Which Method of Assigning Bond Orders in Lewis Structures Best Reflects Experimental Data?

An Analysis of the Octet Rule and Formal Charge Systems for Period 2 and 3 Nonmetallic Compounds

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Lewis structures are an essential part of chemistry. They represent a shorthand method for discussing molecules that has become completely ingrained into our discipline, and techniques for drawing the Lewis structures are universally included in introductory chemistry courses. Implicit in Lewis structures is the concept of bond order *(1)*. This concept is one that all chemists have some level of intuitive understanding, but it lacks either a rigorous or consensus definition *(2–22)*.[1] Lewis's original concept of a covalent bond was a localized pair of electrons shared between two atoms. While this concept remains useful for many applications, it is clearly demonstrable that (except in diatomic or a few other simple, highly symmetric molecules, such as C_2H_2) the localized electron-pair concept is a significant oversimplification of the physical reality of covalent bonds.

Discussions concerning bond order have a long history. At least in recent years, the discussion of bond order can be generally divided into two schools of thought, which may loosely be termed the *theoretical* and *phenomenological* camps. Those in the theoretical camp *(2–15)* have tried to use computational methods to rectify Lewis's original concept with the reality of electron distribution in molecules. While much sophisticated analysis has been invested in this work, several potential difficulties are inherent in this approach. For instance, it is possible that a quantifiable relationship does not exist between the simplistic concept of covalent bond as a shared electron pair and the complex reality of the electron density of molecules or that the relationship is so complex that it defeats the purpose of a simple model. Also, care must be taken to ensure that any resulting model is in accord with the concept of bond order as it is understood by non-theoretical chemists. The concept of bond order is a human creation; it is not a directly observable property of a molecule. As such, it carries a good deal of the accumulated experience of chemists, and any attempt to refine the definition of bond order must retain this accumulated experience or it will be of little value to the chemical community at large. Mayer *(16)* provides a good history of the work concerning computation and bond order.

Those in the phenomenological camp *(17–22)* have taken a more practical, and less theoretical, approach to the problem of bond order. They turn to observable measurements of bonding, such as bond distance, bond enthalpy, IR stretching frequency, or more recently, quantifications of bonding electron density, such as ρ_b. To assign bond order, they compare the contact in question to "prototypical" examples of a single or double bond between that atom pair. While this may be a less conceptually satisfying approach than that of the theoretical camp, it does ensure that the results will be in keeping with the concept of bond order familiar to non-theoreticians. It is probably safe to say that, at times, both camps have not fully appreciated the subtleties of the other's arguments. These discussions have been going on for some time, but still generate considerable interest, as evidenced by the recent article in *Chemical and Engineering News (23)*.

In keeping with the nature of this *Journal*, the scope of this work will be limited to addressing the pedagogically relevant question: *Which system of assigning bond orders in Lewis structures best correlates with experimental measurements of chemical bonding?* In attempting to answer this question, theoretical discussions and a priori assumptions will generally be avoided. Instead, this discussion of bond order will focus on three observable properties of a molecule: bond distance, bond energy, and IR symmetrical stretching frequency.[2] Each of these criteria has been traditionally linked to concept of bond order, as it is understood through the experience of many chemists. The only assumption made is that, in comparing two bonds between the same atom pair, the contact with the higher bond order should have a (i) shorter distance, (ii) higher bond enthalpy, and (iii) higher IR force constant. Therefore, the bonds drawn on Lewis structures should be reflective of these experimental measurements of bonding. Also, by using this variety of quantification techniques, the possibility of error, or anomalous results,[3] caused by a single data source will be greatly reduced.

Bond distance is the most easily obtained of the three physical properties; compilations of gas-phase and crystallographic structures, such as the Cambridge Structure Database *(24)*, MOGADOC gas-phase database *(25)*, and NIST Computational Chemistry Comparison and Benchmark Database *(26)*, are available for most simple compounds. Pauling *(1)* noted that there is an exponential relationship between bond distance and bond order; this relationship can be expressed as

$$\text{bond order} = \exp\left(\frac{r_{ij} - d_{ij}}{b}\right) \qquad (1)$$

where r_{ij} is the single-bond distance between atoms i and j, d_{ij} is the observed (or calculated) distance, and b is a constant. Values for r_{ij}'s, and for the constant b, have been variously calculated *(22)*; however, the 1991 values of O'Keefe and Brese *(27)* will be used in this article. This method has been called the bond distance–bond order technique *(28)*, and bond orders calculated in this way will be referred to as bo_{BDBO} in this article.[4] These bo_{BDBO} values are highly dependent on the parameters, especially r_{ij}, and so the values for a specific pair of atoms may be systematically in error.

Bond energies are very useful values that, between the same atom pair, should be proportional to bond order. For molecules with only one type of bond, accurate bond energies can be calculated from either atomization energies or a Hess's law summation of the enthalpies of formation. However, for molecules containing a variety of bonds, determination of accurate bond energies

Table 1. Bonding Parameters for Selected Nonmetal Oxides

Oxide	Lewis Structure Bond Orders		Bond Distance/Å	bo$_{BDBO}$ (eq 1)	Bond Enthalpy/ (kJ/mol)	IR Sym Stretching Frequency/cm^{-1}	Force Constant/ (mdyn/Å) (eq 2)
	Octet Rule	Formal Charge					
NO	2.0	2.0	1.151	1.71	632	1904	15.99
NO$_2$	1.5	2.0	1.193	1.53	468	1318	7.66
N$_2$O$_4$	1.5	2.0	1.190	1.54	—	1380	8.40
ONNO$_2$ (2-coord N)	2.0	2.0	1.142	1.75	—	1830	14.77
ONNO$_2$ (3-coord N)	1.5	2.0	1.210	1.46	—	1630	11.72
PO	2.0	2.0	1.476	1.83	594	1233	9.47
PO$_2$	1.5	2.0	1.467	1.88	564	1320	10.85
P$_4$O$_6$	1.0	1.0	1.640	1.18	414	953	5.66
P$_4$O$_{10}$ (P–O terminal)	1.0	2.0	1.430	2.07	—	1408	12.35
P$_4$O$_{10}$ (P–O bridge)	1.0	1.0	1.600	1.31	—	1025	6.54
O$_2$	2.0	2.0	1.208	1.15	498	1580	11.79
O$_3$	1.5	2.0	1.278	0.95	303	1110	5.82
SO	2.0	2.0	1.481	1.58	521	1147	8.29
SO$_2$	1.5	2.0	1.432	1.80	536	1151	8.35
SO$_3$	1.33	2.0	1.418	1.87	494	1065	7.15
FO	1.0	1.0	1.354	0.66	220	1029	5.43
OF$_2$	1.0	1.0	1.412	0.56	192	928	4.42
ClO	1.0	1.0/2.0	1.570	1.14	269	854	4.75
ClO$_2$	1.0	1.5/2.0	1.470	1.50	261	1110	8.02
OCl$_2$	1.0	1.0	1.696	0.81	205	686	3.06

is significantly more complex. Therefore, bond energies will only be discussed for those molecules that contain a single type of bond. The force constant, k_{ss}, of the symmetrical stretching frequency (ν_{ss}) should also be proportional to the bond order, and is calculated as

$$k_{ss} = \mu(2\pi c \nu_{ss})^2 \qquad (2)$$

where μ is the reduced mass and c is the speed of light. IR spectra are available for many compounds through the *NIST Web Book (29)*.

The two systems to be investigated for assigning bond order in Lewis structures are the octet rule and formal charge. Both these systems are well known and so will be outlined only briefly here. When assigning bond orders based on the octet rule, the primary concern is to put eight electrons around the central atom. For odd-electron structures, the central atom may have seven electrons, but never nine. In the formal-charge approach, the formal charge of all atoms is to be minimized. For neutral atoms, all formal charges should equal zero. In anions, the sum of the formal charges should equal the charge on the ion, with no formal charge less than –1, and these –1 formal charges are generally on the most electronegative element (i.e., terminal oxygen atoms in oxides, oxoanions, and oxoacids). The difference between these two systems is well illustrated by the example of SO$_2$. The octet rule approach gives a Lewis structure with one single and one double bond, for an S—O bond order of 1.5. In the Lewis structure determined by formal charge, there are two double bonds, so the S—O bond order is 2.0 (a worked example is given in the online material). It should also be stressed that what is being evaluated are two systems for assigning bond

order in Lewis structures, and how well each system correlates to experimental measurements of bonding. There is no suggestion that either system represents the physical basis of chemical bonding. However, by comparing the predictions of these two systems to experimental data, it may be possible to show which system better reflects the observed subtleties of bonding in main-group molecules.

Finally, the types of compounds to be evaluated must show the difference between the two systems. Organic compounds, despite their great importance to chemistry, tend to give the same Lewis structures by either method and would therefore make a poor test set. On the other hand, considerable ambiguity exists concerning bond order in the following classes of inorganic main-group compounds: oxides, halides, oxohalides, oxoanions, and oxoacids. Not only do the two methods for producing Lewis structures give different bond orders in many of these compounds, but these are the types of compounds typically presented to introductory chemistry students when they are learning the topic of Lewis structures. As such, these molecules will be both a valid and appropriate test set for the evaluation of the two methods outlined above.

Results

Pertinent data for the oxides; halides and oxohalides; and oxoanions and oxoacids are collected in Tables 1, 2, and 3, respectively,[5] and full drawings of both the octet rule and formal charge Lewis structures are available in the online material. A close inspection of the data for the oxides (Table 1) reveals two distinct trends. For those compounds with only period 2 atoms,

Table 2. Bonding Parameters for Selected Nonmetal Halides and Oxohalides

Halide or Oxohalide	Lewis Structure Bond Orders		Bond Distance/Å	bo$_{BDBO}$ (eq 1)	Bond Enthalpy/ (kJ/mol)	IR Sym Stretching Frequency/cm^{-1}	Force Constant/ (mdyn/Å) (eq 2)
	Octet Rule	Formal Charge					
NF$_3$	1.0	1.0	1.365	0.82	281	1032	5.07
NCl$_3$	1.0	1.0	1.754	0.89	—	—	—
OCF$_3^-$ C–O	1.0	2.0	1.227	1.55	—	1514	9.28
OCF$_3^-$ C–F	1.0	1.0	1.391	0.83	—	1039	4.69
ONF$_3$ N–O	1.0	2.0	1.158	1.68	—	1783	14.02
ONF$_3$ N–F	1.0	1.0	1.431	0.68	—	731	2.54
O$_2$NF N–O	1.5	2.0	1.180	1.58	—	—	—
O$_2$NF N–F	1.0	1.0	1.467	0.62	—	—	—
O$_2$NCl N–O	1.5	2.0	1.202	1.49	—	—	—
O$_2$NCl N–Cl	1.0	1.0	1.837	0.71	—	—	—
PF$_3$	1.0	1.0	1.561	1.17	504	892	5.53
PF$_5$ equitorial	0.8*	1.0*	1.524	1.30	461	816	4.63
PF$_5$ axial	0.8*	1.0*	1.577	1.12	—	—	—
OPF$_3$ P–O	1.0	2.0	1.436	2.04	—	1417	12.51
OPF$_3$ P–F	1.0	1.0	1.524	1.30	—	873	5.30
PCl$_3$	1.0	1.0	2.043	1.08	323	504	2.48
OPCl$_3$ P–O	1.0	2.0	1.455	1.94	—	1322	10.89
OPCl$_3$ P–Cl	1.0	1.0	1.989	1.24	—	481	2.26
O$_2$PCl P–O	1.5	2.0	1.448	1.98	—	—	—
O$_2$PCl P–Cl	1.0	1.0	1.972	1.30	—	—	—
SF$_2$	1.0	1.0	—	—	366	940	6.22
SF$_4$ equitorial	0.75*	1.0*	1.545	1.33	340	—	—
SF$_4$ axial	0.75*	1.0*	1.646	1.01	—	—	—
SF$_6$	0.67	1.0	1.564	1.26	329	970	6.63
O$_2$SF$_2$ S–O	1.0	2.0	1.405	1.94	—	1269	10.15
O$_2$SF$_2$ S–F	1.0	1.0	1.530	1.38	—	848	5.07
SCl$_2$	1.0	1.0	2.010	1.03	270	525	2.79
O$_2$SCl$_2$ S–O	1.0	2.0	1.443	1.75	—	1205	9.15
O$_2$SCl$_2$ S–Cl	1.0	1.0	2.076	0.86	—	586	3.41
ClF	1.0	1.0	1.628	0.83	251	786	4.51
ClF$_3$ equitorial	0.67*	1.0*	1.597	0.90	175	752	4.13
ClF$_3$ axial	0.67*	1.0*	1.697	0.69	—	529	2.04
O$_3$ClF Cl–O	1.0	2.0	1.400	1.81	—	1061	7.33
O$_3$ClF Cl–F	1.0	1.0	1.598	0.90	—	715	3.73

*Indicates average value for non-equivalent A–X contacts

the Lewis structures based on the octet rule clearly do a better job describing the bond order (bo). For instance, both systems predict a bond order of 2.0 in NO, but in NO$_2$, the octet rule predicts a bond order of 1.5 and formal charge expects a bond order of 2.0. The bond distance, bond energy, and IR force constant all show a weaker bond in NO$_2$ than in NO, so the octet rule system better accounts for the physical data. Similarly, the octet rule Lewis structures assert that the O–O contact in O$_3$ (bo ~ 1.5) should be significantly weaker than in O$_2$ (bo ~ 2.0), where the formal charge Lewis structures predict equally strong O–O contacts (bo ~ 2.0) in both molecules. All of the physical

data for O$_3$ and O$_2$ support a lower bond order for O$_3$.[6] Therefore, when only period 2 elements are involved, the octet rule appears to give a better guide to the correct bond order.

However, when molecules with a period 3 central atom (or binary compounds containing a period 3 atom) are considered, the situation is different. For example, in the sulfur oxides (Table 1), the octet rule predicts a progressive decrease in S–O bond order as one goes from SO (bo ~ 2.0) to SO$_2$ (bo ~ 1.5) to SO$_3$ (bo ~ 1.33), but the formal charge Lewis structures suggest that all the S–O contacts in these three molecules should be of approximately equal strength (bo ~ 2.0). The physical measure-

Table 3. Bonding Parameters for Selected Nonmetal Oxoanions and Oxoacids

Oxoanions and Oxoacids		Lewis Structure Bond Orders		Bond Distance/Å	bo$_{BDBO}$ (eq 1)	Bond Enthalpy/ (kJ/mol)	IR Sym Stretching Frequency/cm^{-1}	Force Constant/ (mdyn/Å) (eq 2)
		Octet Rule	Formal Charge					
HNO$_3$	N–O (terminal)	1.5	2.0	1.211	1.46	—	—	—
HNO$_3$	N–O (H)	1.0	1.0	1.406	0.86	—	879	3.41
NO$_3^-$		1.33	1.67	1.241	1.34	—	1360	8.16
H$_2$SO$_4$	S–O (terminal)	1.0	2.0	1.422	1.85	—	1216	9.32
H$_2$SO$_4$	S-O (H)	1.0	1.0	1.574	1.23	—	831	4.35
HSO$_4^-$	S–O (terminal)	1.0	1.67	1.445	1.74	—	1170	8.63
HSO$_4^-$	S–O (H)	1.0	1.0	1.552	1.30	—	860	4.66
SO$_4^{2-}$		1.0	1.5	1.473	1.61	—	1100	7.63
HClO		1.0	1.0	1.691	0.83	—	1239	9.99
HClO$_4$	Cl–O (terminal)	1.0	2.0	1.408	1.77	—	—	—
HClO$_4$	Cl–O (H)	1.0	1.0	1.635	0.96	—	—	—
ClO$_3^-$		1.0	1.67	1.461	1.54	—	970	6.12
ClO$_4^-$		1.0	1.75	1.427	1.68	—	1060	7.31

NOTE: For those species with only one bond type (NO$_3^-$, SO$_4^{2-}$, ClO$_3^-$, ClO$_4^-$), no experimental data concerning bond enthalpy is available from the standard databases (26, 29).

ments show that SO$_3$ actually has the shortest S—O distance, and SO$_2$ has the highest bond energy and IR force constant. If all three measurements are considered, there is little difference between the S—O bonds in the three compounds, (which are also very similar to the S—O$_{terminal}$ bonds in H$_2$SO$_4$ and HSO$_4^-$; see Table 3) so the bond order prediction of ~2.0, made by formal charge, is confirmed. The phosphorus oxides continue this trend. For PO and PO$_2$, being isoelectric with NO and NO$_2$, the octet rule would predict a similarly weaker P—O bond for PO$_2$. In fact, the P—O contacts alter very little from PO to PO$_2$, exactly as predicted by formal charge. Finally, there are the chlorine oxides. There is some ambiguity concerning the correct formal charge Lewis structure, and so two bond orders are listed. What is clear is that there is some multiple-bond character to the Cl—O contacts in ClO and ClO$_2$, as indicated by comparison to the Cl—O contacts (presumably single bonds) in OCl$_2$. ClO has been studied computationally by Hirsch and Kobrak (30), and their results favored a bond order in the range of 1.5–1.8.

The trend observed above is continued for the nonmetal halides and oxohalides, as shown in Table 2. First, the lower-coordinate fluorides of period 3 nonmetals (PF$_3$, SF$_2$, and ClF, all of which would be expected to have A—X bond orders of ~1.0) may be compared to their hypervalent (31–35) analogues (PF$_5$, SF$_4$, SF$_6$, and ClF$_3$). In each case, an octet rule analysis predicts a bond order of less than one in the hypervalent species, but formal charge anticipates a bond order of 1.0 in every case. A good comparison is between PF$_3$ and PF$_5$. The bond distances, and bo$_{BDBO}$ values, differ little between the two molecules, but the bond enthalpies and force constants show some weakening in PF$_5$. However, between PF$_3$ and PF$_5$, the octet rule predicts a 20% decrease in bond order, but bond enthalpy only decreases by 8.5%. Overall, the comparison of lower-coordination and hypervalent fluorides favors the formal charge bond orders, though not conclusively.

In contrast, when one considers the oxohalides (Table 2), a clear distinction can be made. Consider the phosphine oxides; over the years, a large amount of discussion has been devoted to these compounds, usually focusing on the order of the P—O bond, which has been variously described as anywhere between a

single and a triple bond (4, 36–40). In the context of this article, the dichotomy is simple—the octet rule system predicts a bond order of one and the formal charge system predicts a bond order of two for the P—O bonds. The experimental data clearly and unambiguously favor the formal charge prediction. The P—O bo$_{BDBO}$ are 2.04 and 1.94 for OPF$_3$ and OPCl$_3$, respectively. Furthermore, the IR force constants for P—O symmetric stretch in these compounds are also as expected for a bond order of approximately two. For reference, one may consider the P—O distances and IR stretching frequency in P$_4$O$_{10}$ (Table 1). Additionally, experimental data from other phosphine oxides (40) also suggest a bond order of approximately two in these compounds, so if theoretical arguments are set aside and only physical data are considered, a bond order of two for the P—O bond in phosphine oxides is a clear conclusion. Similarly, in the sulfones, O$_2$PCl, and O$_3$ClF, the experimental data clearly support the formal charge prediction of A—O double bonds in these molecules, with the A—O bo$_{BDBO}$ values ranging from 1.75 to 1.98, and force constants commensurate with a double bond. Electron density calculations carried out by Purser (20) also support the idea that the A—O$_{terminal}$ contacts in oxidized phosphines and sulfones are essentially double bonds.

The oxohalides (Table 2) in this study with a period 2 central atom are OCF$_3^-$, ONF$_3$, O$_2$NF, and O$_2$NCl; these molecules are of considerable theoretical interest (7, 21, 36, 37, 39, 41, 42). In each, the O—A bond is clearly stronger than the A—F (or N—Cl) bond, suggesting a bonding pattern analogous to their isoelectric, phosphorus-centered analogues. The phosphorus-centered analogues have a total of approximately five bonds to the central atom, which would be contrary to the above results indicating that period 2 central atoms always follow the octet rule. However, a closer inspection of these compounds reveals a more complex story. In OPF$_3$, the P—F bonds are actually shorter than the P—F bonds in PF$_3$, but in ONF$_3$, the N—F bonds are *much* longer than the N—F bonds in NF$_3$. Additionally, the IR stretching data indicate substantial bond weakening of the N—F bonds in the oxidized species. If one sums the bo$_{BDBO}$ values in ONF$_3$, the total of the four bonds is 3.72, actually slightly less than what would be expected based on the octet

Table 4. Bonding Parameters for Group 13 Halides and Tetrahalide Anions

Halides and Tetrahalide Anions	Lewis Structure Bond Orders		Bond Distance/Å	bo_BDBO (eq 1)	Bond Enthalpy/ (kJ/mol)	IR Sym Stretching Frequency/cm⁻¹	Force Constant/ (mdyn/Å) (eq 2)
	Octet Rule	Formal Charge					
BF_3	1.33	1.0	1.307	0.98	646	1450	8.55
BF_4^-	1.0	0.75	1.380	0.81	646	1197	5.83
BCl_3	1.33	1.0	1.742	1.02	444	956	4.47
BCl_4^-	1.0	0.75	1.848	0.77	484	766	2.87
AlF_3	1.33	1.0	1.630	0.95	593	935	5.75
AlF_4^-	1.0	0.75	—	—	643	—	—
$AlCl_3$	1.33	1.0	2.060	1.03	426	595	3.20
$AlCl_4^-$	1.0	0.75	2.127	0.86	474	—	—

rule. Therefore, if it is conceded that the N−F bonds may be less that a single bond (bo ~ 0.7), then ONF_3 does follow octet rule expectations, though it may be difficult to predict these bond orders with simple Lewis structures (32). An analogous case can be made for OCF_3^-, where the sum of the bo_BDBO values is 4.04. In the O_2NX molecules, the physical data suggest a N−X bond order of ~1 and a N−O bond order of ~1.5 each, and the sum of the bo_BDBO values at nitrogen is again less than 4.0. Although each of these molecules has been suggested to violate the octet rule, this analysis does not support such a conclusion, and instead shows that the nitrogen oxohalides and OCF_3^- strongly support for the idea that a bond order sum of approximately four is the upper limit for a period 2 central atom.

The oxoanions and oxoacids (Table 3) also support the trends observed above. For nitric acid and the nitrate ion, the octet rule Lewis structures give a good prediction of bond order. However, for the sulfur- and chlorine-centered oxoacids and oxoanions, the formal charge Lewis structures give a clearly superior correlation to the bo_BDBO values and also to the IR force constants. As the Lewis structures based on the octet rule for the sulfur- and chlorine-centered oxoacids and oxoanions predict that all A−O bond orders will be one, they are obviously inadequate to represent the bonding situation in these species.

In the analysis of main-group compounds carried out above, the emerging pattern shows that the octet rule only holds for period 2 central atoms (C, N, and O). Period 3 central atoms are not limited to eight electrons, at least in the context of Lewis structures, and the formal charge system gives a prediction of bond order that better matches the experimental data. One other case to consider is that of the group 13 halides (Table 4). In all cases, the terminal atom has much greater electronegativity than does the central atom, so the A−X bonds are highly polar. A characteristic of these compounds is that the anions have significantly longer A−X distances than do the neutral molecules. This has often been explained (43) in the context of the octet rule: (i) the anions have a bond order of one and (ii) in the neutral molecules, to achieve eight electrons on the central atom, one double A=X bond is made, making the average A−X bond order 1 1/3. The problem with such an explanation is the highly unusual double bond to a terminal fluorine or chlorine. This suggests a negative partial charge the central boron or aluminum and a positive partial charge to the terminal halides. Given the electronegativities of the elements involved, this seems unlikely, as Gillespie has previously observed (33, 44).

Fortunately, a better explanation exists for the bond length difference between the neutral group 13 halides and their anion

analogues, based on the bond valence model (BVM) developed by I. D. Brown (22, 45, 46). Though this model was devised for inorganic materials, it has been shown to also apply to hydrogen bonds and to discrete molecular compounds that contain coordination bonds (28, 47, 48). The highly polar bonds in the group 13 halides can also be treated using the BVM approach (an illustrated example is given in the online material). In this model atoms are treated as individual cations or anions, and the sum of the bo_BDBO values at a central atom is expected to be equal to that atom's charge (or valence). For the group 13 halides, the central boron or aluminum would have a +3 charge and each terminal halide would be -1. In the neutral molecules, there are three contacts that must sum to a total bond valence of three, and the bond order of each A−X contact would be expected to be 1.0. However, in the anion, the central atom will still have a total bond valence of three, but now this is spread over four A−X contacts, so the expected bond order of each A−X bond is 0.75. These expected bond orders show good agreement with the bo_BDBO values in Table 4. This is also in accord with the formal charge prediction of bond order, since an average bond order of 0.75 gives a formal charge of zero for the central atom and an average formal charge of −¼ for the terminal halides: a charge distribution much more in line with chemical intuition than the A=X double-bonded structures cited above. In this case, the octet rule prediction is in error because it forces too many electrons, eight, about the central boron or aluminum. Formal charge gives a more correct prediction of bond order because it accepts that central atoms may have different numbers of electrons in their valence sphere. Data from the $BX_{3-n}H_n$ (X = F or Cl, n = 1 or 2) (17) give further support to these conclusions. If the octet rule is to be obeyed in the series BF_3, HBF_2, and H_2BF, the B−F bond orders should be as follows: BF_3–1.33, HBF_2–1.5, and H_2BF–2.0. However, the observed B−F distances are virtually identical (BF_3–1.309 Å, HBF_2–1.311 Å, and H_2BF–1.316 Å), strongly suggesting that all the bonds are single bonds. The same trends are observed for the chlorine analogues. Since Gillespie (49) has also shown that there is no need to invoke multiple bonding to explain Lewis acidity trends in these species, the conclusion that the group 13 AX_3 molecules contain only single bonds is well supported.

At this point, the results of this study can be summarized as *For main-group compounds, the Lewis structure that minimizes formal charge gives the best prediction of bond order, but period 2 central atoms are limited to a formal maximum of eight valence electrons. Period 3 central atoms may have more than eight valence electrons.*

Such a statement is not new—it was certainly implied by the results of Straub *(18),* and Purser *(19, 20)* also reached a similar conclusion.

Discussion

Statistical Analysis of the Data

While the computation of bo_{BDBO} values is imperfect, they do provide a readily available and self-consistent quantification technique for bond order. Therefore, it may be useful to analyze the difference between bo_{BDBO} and the bond orders as predicted by the two methods of drawing Lewis structures.

A compilation of these values, arranged by central atom, is contained in Table 5. The result of this statistical analysis gives strong support to the general conclusions of this article concerning bond order. For all of the period 3 central atoms (Al, P, S, and Cl) and boron, the formal charge Lewis structures are more accurate in predicting bo_{BDBO} values, with a combined error almost 1/3 of that for the Lewis structures that conform to the octet rule. Only when nitrogen or oxygen are central atoms,[6] and the limitation of eight formal valence electrons becomes an issue, do the Lewis structures based on the octet rule outperform those based on formal charge.

Hypervalence and the Octet Rule

The topic of hypervalence has received a fair amount of attention *(6, 21, 35, 36, 50)* in recent years, possibly because of over-emphasis of the octet rule. As has been shown above, the octet rule only acts as a limit to a few, albeit very important, central atoms: nitrogen, oxygen, and presumably carbon. Noury, Silvi, and Gillespie *(32)* have pointed out that the nature of covalent bonds is the same in both hypervalent compounds (such as SF_6) and those that follow the octet rule (such as SF_2)—nothing in this study suggests otherwise. However, what is different is the sum of the bonding at the central atom. These results show a demonstrable, physical difference between isoelectric species when one central atom is in period 2 and the other is in period 3, examples of such pairs in this study include NO–PO, NO_2–PO_2, ONF_3–OPF_3, O_2NCl–O_2PCl, O_3–SO_2, and FO–ClO. In each of these cases, an increase in $A-O$ (and $A-X$) bond order occurs in the species containing the period 3 atom. Only in the group 13 halides, where the maximum of 8 electrons on the central atom is not an issue, do the period 2- and period 3-centered species have similar bo_{BDBO} values. Since there is a difference in how, for instance, nitrogen and phosphorus behave as central atoms, some term should be retained to express this difference. Possibly the problem lies in the implication that hypervalent species are somehow "unusual" *(7).* Data on the oxides, oxoacids, and oxoanions of As, Se, Te, Br, I, and Xe suggest bonding behavior similar to period 3 central atoms *(18),* so in terms of the main-group nonmetals, hypervalent central atoms appear to be much more common than adherence to the octet rule. Perhaps it would work better if the "unusual" species where considered to be those period 2 central atoms that are limited to eight formal valence electrons.

The physical basis for the eight-electron limitation on period 2 central atoms is not at all obvious. Several researchers have suggested that this may simply be a size issue *(7, 32)*—there is not enough space around a period 2 atom for more than four MOs. Period 3 central atoms, having larger bonding spheres, can potentially accommodate more than four MOs and therefore exceed the eight-electron limitation. When one remembers

Table 5. Mean Unsigned Error, Lewis Structure Bond Order vs bo_{BDBO}

Central Atom	N_{obs}	Error	
		Octet Rule	Formal Charge
N	16	0.18	0.35
O	7	0.39	0.50
total of N, O	23	0.24	0.40
P	15	0.44	0.16
S	16	0.47	0.18
Cl	13	0.33	0.18
Al	3	0.27	0.06
B	4	0.27	0.03
total of P, S, Cl, Al, B	51	0.40	0.16

NOTE: N_{obs} is the number of entries in Tables 1–4 with known A–X distance.

that covalent bonds are actually just the result of the energy reduction caused by orbital rearrangement when two atoms approach each other closely, this explanation has some theoretical justification, at least on a qualitative level. Results by Ponec *(50)* also support such an interpretation. However, this is not the only possible explanation of the observed eight-electron limitation for period 2 central atoms, and so this, or any other, proposal will require significant quantified evaluation before it could be accepted as *the* explanation of the observed effect.

Conclusions and Recommendations

In this study, the bond orders of a diverse selection of main-group, inorganic compounds have been studied, based on experimentally determined bond distances, bond enthalpies, and IR force constants. Overall, the analysis clearly shows that the Lewis structures that minimize formal charge give the best prediction of experimental bond parameters, with the restriction that period 2 central atoms are limited to a formal maximum of eight valence electrons. Based on the above, the following specific recommendations can be made to chemical educators:

- *Formal charge is an essential part of drawing the Lewis structures of main-group compounds*: For central atoms other than C, N, and O, Lewis structures that do not minimize formal charge are suboptimal. It is always more efficient to teach students the correct techniques initially, rather than an over-simplified approach that may or may not be corrected later in their education.

- *The octet rule limits the formal valence electrons on period 2 central atoms*: B, C, N, and O may have no more than eight electrons, but they may have less (seven in radicals, six on B and on C in carbenes, etc.).

- *Species that do not conform to the octet rule are common for most of the main-group elements*: So-called hypervalent or electron-deficient species are not unusual for central atoms other than C, N, or O. Presenting Lewis structures of compounds such as BF_3, SO_2, or ClO_4^- that conform to the octet rule contradicts the experimental evidence and should be discontinued. Except for those central atoms limited by the octet rule, the Lewis structure that minimizes formal charge gives the best fit to experimental data, and these structures only should be presented to chemistry students.

Notes

1. The definition of bond order given in general chemistry textbooks, based on molecular orbital theory, gives an appropriate definition of bond order for diatomic molecules, and is probably superior to Lewis structures determined by either the octet rule or the formal charge approach. However, this definition is a special case, and is not easily applicable to molecules with more than two atoms.

2. Use of experimental methods in this work to quantify bond order is *not* meant to indicate that the "phenomenological" camp has superior arguments, but simply because a more practically oriented approach is better suited to answer to the title question. To determine *why* the results are as observed, one clearly must turn to computational methods.

3. It is possible to get anomalous results with each of these physical methods. For instance, "longer but stronger" bonds have been reported *(51)*, and the coupling of IR modes can lead to anomalously high stretching frequencies *(52)*.

4. Two types of bond orders are discussed in the article: the values of bo_{BDBO} are calculated from eq 1 and the values of bo are obtained from the Lewis structures.

5. The bond order predictions from the Lewis structures in Tables 1–4 are given as the average of equivalent A–X contacts. If one uses the process of drawing resonance structures, the identical result will be obtained.

6. It is highly probable that the bo_{BDBO} values for O_2 and O_3 are systematically in error.

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