_{B,n} c_{im}c_{in}S_{mn})] \tag{1}$$

in which δ_A is the charge on atom A, n_i is the number of electrons in molecular orbital i, c_{im} (c_{in}) are the coefficients of atomic orbital m(n) on atom B(A) in molecular orbital i, and S_{mn} is the overlap between orbitals m and n. This definition is normally referred to as a "population analysis" since it sums over orbital populations. Although relation 1 is still widely used, some serious questions remain as to the meaning of the results.[2] The most often mentioned of these is the arbitrary division of overlap charge, i.e., the $c_{im}c_{in}S_{mn}$ terms, equally among bonded atoms. Even with these uncertainties, however, the method remains useful in identifying trends.

There have been various other methods proposed to circumvent some of the problems associated with (1).[5] These include both modifications of the overlap partitioning formula as well as schemes for directly integrating electron density over variously defined regions of space. In one such case the atom has been defined in terms of the minimum in the electron density function between bonded atoms.[17] Integration is then carried out over these atomic regions to yield values for charge. For linear systems the covalent radius can be used to separate atomic regions.[18] The use of a tetrahedral region about the carbon atom has also been used for some molecules.[19] In addition to these types of approaches, the use of optimum atomic radii obtained from electron density calculations has also been suggested as a means of representing electron densities.[20] Some of these methods have achieved reasonable success in correlating experimental data.

One method which appears to overcome some of the problems associated with (1) was developed in the mid-1970's by Politzer.[2,11] In this approach the molecule is first broken up into regions corresponding to individual atoms. These regions are based on free atom charge distributions. The molecular electron density (ρ) is then integrated over the region belonging to the atom

$$\delta_A = \int_A \rho \tag{2}$$

Politzer used this basic procedure to obtain reasonable atomic charges for a series of linear molecules.

Other schemes based on electronegativity equalization have also been developed to circumvent some of the difficulties associated with the purely theoretical methods.[3,12,13,21,22] Sanderson's scheme is about the simplest.[3] Atom charge is calculated directly from the difference in electronegativity between the isolated and bound states. The method, however, assigns the same charge to each atom of the same type within the molecule, e.g., all H atoms in CH_3OH are assigned the same charge. This of course is not in conformity with experience. All total equalization scheme suffer from the same defect. A partial electronegativity equalization method (PEOE) has been developed recently that overcomes this problem.[12] This is described below.

In addition to these theoretical methods, various experimental methods have been used to estimate atomic charge. These include NMR, NQR, Mossbauer, and IR spectroscopy.[1] All have suffered from the interference of effects like orbital hybridization. Recent developments in ESCA, however, indicate that this can be a powerful tool in this area.[13,16]

In closely related work, several recent articles have introduced a method for calculating electronegativity which is at once simple and widely applicable.[23] This work also indicated in a preliminary fashion that the same procedure can be used to calculate reasonable atomic charges. The present work expands this observation and demonstrates the utility of that method in this area as well as with electronegativity. It compares results from this method to values obtained with Mulliken's and Politzer's methods as well as from ESCA and PEOE results. In addition the method is shown to be capable of treating resonance effects, e.g., in NNO, and also electron pair donor acceptor bonding in a natural manner.

Calculation Procedure

In previous work[23] it was shown that the electronegativity of an orbital i on atom A can be expressed as

$$\chi_{A,i}(\delta_{A,i}) = \chi_{A,i}{}^0(1 + 0.5\sum_{j\neq i}\delta_{A,j} + 1.5\delta_{A,i}) \tag{3}$$

in which $\chi_{A,i}{}^0$ is the neutral atom electronegativity of orbital i on A, $\delta_{A,i}$ is the charge in i (i.e., 1 minus orbital occupation), and $\delta_{A,j}$ are the charges in the other bonded orbitals on A. The charge on atom A is given by the sum of the charges in each orbital

$$\delta_A = \sum_k \delta_{A,k} \tag{4}$$

where k includes both i and j orbitals in (3).

The method used in the present paper relies on this definition and is exactly as presented previously. For any molecule (M) or group (G) the atomic charges are calculated by applying two constraints to each bond in M or G. For each bond it is required that first the electronegativities for both atomic orbitals involved in the bond are equalized and second that charge is conserved in the orbitals. These principles can also be stated as follows. For every bond i in M or G between atoms A and B

$$\chi_A(\delta_{A,i}) = \chi_B(\delta_{B,i}) \tag{5}$$

$$\delta_{A,i} + \delta_{B,i} = 0 \tag{6}$$

(5) requires electronegativity equalization and (6) charge conservation. Note that there are two unknowns per bond, i.e., $\delta_{A,i}$ and $\delta_{B,i}$, and two equations. Thus each orbital charge is specified. This information and eq 4 yield values for the charges of each atom.

Note that (6) can be substituted into (5) to give

$$\chi_{A,i}(\delta_{A,i}) = \chi_{B,i}(-\delta_{A,i}) \tag{7}$$

Thus there is only one simple linear equation per bond which must be solved in order to obtain a complete set of atomic charges for the molecule or group. Note also that the method represents a partial rather than a total electronegativity equalization scheme. This is because it requires equalization separately in each bond and not throughout the molecule and also because it distinguishes among orbitals by using the different charge coefficients in (3). As has been shown previously, this fact allows for a more realistic treatment of group electronegativity.[23] In the present context it also provides for the circumventing of the problem with total electronegativity equalization schemes mentioned above. Specific examples of the use of this method are given in ref 23b.

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As presented thus far the method is able to treat the normal chemical bonding situation, i.e., the case in which the two atomic orbitals involved in the bond are half-filled prior to bonding. This, however, is not sufficient to treat all situations. For example, consider the case of ClCN. A careful theoretical analysis of this molecule[11] indicates that there may be significant bonding between filled p orbitals on Cl and the p orbitals on the C that also take part in the π-CN bonds. Likewise in the case of NNO it is likely that there is bonding between filled p orbitals on the central N atom and half-filled orbitals on the other N and O atoms. The present method accounts for these situations easily.

This can be seen by first noting that orbital electronegativity can be expressed as[24]

$$\chi_{A,i} = B_{A,i} - A_A n_{A,i}/2 \qquad (8)$$

where $n_{A,i}$ is the occupation of the i orbital. This equation is satisfied for the present system if the following relations are used,

$$B_{A,i} = \chi_{A,i}^0(2.5 + 0.5\sum_{j\neq i}\delta_{A,j}) \qquad (9)$$

$$A_A = 2 \times 1.5\chi_{A,i}^0 \qquad (10)$$

This is easily seen for a half-filled orbital (i.e., in which $n_{A,i} = 1$ and therefore $\delta_{A,i} = 0$) by substituting (9) and (10) into (8). This yields eq 3 with $\delta_{A,i} = 0$. Likewise for empty and filled orbitals (i.e., $n_{A,i} = 0$ and 2, respectively) the electronegativity becomes respectively

$$\chi_{A,i} = \chi_{A,i}^0(1 + 0.5\sum_{j\neq i}\delta_{A,j} + 1.5(1)) \qquad (11)$$

$$\chi_{A,i} = \chi_{A,i}^0(1 + 0.5\sum_{j\neq 1}\delta_{A,j} + 1.5(-1)) \qquad (12)$$

Next note that these equations refer to the atomic orbital before bonding, i.e., prior to any charge transfer. After bonding occurs charge $\delta_{A,i}$ accumulates in orbital i. This is treated as follows. If $n_{A,i}^0$ is the occupation prior to bonding then

$$n_{A,i} = n_{A,i}^0 - \delta_{A,i} \qquad (13)$$

This allows the general equation to be written as

$$\chi_{A,i}(\delta_{A,i}) = \chi_{A,i}^0(2.5 - 1.5n_{A,i}^0 + 0.5\sum_{j\neq 1}\delta_{A,j} + 1.5\delta_{A,i}) \qquad (14)$$

This equation can also be applied by using nonintegral values for $n_{A,i}^0$. This is useful in cases which have traditionally been treated with use of resonance theory. The case of NNO is one such example which will be illustrated below.

For a specific example of the application of these ideas consider the case of ClCN. It will be assumed that there are four different kinds of bonds in this molecule, i.e., ClC σ, ClC π, CN σ, and CN π. Cl will use sp^3 and p orbitals in its σ and π bonds, respectively. Both C and N will use sp and p orbitals in their σ and π bonds, respectively. The appropriate electronegativity values[19a] are $\chi_{Cl\sigma} = 3.92$, $\chi_{Cl\pi} = 3.07$, $\chi_{C\sigma} = 3.17$, $\chi_{C\pi} = 1.78$, $\chi_{N\sigma} = 4.42$, $\chi_{N\pi} = 2.40$. The equations for the normal σ and π bonds are

$$3.92(1 + 2 \times 0.5 \times 0.12\delta_{Cl\pi} + 1.5\delta_{Cl\sigma}) = 3.17(1 - 2 \times 0.5 \times 0.12\delta_{Cl\pi} + 2 \times 0.5\delta_{C\pi} + 0.5\delta_{C\sigma} - 1.5\delta_{Cl\sigma}) \qquad (15)$$

$$3.17(1 - 2 \times 0.5 \times 0.12\delta_{Cl\pi} - 0.5\delta_{Cl\sigma} + 2 \times 0.5\delta_{C\pi} + 1.5\delta_{C\sigma}) = 4.42(1 - 2 \times 0.5\delta_{C\pi} - 1.5\delta_{C\sigma}) \qquad (16)$$

$$1.78(1 - 2 \times 0.5 \times 0.12\delta_{Cl\pi} - 0.5\delta_{Cl\sigma} + 0.5\delta_{C\sigma} + 0.5\delta_{C\pi} + 1.5\delta_{C\pi}) = 2.40(1 - 0.5\delta_{C\sigma} - 0.5\delta_{C\pi} - 1.5\delta_{C\pi}) \qquad (17)$$

Equations 15 and 16 are the electronegativity equalization relations for the ClC σ and CN σ bonds, respectively. Likewise (17) is for the CN π bonds. $\delta_{Cl\sigma}$ and $\delta_{Cl\pi}$ are the charges accumulated on the Cl atom in its σ and π bonds to C. Of course the charges accumulated on the C atom in these two bonds are $-\delta_{Cl\sigma}$ and $-\delta_{Cl\pi}$. $\delta_{C\sigma}$ and $\delta_{C\pi}$ are the charges transferred to C through its σ and π bonds to N. Since the two CN π bonds are equivalent there is only one equation.

Note that it has been assumed that the two ClC π bonds have a bond order of 0.12. This has been done to reflect the results of a careful theoretical analysis by Politzer which suggests that some π bonding occurs between the C and Cl.[11] The data in that paper do not indicate any π bonding to be exceptionally strong. Thus a value of 0.12 was used for each of the two equivalent π bonds to give a total of about 25% π bonding between the C and Cl. Since the bonding is not total neither will any charge transfer. Thus the charge accumulation due to this bonding was reduced accordingly.

The equation for the ClC π bonds is

$$3.07(2.5 - 3.0 + 0.5\delta_{Cl\sigma} + 0.12 \times 0.5\delta_{Cl\pi} + 1.5\delta_{Cl\pi}) = 1.78(1 + 0.5\delta_{C\sigma} + 2 \times 0.5\delta_{C\pi} - 0.5\delta_{Cl\sigma} - 0.5 \times 0.12\delta_{Cl\pi} - 1.5\delta_{Cl\pi}) \qquad (18)$$

Notice that in eq 18 Cl becomes a π electron donor as compared to the C atom. The respective atomic electronegativities for Cl and C are −3.07 (0.5) and 1.78. This means that contrary to what would normally be expected in a ClC bond, electrons will flow to theC atom from the Cl. As will be seen below this is completely consistent with both Politzer's analysis as well as experiment.

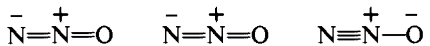
Solving (15) through (18) gives $\delta_{Cl\sigma} = -0.087$, $\delta_{Cl\pi} = 0.509$, $\delta_{C\sigma} = -0.037$, $\delta_{C\pi} = 0.10$. These in turn result in the following atom charges: $\delta_{Cl} = 0.035$, $\delta_C = 0.128$, $\delta_N = -0.163$. Note that the Cl charge is actually positive due to the back-bonding.

This example also illustrates the fact that partial bonding, i.e., bond orders less than 1, can be treated with the present system. In order to reflect this eq 14 needs to be generalized to

$$\chi_{A,i}(\delta_{A,i}) = \chi_{A,i}^0(2.5 - 1.5n_{A,i}^0 + 0.5\sum_{j\neq i} b_j\delta_{A,j} + 1.5\delta_{A,i}) \qquad (19)$$

in which b_j is the bond order of the bond involving the orbital j on atom A.

Next consider NNO. This molecule has two different N atoms. These will be distinguished as N(T) (terminal) and N(C) (central). The best way to treat this molecule appears to be in terms of resonance theory.[25] The major resonance forms are



$$\overset{-}{N}=\overset{+}{N}=O \qquad \overset{-}{N}=\overset{+}{N}=O \qquad N\equiv\overset{+}{N}-\overset{-}{O}$$

I II III

The first two structures differ in that the N(T)N(C) π bond uses p_x orbitals in one case and p_y in the other. Of course the N(C)O π bond will use the other p orbital for its bonding. Because of the energy similarities each structure is believed to contribute equally.[25]

It can be seen that there are four different kinds of bonds formed: one N(T)N(C) σ, one N(C)O σ, two N(T)N(C) π, and two N(C)O π. Not all of these will have a bond order of 1 in the molecule. In order to determine the bond orders to use a simple assumption will be made, i.e., the bond order is equal to the number of resonance structures containing that bond divided by the total number of structures considered (three in this case). Since both N(T)N(C) σ and N(C)O σ bonds appear in all three forms their bond order will be 1. Each of the N(T)N(C) π bonds appear in two structures, thus $b_{NN\pi} = {}^2/_3$. Each N(C)O π appears in one structure, thus $b_{NO\pi} = {}^1/_3$.

N(T) takes part in three bonds: one σ and two π. Each of its orbitals used in these bonds is half-filled prior to bonding. It will be assumed to use sp and p hybrids. Thus $\chi_{N(T)\sigma} = 4.42$ and $\chi_{N(T)\pi} = 2.40$.

The O atom also has three bonds: one σ and two π. It will be assumed to use sp^3 and p orbitals. Thus $\chi_{O\sigma} = 4.53$ and $\chi_{O\pi} = 3.15$. The sp^3 orbital will be half-filled before bonding. The p orbitals will resonate between empty and half-filled (i.e., between structures I and III or II and III above). Thus there will be two

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equations to be solved for each O π bond.

$$3.15(1 + 0.5\delta_{O\sigma} + 0.50 \times 0.33\delta_{O\pi}' + 1.5\delta_{O\pi}'') = \chi_{N(C)\pi}(-\delta_{O\pi}'') \quad (20)$$

$$3.15(2.5 + 0.5\delta_{O\sigma} + 0.5 \times 0.33\delta_{O\pi}'' + 1.5\delta_{O\pi}') = \chi_{N(C)\pi}(-\delta_{O\pi}') \quad (21)$$

However, these can be combined as

$$3.15(1.75 + 0.5\delta_{O\sigma} + 0.5 \times 0.33\delta_{O\pi} + 1.5\delta_{O\pi}) = \chi_{N(C)\pi}(-\delta_{O\pi}) \quad (22)$$

where $\delta_{O\pi}$ is $(\delta_{O\pi}' + \delta_{O\pi}'')/2$. Note that the expression for the corresponding N(C) π orbital has been simplified for clarity. However, exactly the same arguments hold as with the O π orbitals. Note also that (22) is equivalent to (19) with $n_{A,i}{}^0 = 0.5$, i.e., the average of an empty and a half-filled orbital i. Thus each π bond between O and N(C) can be seen as involving a p orbital on O with an initial occupation of 0.5 e. This of course is best interpreted as representing a resonance between two structures involving an empty and a half-filled orbital, respectively.

N(C) is involved in six formal bonds: one N(T)N(C) σ, one N(C)O σ, two N(T)N(C) π, and two N(C)O π. Each σ bond will use an sp orbital for bonding. Thus $\chi_{N(C)\sigma} = 4.42$. These will be half-filled prior to bonding. The appropriate electronegativity equalization equations for the NN and NO bonds are

$$4.42(1 + 2 \times 0.5 \times 0.67\delta_{N(T)\pi} + 1.5\delta_{N(T)\sigma}) = 4.42(1 - 2 \times 0.5 \times 0.67\delta_{N(T)\pi} + 2 \times 0.5 \times 0.33\delta_{N(C)\pi} + 0.5\delta_{N(C)\pi} - 1.5\delta_{N(T)\sigma}) \quad (23)$$

$$4.42(1 - 0.5\delta_{N(T)\sigma} - 2 \times 0.67 \times 0.5\delta_{N(T)\pi} + 2 \times 0.5 \times 0.33\delta_{N(C)\pi} + 1.5\delta_{N(C)\sigma}) = 4.53(1 - 2 \times 0.5 \times 0.33\delta_{N(C)\pi} - 1.5\delta_{N(C)\sigma}) \quad (24)$$

Since the N(C) atom uses two electrons in its σ bonding it has three remaining for involvement in the π bonds. There are two p orbitals available. Thus it will be assumed that each of these orbitals has an effective orbital population of 1.5 prior to charge redistribution upon bonding. This is interpreted as implying a resonance between half and completely filled orbitals. Thus assigning $n_{N(C)p}{}^0 = 1.5$ gives the following equations for the N(T)N(C) and N(C)O bonds

$$2.40(1 + 0.5\delta_{N(T)\sigma} + 0.5 \times 0.67\delta_{N(T)\pi} + 1.5\delta_{N(T)\pi}) = 2.4(0.25 - 0.5\delta_{N(T)\sigma} - 0.5 \times 0.67\delta_{N(T)\pi} + 0.5\delta_{N(C)\sigma} + 2 \times 0.33\delta_{N(C)\pi} + 1.5\delta_{N(T)\pi}) \quad (25)$$

$$2.40(0.25 - 0.5\delta_{N(T)\sigma} - 2 \times 0.67 \times 0.5\delta_{N(T)\pi} + 0.5\delta_{N(C)\sigma} + 0.5 \times 0.33\delta_{N(C)\pi} + 1.5\delta_{N(C)\pi}) = 3.15(1.75 - 0.5\delta_{N(C)\sigma} - 0.5 \times 0.33\delta_{N(C)\pi} - 1.5\delta_{N(C)\pi}) \quad (26)$$

Equations 23–26 can now be solved to obtain the atomic charges. This gives $\delta_{N(T)\sigma} = 0.107$, $\delta_{N(T)\pi} = -0.155$, $\delta_{N(C)\sigma} = -0.125$, $\delta_{N(C)\pi} = 0.529$ and final atom charges of $\delta_{N(T)} = -0.101$, $\delta_{N(C)} = 0.326$, $\delta_O = -0.224$. As will be seen below these results are in conformity with Politzer's work. This molecule represents a good example of the versatility of the present method to successfully treat both resonance effects and various orbital populations.

Since several different concepts have been introduced by means of these examples, the overall method will be summarized for clarity.

(1) Determine the number of bonds in the molecule and the bond order (*b*) for each. This can be done by using either classical bonding or resonance schemes or a combination of both.

(2) Assign each atom the appropriate orbital hybridization for each of its bonds. Use this to assign electronegativity (χ^0) for each orbital.

(3) Assign each bonding atomic orbital the appropriate occupation (n^0) prior to any charge transfer due to bonding. This will be one for the normal bond, 0 for an empty orbital and 2 for a filled orbital. Equivalent orbitals (e.g., a p_x and p_y) which can assume more than one occupation prior to bonding can be assigned an intermediate n^0 value.

(4) Assume charge conservation holds for each bond (eq 6). Write the appropriate electronegativity equalization eq 7 for each bond by using 19 and the information from steps (1), (2), and (3). For a system with *N* different kinds of bonds this will give *N* linear equations in *N* orbital charges.

(5) Solve these equations for orbital charges. Use eq 4 to obtain the charge for each atom.

Table I. Comparison of H Atom Charge,[a] ab Initio with Use of Mulliken Population Analysis vs. Present Method Results

molecule	Marriott[b]	present method
HLi	−0.18	−0.234
HCH_3	0.17	0.037
HCH_2Me	0.16	0.042
$HCHMe_2$	0.15	0.043
$HCMe_3$	0.16	0.043
$HCHCH_2$	0.17	0.072
HCCH	0.28	0.138
HCH_2NH_2	0.16	0.053
HCH_2OH	0.15	0.065
HCH_2F	0.16	0.073
HCH_2CN	0.23	0.062
HCN	0.31	0.185
HCHO	0.14	0.121
HCOMe	0.14	0.127
HCO_2H	0.18	0.157
HCO_2Me	0.19	0.158
$HCONH_2$	0.14	0.145
HCOF	0.18	0.167
HCF_3	0.17	0.158
HNH_2	0.33	0.133
HNHMe	0.34	0.138
$HNMe_2$	0.34	0.143
HNHCHO	0.39	0.151
$HNHNH_2$	0.34	0.136
HNO_2	0.40	0.249
HNCO	0.42	0.233
HOH	0.43	0.201
HOMe	0.44	0.207
HOCOMe	0.46	0.223
HF	0.52	0.259
$HSiH_3$	−0.13	−0.019
HSH	0.12	0.051
HSMe	0.10	0.057
HCl	0.28	0.204
corr coef		0.85

[a] Data for first H atom in each molecule. Me = CH_3. [b] Reference 26.

Results and Discussion

Recently an extensive series of theoretical values was reported for the atomic charge on H in HX molecules (where X represents various atoms or groups).[26] These were obtained with use of a Mulliken population analysis of results of ab initio molecular orbital calculations. This work was done in order to develop a convenient measure of substituent electronegativity. Table I compares these results to values obtained by using the present method. A correlation coefficient is also presented relating the two sets of results.

It is apparent that there is a reasonable amount of correlation. However, it can also be seen that there are differences. For example, the present scale attributes more electron-withdrawing character to CHO and $COCH_3$ in comparison to CH_3 than does Marriot. With the unresolved difficulties inherent in the Mulliken scheme (see above), it is uncertain as to whether a good correlation is desirable. It is clear, however, that overall trends should at least be reproduced. This as can be seen is done with the current scheme.

As mentioned above a partial electronegativity equalization scheme (PEOE) has been developed recently specifically to calculate atomic charges in molecules.[12] In this method the charge

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(26) Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959.

Table II. Comparison of Atomic Charges and Experimental Core Binding Energies for Carbon

molecule	E_B,[a] eV	PEOE[b]	present method
CH_4	0	-0.05	-0.148
$\mathrm{CH_3CH_3}$	-0.2	-0.046	-0.126
$\mathrm{CH_2CH_2}$	-0.1	-0.037	-0.144
$\mathrm{C_2H_2}$	0.4	-0.022	-0.138
$\mathrm{CH_3F}$	2.8	0.053	0.015
$\mathrm{CH_2F_2}$	5.6	0.162	0.196
$\mathrm{CHF_3}$	8.28	0.274	0.397
$\mathrm{CF_4}$	11.0	0.382	0.623
$\mathit{C}\mathrm{H_3CH_2F}$	0.2	-0.024	-0.109
$\mathrm{CH_3}\mathit{C}\mathrm{H_2F}$	2.4	0.058	0.0
$\mathit{C}\mathrm{H_3CF_3}$	1.1	0.022	-0.054
$\mathrm{CH_3}\mathit{C}\mathrm{F_3}$	7.6	0.273	0.425
$\mathrm{CH_3OH}$	1.6	0.009	-0.021
$\mathrm{CH_3OCH_3}$	1.4	0.012	-0.017
$\mathrm{H_2CO}$	3.3	0.051	0.069
$\mathit{C}\mathrm{H_3CHO}$	0.6	-0.025	-0.075
$\mathrm{CH_3}\mathit{C}\mathrm{HO}$	3.2	0.057	0.094
$\mathit{C}\mathrm{H_3COCH_3}$	0.5	-0.033	-0.071
$\mathrm{CH_3}\mathit{C}\mathrm{OCH_3}$	3.1	0.065	0.118
HCN	2.6	0.032	0.046
$\mathit{C}\mathrm{H_3CN}$	2.1	-0.029	-0.035
$\mathrm{CH_3}\mathit{C}\mathrm{N}$	2.1	0.041	0.071
corr coef		0.986	0.988

[a] Reference 12. [b] Reference 12. Values chosen were those that gave the best correlation with E_B data.

acquired by an atom is calculated in steps or cycles. In the case of a diatomic molecule the charge transferred is

$$q^\alpha = (1/2)^\alpha(\chi_B{}^\alpha - \chi_A{}^\alpha)/\chi_A{}^+ \tag{27}$$

where α is the number of the cycle and $\chi_A{}^+$ is the greater of the two atomic electronegativities. With polyatomic systems terms such as in the right-hand side of (27) are added together for each atom bonded to the atom of interest to give each q^α. The overall charge for an atom is simply the sum of the q^α over all cycles for that atom. Note that the $(1/2)^\alpha$ factor in (27) prohibits complete electron transfer in any bond by prohibiting complete electronegativity equalization. Hence the name "partial equalization of electronegativity" (PEOE).

The same authors suggest a full electronegativity equalization scheme (FEOE).[12] This method uses a set of linear equations as in the present scheme. But each equation contains a summation over (q_j/r_{ij}) terms for every atom in the molecule. This requires interatomic distances between every atom j and the atom under consideration (i). Since the results obtained from this method are not significantly different than those from the PEOE method, they will not be discussed further.

Table II contains PEOE values as well as results from the present method. In addition it presents experimental ESCA results of C-1s binding energies in the molecules given.[12] As mentioned above this technique holds the most promise of any experimental method for being easily related to atomic charge values.[1,16] Normally empiricial correlations with ESCA data take into account the charge on the atom of interest as well as the charges on the other atoms in the molecule.[12,13,16] It has been shown however, that with the set of molecules in Table II it is reasonable to compare calculated charges directly to the binding energy.[13] Thus, a correlation coefficient has been obtained for both calculational schemes vs. the ESCA data. Note the values obtained from the present method assumed that the F atom uses 10% s character in its bonding with the atoms contained in the table. If 0% s were used a poorer correlation (0.975) results. These results are quite consistent with other work.[12,23,27] Thus it appears that F uses about 10% s character in its bonds.

It can be seen that both methods correlate very well with the data. Previous work has shown that Mulliken population analysis on STO-3G wave functions with the same set of molecules gave only a 0.938 correlation coefficient.[13] These results indicate that the present method appears to offer a better representation of atomic charges than STO-3G and as good as the PEOE method.

Table III. Comparison of Atom Charges

molecule	atom	politzer[a]	present method
LiCCH	Li	0.49	0.36
	C	-0.36	-0.29
	C	-0.23	-0.19
	H	0.10	0.12
HCCH	H	0.14	0.14
	C	-0.14	-0.14
FCCH	F	-0.05	-0.06
	C	0.09	0.02
	C	-0.19	-0.11
	H	0.15	0.15
ClCCH	Cl	0.03	0.0
	C	-0.02	-0.02
	C	-0.15	-0.12
	H	0.15	0.14
HCN	H	0.18	0.19
	C	0.0	0.05
	N	-0.18	-0.23
FCN	F	-0.02	-0.03
	C	0.23	0.18
	N	-0.21	-0.15
ClCN	Cl	0.08	0.04
	C	0.10	0.13
	N	-0.19	-0.16
NCCN	N	-0.10	-0.13
	C	0.10	0.13
NCCH	N	-0.16	-0.15
	C	0.09	0.10
	C	-0.05	-0.02
	C	-0.06	-0.09
	H	0.18	0.15
SCO	S	-0.14	-0.07
	C	0.34	0.35
	O	-0.20	-0.28
OCO	O	-0.23	-0.25
	C	0.46	0.49
NNO	N	-0.08	-0.10
	N	0.33	0.33
	O	-0.25	-0.22
corr coef			0.978

[a] References 2 and 11.

Table III compares data obtained from Politzer's improved calculational scheme and the present method. Again a correlation coefficient has been calculated. It can be seen that the results are once again very good. The correlation coefficient was calculated without using the LiCCH results. This gives only a slightly better correlation (0.978 vs. 0.977) but it gives a much different equation relating the present data to Politzer's

$$\delta_{\mathrm{Pol}} = 0.98\delta \tag{28}$$

With the LiCCH data it is found that $\delta_{\mathrm{Pol}} = 0.92\delta$. Equation 28 represents more of the data better. It is both surprising and gratifying to see not only a very good correlation but also a relation that indicates essentially an identity between Politzer and the current system.

Note also that FCCH, FCN used 10% s character for F in conformity with the above results. In ClCCH and ClCN the Cl atom was assumed to use 25% s character. All four of these molecules reproduce Politzer's numbers very well. These molecules will be looked at more deeply because the results indicate an important and useful characteristic of the current scheme.

As was shown above ClCN was assumed to have 24% π bonding in the CCl bond. This was also done with the other molecules in this series. The halogen atoms used filled p orbitals in this bonding. As can be seen from eq 14, with $n_{A,i}{}^0 = 2$ the orbital is an electron donor (i.e., its atomic orbital electronegativity is negative). Thus, the π bonding serves to remove electrons from the halogen and transfer them to C. This gives F a low negative and Cl a positive charge in agreement with Politzer and experiment.[11] If no π bonding was assumed then Cl would be negative and F more negative. This would of course disagree with the other

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(27) Foster, J. P.; Weinhold, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

work. The method then not only reproduces the charge relationship but also supports the contention of π back-bonding in the halogens.

It can be argued that the same results would be obtained by assuming no FC or ClC π bonding and 0% s character in the halogen orbital involved in the σ bond. This would contradict the ESCA results presented above and electronegativity data presented in a separate paper.[23] Thus another assumption would be required to explain why F (or Cl) used different hybrids for different bonds. This of course is possible but unnecessary in light of Politzer's results.

Huheey also compared results he obtained for some of the molecules in Table III to Politzer's data.[28] He utilized an energy minimization method which allowed for three contributions, i.e., electronegativity energy, a Madelung potential energy using point charges, and a covalent energy term. His values also compared favorably with Politzer's. The present method does not require the use of all of the energy terms and thus requires much less input data. It also suggests that the ionic terms are not needed for the low polarity bonds. It does, however, indicate a possible direction to modify the present scheme to account more reasonably for high polarities such as in LiCCH.

Summary

A method is presented that allows the calculation of atomic charges in molecules to be done in a simple manner. Three relations are involved, viz., a definition of orbital electronegativity (eq 19), a bond electronegativity equalization scheme (eq 5), and a charge conservation principle (eq 6). It is shown that both empty and filled orbitals as well as variable bond orders are treated in a natural manner. This is done with the addition of b_i and $n_{A,i}^0$ terms in eq 19. Use of these relations leads to a series of simultaneous equations which are linear in orbital charge.

Results obtained from this method are compared to other theoretical (Mulliken population analysis, Politzer electron count method, and the PEOE method) and experimental ESCA data. It is shown that very good correlation is obtained. It is also shown that the method can provide a useful technique for analyzing bonding situations for type of bond and orbital used.

It should be noted that this scheme is designed to treat only inductive (through bond) effects. The treatment of properties which are sensitive to field effects (through space)[26,29] is thus outside of its scope.

Registry No. HLi, 7580-67-8; HCH_3, 74-82-8; HCH_2Me, 74-84-0; $HCHMe_2$, 74-98-6; $HCMe_3$, 75-28-5; $H_2C{=}CH_2$, 74-85-1; $HC{\equiv}CH$, 74-86-2; $MeNH_2$, 74-89-5; MeOH, 67-56-1; MeF, 593-55-3; MeCN, 75-05-8; HCN, 74-90-8; HCHO, 50-00-0; HAc, 75-07-0; HCO_2H, 64-18-6; HCO_2Me, 107-31-3; $HCONH_2$, 75-12-7; HCOF, 1493-02-3; HCF_3, 75-46-7; NH_3, 7664-41-7; H_2NNH_2, 302-01-2; $HNMe_2$, 124-40-3; H_2NCHO, 75-12-7; HNO_2, 7782-77-6; HNCO, 75-13-8; H_2O, 7732-18-5; HOAc, 64-19-7; HF, 7664-39-3; $HSiH_3$, 7803-62-5; H_2S, 7783-06-4; HSMe, 74-93-1; HCl, 7647-01-0; CH_2F_2, 75-10-5; CHF_3, 75-46-7; CF_4, 75-73-0; EtF, 353-36-6; MeAc, 67-64-1; $MeCF_3$, 420-46-2; MeOMe, 115-10-6; $LiC{\equiv}CH$, 1111-64-4; $FC{\equiv}CH$, 2713-09-9; $ClC{\equiv}CH$, 593-63-5; FCN, 1495-50-7; ClCN, 506-77-4; NCCN, 460-19-5; SCO, 463-58-1; OCO, 124-38-9; NNO, 10024-97-2.

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Theoretical Studies of Reactions of H_2SiNH and Its Isomer $HSiNH_2$

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Abstract: The structure and reactivity of unsaturated singlet silicon-nitrogen compounds is theoretically investigated. Ab initio calculations demonstrate that the planar silylene $HSiNH_2$ is the global minimum on the $SiNH_3$ surface, with the planar doubly bound species H_2SiNH 18 kcal/mol higher in energy. The internal rotational barriers are computed to be 26.9 kcal/mol for $HSiNH_2$ and 37.9 kcal/mol for H_2SiNH. However, the barrier for the inversion of H_2SiNH is only 5.6 kcal/mol, so that inversion is favored over rotation for this species. The isomerization connecting H_2SiNH to $HSiNH_2$ has a barrier of 60 kcal/mol. The transition-state structures, as well as the exothermicities of the concerted hydrogenation processes of both compounds, are also examined.

I. Introduction

In recent years, there has been considerable interest in the study of reactive intermediates which possess multiple bonds to silicon. Silicon-silicon and silicon-carbon double bonds in particular have been well-studied both experimentally and theoretically.[1,2] However, relatively little attention has been paid to the silicon-nitrogen double bond.

The substituted silanimine, R_2SiNR, was observed in both gas-phase pyrolysis and photolysis by Sommer.[3,4] Wiberg has also reported some evidence for the formation of compounds containing silicon-nitrogen double bonds.[5] To our knowledge, no other experimental data for such species or its properties have been reported in the literature. While several calculations have been performed on the related triply (HSiN)[6,7] and singly (H_3SiNH_2)[8] bound species, no theoretical study of silanimine has appeared to date.

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