Lewis Structure Representation of Free Radicals Similar to ClO

Warren Hirsch* and Mark Kobrak

Department of Chemistry, Brooklyn College of CUNY, Brooklyn, NY 11210; *whirsch@brooklyn.cuny.edu

At the level of introductory chemistry, oxidation numbers and formal charges are tools useful in analyzing the electronic structure of molecules. Oxidation numbers are assigned by giving a negative charge to the more electronegative atom in a diatomic molecule, while formal charges are assigned by assuming that electrons in a bond are shared equally between atoms, regardless of relative electronegativities. Electronegativity may be defined as the ability of an atom in a bond to attract electrons toward itself and is therefore a relative scale. Various scales are in use including those of Pauling, Mulliken, Allred–Rochow, and Sanderson *(1–4)*. The formal charge of an atom in a molecule can be calculated by taking the number of valence electrons originally surrounding the unbonded atom and subtracting the sum of the unshared electrons and half of the bonded electrons. When choosing the best possible Lewis structures, the conventional approach is to select species with lower absolute values of formal charges. These concepts, in combination with more advanced concepts such as conjugation and coordination are sufficient to interpret most observed chemical processes, and practicing chemists generally do not attempt more rigorous quantum chemical calculations unless high levels of accuracy are desired. The simple ideas above, therefore, provide a useful framework for understanding chemistry, as evidenced by their continued inclusion in introductory chemistry *(5)*.

However, despite their success, these concepts can fail even for simple systems. Students often find cases in which the rules are ambiguous or contradictory, and understanding these exceptions is important pedagogically. Some interesting examples of ambiguous cases are the ClO radical and its isoelectronic analogues. In the analysis of the Lewis structure of ClO, regardless of the scale chosen, students will recognize that oxygen is the more electronegative atom from an examination of periodic trends. Therefore, if one assumes a single bond and that the location of the unpaired electron is determined by electronegativity, it ought to be situated on the chlorine atom, since the more electronegative oxygen atom will attract enough electrons to form an octet (Figure 1A). However, in this structure, the formal charges are +1 and -1 for Cl and O, respectively, when calculated by the method described above. If the unpaired electron's location is determined by formal charge, it ought to be on the oxygen atom (Figure 1B), since this structure leads to a formal charge of zero on both atoms. Another possibility is an increase in the bond order to two, which lowers the formal charges to zero. In that case, the chlorine atom has an odd number of electrons and its valence shell exceeds an octet (Figure 1C). One might also consider a three-electron bond, as Pauling *(6)* did (Figure 1D). In that case, the formal charge would be +0.5 for oxygen and -0.5 for chlorine, and the halogen would still exceed an octet.

We propose to use density functional computational methods, in conjunction with a variety of other computational analysis methods, to accurately describe the electronic
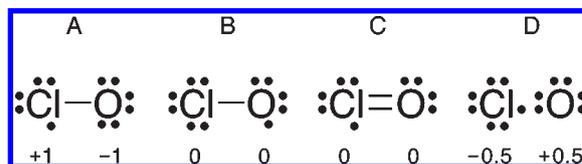

Figure 1. Some possible Lewis structures for ClO with formal charges of Cl and O.

structures for these species and attempt to interpret the results in a Lewis structure framework. The structures shown in Figure 1 represent possible resonance structures of ClO and its analogues. The interpretation will be based on the comparison of the computed results to the Lewis structures in Figure 1, with the goal of identifying which resonance structures most strongly contribute to the behavior of the system. In addition to the pedagogical value of the clarification of Lewis structures, halogen oxide molecules are of interest since they promote stratospheric ozone depletion and tropospheric ozone production *(7–10)*. A simple Lewis structure interpretation of these species may therefore be of interest to students of atmospheric chemistry.

Computational Methods

Calculations were performed to determine the equilibrium geometry of the molecules at the hybrid Hartree–Fock density functional level B3LYP using Gaussian 98 software with the basis set 6-311G++ (3df.3pd). The reliability of the B3LYP scheme is well-established for the prediction of structure, heats of formation, and vibrational properties of molecules. It has been used to study various chlorine oxide molecules with both full and open shells *(11)*. The computed equilibrium bond lengths of the molecules compare favorably to NIST experimental equilibrium bond length values *(12)*. Unfortunately, the above basis set did not allow computations with iodine atoms.

The Pauling electronegativity scale revised by Allred *(13)* was used to calculate the electronegativity differences between halogen and chalcogen atoms. Charge densities and spin densities at equilibrium were computed with the Mulliken, AIM (atoms in molecules), and NBO (natural bond orbital) methods. The AIM theory is a topological theory *(14)* that permits the estimation of bond orders in addition to the charge and spin densities *(15)*. The basis set used for AIM calculations was 6-31G+(d, p), at the bond length fixed by the geometric optimization method above. NBOs are localized orbitals that describe Lewis-type molecular structures. For radical structures electrons of opposite spins are considered to be in separate orbitals—leading to interesting consequences that will be discussed later. The NRT (natural resonance theory) option of NBO theory also permits numerical estimates of bond orders. These were not performed in the present work *(16)*.

The correlation coefficients between the electronegativity differences, $\Delta\chi$, and both the charge and spin densities computed by the three methods were determined, allowing for a comparison of the reliability of results given by these methods. The results of the calculations are listed in Table 1.

Results and Discussion

The halogen spin densities calculated by the three methods show significant correlation with the electronegativity differences. In Figure 2, we plot the Mulliken spin density on the halogen atom versus the Pauling electronegativity difference between the group 16 (chalcogen) atom and the group 17 (halogen) atom ($\Delta\chi = \chi_{16} - \chi_{17}$) for the nine isoelectronic compounds. It is evident that the spin density on the halogen atom increases as the electronegativity difference increases. The atomic charges of the halogen calculated by both the AIM and NBO methods also correlated strongly with the electronegativity difference, though the correlation in the Mulliken charges was considerably weaker. In the case of SBr, only AIM theory gives a negative charge for bromine, consistent with the fact that bromine is more electronegative than sulfur.

One should note that for *all* of the calculations, regardless of the sign or magnitude of the electronegativity difference, the chalcogen atom had a greater spin density than that of the halogen atom. Based on analysis of the Lewis structures in Figure 1, this indicates that formal charge is a more important factor than electronegativity in the configuration of the odd electron. According to the Mulliken calculations for ClO, approximately 70% of the spin density resides on the oxygen atom, making structure B the best structure of those in Figure 1. The linear correlation coefficient for the nine points on the plot is $r = 0.949$, indicating a confidence level of better than 99.9% certainty in the hypothesis that increasing electronegativity difference augments the halogen spin density. In fact, for SeF, which had the most negative electronegativity difference of all the molecules studied (−1.43), about 94% of the spin density resides on the Se atom and only about 6% on the F atom.
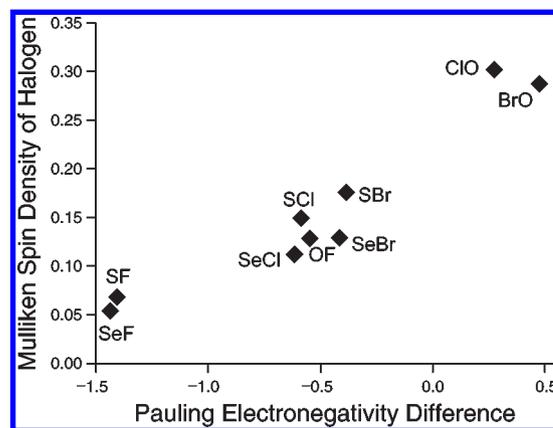

Figure 2. Effect of Pauling electronegativity difference on Mulliken spin density of halogen.

For OF, about 87% of the spin density is on the oxygen atom, indicating that structure B is the most strongly contributing resonance form. However, structure B does not adequately depict the bond order. The AIM bond order for OF was computed to be 1.5, consistent with simple molecular orbital theory, taking one half the difference between the number of electrons occupying bonding and antibonding MOs:

$$\sigma(2s)^2 \; \sigma^*(2s)^2 \; \sigma(2p_x)^2 \; \sigma^*(2p_x)^2 \; \pi(2p_y)^2 \; \pi(2p_z)^2 \; \pi^*(2p_y)^1$$

This MO method is included in most general chemistry textbooks *(17)*. Ordinary Lewis structures are inadequate to describe this molecule since, in the case of OF, hypervalency is not possible on either atom because of the absence of low-lying d orbitals. Structures similar to C or D in Figure 1 are therefore prohibited. In fact, analysis using NBO theory shows that in the case of ClO, where hypervalency in the case of the chlorine atom is possible, there is very little contribution from d orbitals. This was true for all of the molecules studied.

Table 1. Properties of Halogen Monoxides and Analogs

Molecule	Equilibrium Bond Length Calc/Å	Equilibrium Bond Length NIST/Å	Pauling $\Delta\chi$	Halogen						AIM Bond Order
				Mulliken Spin Density	Mulliken Charge	AIM Spin Density	AIM Charge	NBO Spin Density	NBO Charge	
SeF	1.76	—	−1.43	0.053	−0.355	0.089	−0.594	0.064	−0.510	1.1
SF	1.62	1.60	−1.40	0.067	−0.175	0.114	−0.597	0.083	−0.458	1.2
SeCl	2.14	—	−0.61	0.112	−0.254	0.134	−0.252	0.119	−0.187	1.4
SCl	1.99	1.98	−0.58	0.148	0.110	0.168	−0.156	0.150	−0.087	1.5
OF	1.35	1.35	−0.54	0.128	−0.056	0.149	−0.110	0.133	−0.081	1.5
SeBr	2.29	—	−0.41	0.128	−0.069	0.158	−0.150	0.137	−0.081	1.5
SBr	2.15	—	−0.38	0.175	0.045	0.193	−0.033	0.168	0.018	1.6
ClO	1.58	1.58	0.28	0.301	0.183	0.283	0.445	0.292	0.433	1.7
BrO	1.73	1.73	0.48	0.286	0.553	0.298	0.524	0.286	0.495	1.7
Correlation Coefficient with $\Delta\chi$				0.949	0.881	0.945	0.987	0.948	0.987	0.96

NOTE: The sum of the spin densities of both atoms in the molecule equals one and that the sum of the atomic charges equals zero. $\Delta\chi = \chi_{16} - \chi_{17}$.
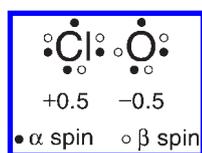
Figure 3. A novel Lewis representation of ClO.

NBO theory considers electrons of opposite spins to be in separate, singly occupied orbitals. The nonbonding electrons are localized on the atoms, while the bonding orbitals are two-center. This leads to two separate Lewis structures, corresponding to the two spin directions. Since the number of electrons is odd, the number of electrons is different for each structure. The α structure has the majority of the electrons and the β structure has the minority. For ClO (in fact for all of the nine compounds except SF and SeF) the α structure has one singly occupied σ bond and six singly occupied nonbonding orbitals—three on each atom. The β structure has a σ bond and a π bond and two nonbonding orbitals on each atom. The NBO treatment not only embraces the "different orbitals for different spins" concept, but also the "different hybrids for different spins" concept *(18)*. Using the latter concept, the α structure with a single bond and six nonbonding sites may be considered to be akin to the ClO⁻ anion. The β structure with two bonds and four nonbonding sites may be considered akin to the singlet ClO⁺ cation. This treatment is at variance with that of valence bond theory, where resonance structures are different forms of the *same* molecule. The bond lengths for the species ClO⁻, ClO, and ClO⁺ were calculated to be 1.69 Å, 1.58 Å, and 1.47 Å, respectively, indicating that the bond order of the ClO radical is between that of the singly bonded anion and the doubly bonded cation. The AIM bond orders for these species were calculated to be 1.4, 1.8, and 2.1, respectively, giving further support to this idea, although the numerical values should be considered to be relative, rather than exact. The superposition of α and β structures leads to average formal charges of +0.5 and −0.5 of the chlorine and oxygen atoms, respectively.

Interestingly, if structures B and C (both having zero formal charges on each atom) are combined, one may represent the results as the hybrid structure shown in Figure 3, which has a three-electron bond and an odd electron on each atom. This is essentially the result obtained from NBO theory. This structure violates the usual rules for drawing Lewis structures, which requires electrons to be paired, if possible. However, each atom has an octet, so that hypervalency, involving d electrons, need not be invoked. The total spin of the molecule is also equivalent to one unpaired electron owing to cancellation of opposite spins.

It remains to account for the greater spin density on the chalcogen atom and also the trend in the spin density of the halogen atom versus the electronegativity difference. The unpaired electron in the three-electron bond, which is in a pi orbital, will be more strongly attracted to the halogen with a charge of +0.5 than to the oxygen with a charge of −0.5. Since

it has a β spin, it will partially cancel the α spin of the unpaired electron on the halogen, therefore leaving the chalcogen with the greater spin density. The greater the electronegativity difference between the chalcogen and halogen atoms, the greater this effect will be. As the difference between the chalcogen and halogen electronegativities increases, the β pi electron will become more polarized toward the chalcogen, diminishing the spin cancellation on the halogen, and therefore increasing the halogen spin density. This explains the trend observed in Figure 2.

According to NBO analysis, the molecules SF and SeF each contain a single bond and an unpaired electron on the chalcogen atom. Therefore, they are both well represented by structure B in Figure 1. The AIM bond orders for SF and SeF are 1.2 and 1.1, respectively, lending further credence to the existence of a single bond. It is likely that p orbital overlap between the second row fluorine and the third and fourth row sulfur and selenium atoms is poor, making pi bonding difficult.

Conclusions

In the general chemistry classroom, if one has to present a single *simple* Lewis structure for a radical formed from a halogen atom and a chalcogen atom, the best structure is akin to Figure 1B—that is, a single bonded molecule with the odd electron on the chalcogen atom. For SF and SeF, the description is adequate. However, for the other seven molecules studied, the bond order is not represented accurately. Formal charge and hypervalency considerations may be included in the discussion of structures akin to Figures 1A, 1C, and 1D. For innovative instruction, and a bright group of students, the novel structure in Figure 3 is proposed. In the physical chemistry or computational chemistry classroom, a discussion of how these conclusions are reached may prove to be interesting. The effect of the electronegativity difference on the halogen spin density may be included in the context of NBO Theory.

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