Notes

Hypervalence and the Octet Rule

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Introduction

Musher[1] originally defined hypervalent molecules as those formed by the non-metals of groups V–VIII (15–18) of the periodic table in any of their valences other than their lowest stable valences of 3–0, respectively. More simply and more comprehensively, a hypervalent molecule is defined as a molecule in which the octet rule is not obeyed in the sense that there are more than four pairs of electrons in the conventional Lewis diagram for the molecule.[2] According to this definition, species such as SiF_5^-, PCl_5, SF_6, and XeF_4 are hypervalent.

Hypervalence and ab Initio Calculations

However, in several recent papers[3,4] the results of ab initio calculations were used as a basis for the claim that hypervalence is an unnecessary concept. The results of these calculations show that, because of the ionic character of the bonds in hypervalent molecules such as SF_6 and PCl_5, there are *effectively* fewer than six electron pairs in the valence shell of the central atom. For example, in SF_6 the charge on sulfur is computed to be +3.62 and the charge on each fluorine is found to be −0.63. This result was interpreted to mean that the *effective* number of electron pairs in the valence shell of sulfur is only 2.4 and that sulfur therefore obeys (or rather does not exceed) the octet rule. However, this conclusion is at variance with the octet rule as proposed by Lewis.[5] Lewis took no account of bond polarity and regarded molecules such as SF_6 and PCl_5 as exceptions to the octet rule because in their Lewis diagrams they have six and five electron pairs, respectively, in the valence shell of the central atom. Unless the octet rule is given an interpretation different from that proposed by Lewis, these molecules must be regarded as exceptions to the octet rule.

Interpretation of the Octet Rule

In these recent discussions of hypervalence, it is assumed that an atom obeys the octet rule if it does not have *more* than four electron pairs in its valence shell although it may have *fewer* than four pairs as indicated by the calculated *effective* number of 2.4 pairs in the valence shell of sulfur in SF_6. Similar ab initio calculations have given values of +1.6 for the charge on carbon and −0.40 for the charge on each fluorine in the CF_4 molecule,[3] corresponding to an effective number of 2.4 pairs of electrons in the valence shell of carbon. However, Lewis proposed that an atom in a molecule obeys the octet rule if there are four pairs of electrons—fully shared, partially shared, or unshared—and not more than four pairs or fewer than four pairs in its valence shell. Indeed, molecules such as BF_3, in which there are only three pairs of electrons (in the Lewis sense) in the valence shell of boron, have long been considered to be exceptions to the octet rule. But, according to the new interpretation of the octet rule, it appears that the boron atom would be considered to obey the octet rule, and the observation that BF_3 is an electron pair acceptor, whereas CF_4 is not, would be left unexplained.

The Octet and Duodecet Rules

If the meaning of the octet rule is changed as some authors appear to have done, then it should no longer be assiciated with the name Lewis. However, there are sound reasons for not supplanting Lewis's original concept. Four shared pairs of electrons completely fill the valence shell of carbon so that CF_4 is a rather unreactive molecule. In contrast, it takes six pairs of electrons in the valence shell of sulfur in SF_6 to attain the same lack of reactivity. Indeed, there is much evidence to suggest that, whereas the valence shells of C, N, O, and F in period 2 are completely filled by four pairs of electrons, six pairs of electrons are needed to completely fill the valence shells of all the period 3 and 4 elements such as P, As, S, and Se. Thus PF_5 and PCl_5 are reactive molecules that are readily attacked by water and form the anions PF_6^- and PCl_6^-, respectively, behaving as Lewis acids just like BF_3 and BCl_3. One of us has suggested that it is more relevant to use a duodecet rule[7] for the period 3 and 4 elements rather than the octet rule which is only valid for period 2 elements just as the corresponding rule for period 1 elements is a duet rule.

Participation of d Orbitals

The long-lasting debate on the "extent of participation of d orbitals" in the bonding of hypervalent molecules has tended to further confuse the discussion. It is well-known that a reasonably good approximate molecular orbital or valence bond description of the bonding in hypervalent molecules can be given in terms of s and p orbitals only, although more exact descriptions require basis sets that include d functions, and of course the most exact ab initio calculations require a very large set of highly modified s, p, and d "atomic" orbitals. But it is not correct to maintain that, because the bonding in a molecule can be approximately described on the basis of s and p orbitals only, such a molecule obeys the octet rule. The SF_6 molecule can be described in terms of the valence bond model by using resonance structures with four covalent and two ionic bonds or by a molecular orbital model that uses only s and p orbitals on the sulfur atom. But this does not alter the fact that there are six polar bonds in the molecule; in other words, there are six pairs of electrons that are unequally shared between the valence shell of the sulfur atom and the valence shells of each of six fluorine atoms. That there are indeed six bonds is clearly shown, for example, by the existence of six bond paths in Bader's topological analysis of the electron density in this and related molecules.[6] So according to Lewis's original formulation of

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(1) Musher, J. L. *Angew. Chem., Int. Engl.* **1969**, *8*, 54.

(2) See, for example: Atkins, P. W.; Shriver, D. E.; Langford, C. H. *Inorganic Chemistry*; W. H. Freeman: New York, 1990; p 38.

(3) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. Extensive references to earlier work on hypervalency are given in this paper.

(4) Cioslowski, J.; Mixon, S. T. *Inorg. Chem.* **1993**, *32*, 3209.

(5) Lewis, G. N. *Valence and the structure of atoms and molecules*; Chemical Catalog Co.: New York, 1923.

(6) Robinson, E. A. *THEOCHEM* **1989**, *186*, 9.

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the octet rule, and the definition of hypervalence, SF_6 and related molecules are indeed hypervalent.

Is Hypervalence a Useful Concept?

It is, nevertheless, worthwhile to ask if hypervalence is a necessary or even a useful concept. In our opinion it is not. We suggest that it is better to recognize that there are many exceptions to the octet rule as originally formulated and as Lewis recognized when he said that "the rule of eight, in spite of its great importance, is less fundamental than the rule of two, which calls attention to the tendency of electrons to form pairs".[5] We propose that it is more useful to recognize that a duet rule applies to the period 1 elements, an octet rule to the period 2 elements, and a duodecet rule to the period 3 and 4 elements. In view of the similarity in properties of SF_6 and CF_4, there can be no fundamental difference between the bonding in these two molecules—both have highly polar bonds. However, calling the former a hypervalent molecule and the latter a "normal" molecule is often taken to mean that there *is* a significant difference in the nature of the bonding. For example, the bonds in SF_6 are often described as three 3-center−4-electron bonds while those in CF_4 are described as "normal" 2-electron bonds. Similarly the description of the axial bonds in PF_5 as a 3-center−4-electron bond (or effectively two half-bonds) while the equatorial bonds are described as "normal" 2-electron bonds is inconsistent with the small difference in the lengths of the axial bonds (157.7 pm) and the equatorial bonds (154.3 pm). Just as there is a great similarity between the unreactive molecules CF_4 and SF_6, there is, likewise, is a great similarity between the much more reactive molecules BF_3 and PF_5, which are exceptions to the octet and duodecet rules, respectively, in the sense that they both have incomplete valence shells. These similarities are obscured by the concept of hypervalence and by the recent reformulation of the octet rule but are made clear by the original Lewis octet rule and the analogous duodecet rule. Similarly, the difference in properties between CF_4 and SiF_4 is only readily understandable when CF_4 is regarded as having a filled valence shell and SiF_4 as having an incomplete valence shell. However, the usefulness of the octet and duodecet rules should not be taken to mean there are no exceptions. Certainly, ions such as $SeCl_6^{2-}$ and $TeBr_6^{2-}$ appear to be exceptions to the duodecet rule, and possible reasons for this have been discussed.[8] Although it would probably be less useful to formulate a 14-electron or similar rule for the elements of period 5 and beyond, such as XeF_6 and IF_7, it is also not useful to consider such molecules to be hypervalent.

Conclusions

In our opinion, the interpretation of the results of ab initio calculations to indicate that molecules such as SF_6 do not violate the octet rule, and need not therefore be considered to be hypervalent, is misleading and is not consistent with Lewis's original formulation of the octet rule. Molecules such as SF_6 do indeed violate the octet rule as formulated by Lewis, and this has important consequences that need to be discussed. Nevertheless, hypervalence is not a useful concept for this purpose, whereas the original Lewis octet rule and an analogous duodecet rule for this period 3 and 4 elements form a useful basis for this discussion. The concept of hypervalence obscures the fundamental similarity between molecules such as CF_4 and SF_6 that obey the octet and duodecet rules, respectively, and the similarities between those such as BF_3 and PF_5 that do not obey these rules. Moreover, the conclusion from ab initio calculations that both CF_4 and SiF_4 obey (or rather do not exceed) the octet rule obscures the fact that SiF_4 is an electron pair acceptor whereas CF_4 is not. Finally, hypervalence has sometimes been taken to imply a fundamental difference between the bonding in hypervalent molecules and in non-hypervalent molecules which does not exist.

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(7) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1991.

(8) Gillespie, R. J.; Hargittai, I. *The VSEPR of Molecular Geometry*; Allyn and Bacon: Boston, 1991.