The [p–π*]σ and [s–π*]σ Bonds. FNO and O_2F_2

Richard D. Spratley and George C. Pimentel

Contribution from the Chemistry Department, University of California, Berkeley, California. *Received November 18, 1965*

Abstract: There is remarkable difference between the bond orders in the related pair of molecules, HNO and FNO. The same difference appears in the related pair, H_2O_2 and F_2O_2. These differences can be attributed to electron sharing in the antibonding π* orbitals of the parent molecules, NO or O_2. In such a case, a weak bond is formed with an atom of high electronegativity, such as F, and the parent molecule is little affected. Atoms with lower electronegativity, such as H or Li, bond more strongly by releasing more electron density into the π* orbital, weakening the parent molecule bond. Such bonds, called [p–π*]σ and [s–π*]σ bonds, also account for the variety of oxygen–fluorine compounds now known, their structures, and their labile chemistry. The existence and structures of a number of presently unknown molecules are predicted.

The fluorine and hydrogen molecular counterparts, FNO-HNO and F_2O_2–H_2O_2, have formulas compatible with conventional valence rules. Yet the bonding differs strikingly in each pair, as indicated by the bond lengths and stretching force constants shown in Table I. To add to our understanding of these differences, lithium nitroxide, the lithium counterpart of HNO, was produced under matrix conditions in this laboratory.[1] The trend established by FNO and HNO was continued. Other examples are the free radicals FO_2 and HO_2 which, though related in formulas, display a striking contrast in their vibrational potential functions (see Table I). The need for a correlating theory that accounts for the bonding, as well as the empirical formulas, is obvious.

Linnett and co-workers have discussed the bonding of FNO and other nitrosyl compounds[2] and of O_2F_2[3] within the framework of his double quartet scheme. In the latter case, the proper choice among ten contributing structures cannot be made *a priori*, thus tempering confidence in the explanation.

Table I. Vibrational Frequencies, Stretching Force Constants, and Bond Lengths of Some N–O and O–O Bonds

Molecule	ν_{N-O} or ν_{O-O}, cm^{-1}	k_{N-O} or k_{O-O}, mdyne/A	r_{N-O} or r_{O-O}, A	Ref (ν and k, r)
NO	1876	15.5	1.15	*a*, *a*
FNO	1844	14.7	1.13	*b*, *c*
ClNO	1799	14.1	1.14	*b*, *d*
BrNO	1801	14.1	1.15	*b*, *e*, *f*
HNO	1570	10.5	1.21	*g*, *h*
LiON	1352	8.0	...	1, ..
O_2	1556	11.4	1.21	*a*, *a*
FO_2	1500	10.5	...	*i*, *j*, 19
F_2O_2	...	...	1.22	.., 4
HO_2	1389	6.1	...	6, ..
H_2O_2	877	4.6	1.48	*k*, *l*

[a] G. Herzberg, "Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules," Van Nostrand Co., Princeton, N. J., 1950. [b] J. P. Devlin and I. R. Hisatsune, *Spectrochim. Acta*, **17**, 206 (1961). [c] C. V. Stephenson and E. A. Jones, *J. Chem. Phys.*, **20**, 135 (1952). [d] J. D. Rogers, W. J. Pietenpol, and V. Williams, *Phys. Rev.* **83**, 431 (1951). [e] W. G. Burns and H. J. Bernstein, *J. Chem. Phys.*, **18**, 1669 (1950). [f] J. A. Ketelaar and K. J. Palmer, *J. Am. Chem. Soc.*, **59**, 2629 (1937). [g] H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958). [h] F. W. Dalby, *Can. J. Phys.*, **36**, 1336 (1958). [i] R. D. Spratley, Ph.D. Dissertation, University of California, Berkeley, 1965. [j] A. Arkell. *J. Am. Chem. Soc.*, **87**, 4057 (1965). [k] E. Hirota, *J. Chem. Phys.*, **28**, 839 (1958). [l] R. L. Redington, W. B. Olson, and P. C. Cross, *ibid.*, **36**, 1311 (1962).

Jackson[4] offered two models for the bonding in O_2F_2. In a valence bond treatment, he invokes significant contribution from ionic structures. In another approach, he elaborates a three-center molecular orbital proposal made by Lipscomb, apparently in private communication to Jackson.[4] More recently, Kasai and Kirshenbaum[5] paraphrased this three-center molecular orbital idea as they discussed the bonding of OOF. These authors refer to possible interaction between the fluorine p orbital and one of the antibonding π orbitals.

We have developed a molecular orbital explanation that is, apparently, quite similar to that offered by Kasai and Kirshenbaum for O_2F. In the present work we have, however, attempted to encompass a much larger range of molecules. We propose that the bonding in all of the molecules in Table I can be considered in terms of electron sharing in the antibonding orbitals of the diatomic parent molecules, NO or O_2. This idea, coupled with familiar electronegativity arguments, permits us to understand the bonding trends in these molecules.

The Proposed Bond

In the simplest molecular orbital description of the first row diatomic molecules, the 2s orbitals are considered to be nonbonding and the orbital occupancies are represented as follows.

$$\text{NO} \quad (\sigma_z)^2(\pi_x)^2(\pi_y)^2(\pi_x^*)^1 \tag{1}$$

$$\text{O}_2 \quad (\sigma_z)^2(\pi_x)^2(\pi_y)^2(\pi_x^*)^1(\pi_y^*)^1 \tag{2}$$

The spatial charge distribution attributed to the outermost electron, placed in a singly occupied antibonding π* orbital, is considered to involve two nodal planes. The resulting four-lobe distribution is shown in Figure 1. Nitric oxide has one such singly occupied π* orbital; oxygen has a second, oriented in a plane perpendicular to the first.

Bonding to Nitric Oxide. A monovalent atom (F, H, Li, etc.) could overlap its partially occupied

---

(1) W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2361 (1966).

(2) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961); J. W. Linnett and R. M. Rosenbert, *Tetrahedron*, 20, 53 (1964).

(3) J. W. Linnett, *J. Chem. Soc.*, 4663 (1963).

(4) R. H. Jackson, *ibid.*, 4585 (1962).

(5) P. H. Kasai and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **87**, 3069 (1965).

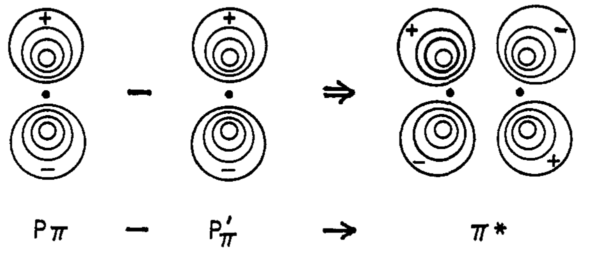


Figure 1. Electron distribution attributed to the π* molecular orbital.

valence orbital with *one* of the four lobes of the singly occupied π* orbital. The resulting sharing of electrons would lower the energy and form the new bond. The bond orders in the resulting triatomic molecule would, then, depend upon the net movement of electrons into the NO antibonding orbital. Figure 2 portrays schematically the result, taking account of the electron-donating properties of the monovalent atoms. The highly electronegative fluorine atom (4.0 on the Pauling scale) releases very little electron density and therefore forms a weak F–N bond. Because of the small release of the fluorine electron into the π* orbital the N–O bond order is reduced only very slightly. (In principle, the fluorine might *withdraw* electrons from the π* orbital, leaving a *stronger* N–O bond, but the facts indicate the opposite.) Chlorine and bromine, with lower electronegativities (3.0 and 2.8, respectively), should bond to NO with somewhat greater release of electron density into the π* antibonding orbital. Hence ClNO and BrNO should exhibit weaker NO bonds than in FNO, just as is suggested by the vibrational frequencies shown in Table I. The effect should also be evident in the bond lengths, but it is not. However, both the expected effect (~0.01 A) and the reverse trend seen in Table I are probably within the experimental uncertainties.

Hydrogen (electronegativity 2.1) surrenders still more of its electron density to the π* orbital, forming a more normal H–N bond and reducing significantly the N–O bond order. Lithium, with its very low electronegativity (1.0), releases its electron almost completely to the nitric oxide π* orbital, weakening still further the N–O bond. Having done so, the positive lithium ion then apparently attaches itself to oxygen, possibly indicating it is the more negative atom of the heteronuclear NO^-.

In all three cases, perfect spin pairing is suggested. However, when the ligand bonds only to a portion of the π* orbital as in the weaker bonds (*e.g.*, in FNO), diamagnetism may persist. We name these bonds after the parent orbitals (in brackets) and add the σ symbol to indicate the axial nature of the electron distribution that holds the X atom to NO.

Bonding to Oxygen. Obviously, the same scheme can be applied to O_2 with the added feature that now there are two singly occupied π* orbitals which can engage in this type of bonding. After one fluorine atom has formed a weak F–O bond to the oxygen π_x^* orbital, a second fluorine can form a similar weak F–O bond with one lobe of the oxygen π_y^* orbital. Intuitively we expect this to occur at the opposite end of the molecule, which would give O_2F_2 a skewed structure and a dihedral angle near 90°, as observed. Since two fluorines so bonded affect the O–O bond very little in O_2F_2, one fluorine should also affect it little (and even less) in O_2F.

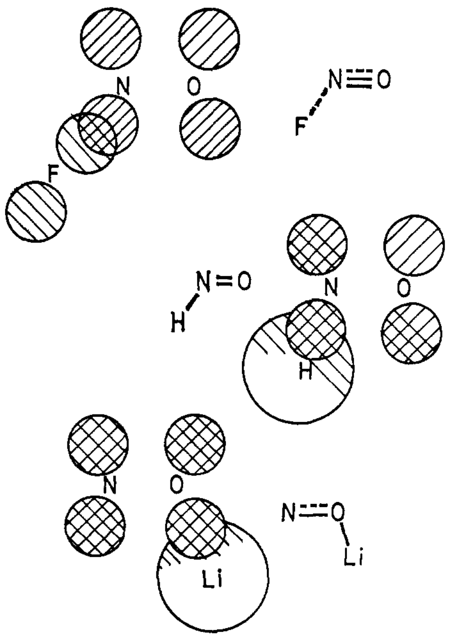


Figure 2. A representation of the electron distribution in the molecules XNO. (Diagonal lines represent electron spin and probability distribution.)

Hydrogen atoms would bond with geometry similar to that of O_2F_2, but with a much weaker O–O bond, by the same argument applied to HNO. Now, however, the large effect caused by the attachment of two H atoms to O_2 implies a significant difference between H_2O_2 and HO_2. In fact, the O–O stretching force constant found for HO_2 by Milligan and Jacox[6] is noticeably higher than that for H_2O_2.

Charge Distribution. This treatment implies that there is charge movement toward the O_2 (or NO) and more such movement for H_2O_2 than for O_2F_2. These two dipole moments are known and that for H_2O_2, 2.1 D.,[7] is higher than that for O_2F_2, 1.44 D.[4] Interpreted in terms of the vector addition model, the O_2F_2 dipole moment requires a transfer of 0.14 electron charge from F to O. The hydrogen peroxide moment requires a transfer of 0.42 charge.

We see that the postulated bonding involvement of the π* electrons provides a framework that encompasses both the bond orders and the charge distributions, where known, in all of the molecules listed in Table I.

Implications and Applications

Fortunately there are quite a number of implications that follow from the bonding model. Some of these furnish predictions that will provide tests, as more data appear, and measure the usefulness of the model.

Other XNO and XO_2 Compounds. Since the effect on either NO or O_2 is slight as fluorine bonds to it, these three species must have comparable electron-attracting power. It is thus implied that NO and O_2 might take the role of the fluorine atom in similar compounds. A substitution of NO for F in FNO

---

(6) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **38**, 2627 (1963).

(7) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

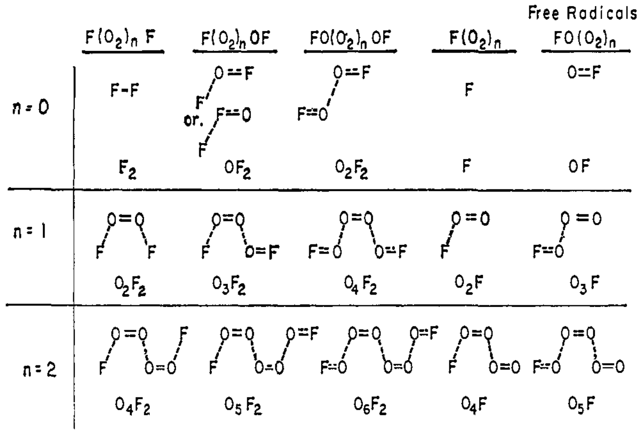
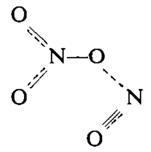


Figure 3. Families of fluorine–oxygen compounds.

gives $(NO)_2$ and, if NO is like fluorine in electron-attracting power, the dimer bond should be weak, as it is. (The heat of dimerization has been estimated to be 4 kcal/mole.[8]) A similar substitution of O_2 for F in FNO (or NO for F in O_2F) gives us O_2NO. Again a weak bond is predicted. This compound, $O_2 \cdot NO$, has been reported by Guillory and Johnston[9] and the NO stretching frequency, 1840 cm^{-1}, is close to that of FNO, consistent with the prediction. Finally, if we consider substituting O_2 for F in the compound O_2F, we obtain the controversial O_4 molecule, considered to have a dimerization energy in condensed phase of only 125 cal/mole.[10]

One additional implication is that two NO molecules might substitute for fluorine in O_2F_2. This would give the compound $ON \cdot O_2 \cdot NO$, with the empirical formula N_2O_4. This proposal brings to mind the isomeric N_2O_4 molecules postulated by Crawford and coworkers[11,12] as well as by Baldeschwieler and Pimentel.[13] Although four isomeric N_2O_4 structures were postulated, an extended $ON \cdot O_2 \cdot NO$ structure was not among them. Nevertheless, there is one feature in the spectrum assigned to the *cis*-nitrite structure, $O_2N—O—N=O$ (Crawford's species D, Baldeschwieler's species A), that attracts attention. This spectrum includes an absorption at 1829 cm^{-1}, far above the usual region for the characteristic nitrite absorptions of CH_3ONO and HONO. Baldeschwieler[13] showed that this absorption displayed an oxygen-18 isotopic shift appropriate to nitric oxide weakly bonded to some other group. Furthermore, he found that infrared irradiation at 20°K caused an isomerization of this substance to another species with a spectrum more like those of the familiar nitrites (Baldeschwieler's species B). The structure of A was represented



1

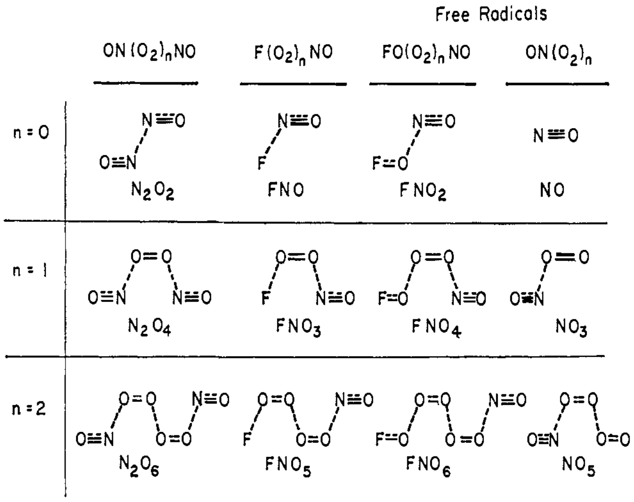
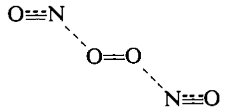


Figure 4. Families of nitric oxide–oxygen–fluorine compounds.

Whether the structure **1** is correct or whether the molecule is actually structure **2**



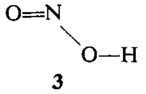
2

we believe the 1829-cm^{-1} NO stretching frequency relates the bonding in this molecule to our present discussion.

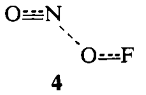
Oxygen–Fluorine Compounds. It is interesting to seek other diatomic molecules that might substitute for O_2 and NO. One obvious case is the diatomic molecule OF, predicted in the simple MO treatment to have a 1.5 order bond and an orbital occupancy

$$\text{OF} \qquad (\sigma_z)^2(\pi_x)^2(\pi_y)^2(\pi_x^*)^2(\pi_y^*)^1 \qquad (3)$$

Once again, we find a singly occupied π^* orbital which can accept electrons to form weak bonds, as do O_2 and NO. Thus, for an example, one can predict the existence of a molecule ONOF, the fluorine analog of nitrous acid, but with very different bonding.



3



4

More important, we find an array of compound types involving weak bonds between the units F, NO, O_2, and OF, as pictured in Figures 3 and 4. Among the families in Figure 3, we find the interesting situation that every structure in the third column has an isomeric counterpart in the first column. Although it is possible that only one of the two will be stable, the situation is strongly reminiscent of the isomeric structures actually found for N_2O_4[11–13] and for N_2O_3.[11] Most impressive, however, is the presentation of a working hypothesis to explain the proliferation of fluorine–oxygen compounds suggested by the work of Von Grosse, *et al.* These workers have reported evidence for ozone difluoride

---

(8) O. K. Rice, *J. Chem. Phys.*, **4**, 367 (1936); A. L. Smith and H. L. Johnston, *J. Am. Chem. Soc.*, **74**, 4696 (1952).

(9) W. Guillory and H. S. Johnston, *ibid.*, **85**, 1695 (1963).

(10) G. N. Lewis, *ibid.*, **46**, 2027 (1924).

(11) W. G. Fateley, H. A. Bent, and B. Crawford, Jr., *J. Chem. Phys.*, **31**, 204 (1959).

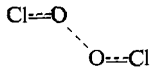
(12) R. V. St. Louis and B. Crawford, Jr., *ibid.*, **42**, 857 (1965).

(13) J. D. Baldeschwieler, Ph.D. Dissertation, University of California, Berkeley, 1959.

(O_3F_2)[14-16] and for O_4F_2.[17] Not only the existence of these compounds (and of O_2F_2) but also their extremely labile chemistry is consistent with the adduct-like structures pictured in Figure 3.[18] We note that the weak interactions between O_2F molecules suggested by the matrix spectra of Spratley, *et al.*,[19] are also explained by one of the O_4F_2 structures.

Oxygen–Chlorine and Oxygen–Bromine Compounds. Chemists traditionally differentiate fluorine from the other halogens in view of some of its rather unique properties. We suggest that this distinctiveness of fluorine may prove to be less marked than now supposed. The similarity of the XNO molecules is one piece of evidence in this direction (see Table I).

Accordingly, the bonding in the as yet unknown molecules Cl_2O_2 and Br_2O_2 acquire great interest. Aside from the conventional single bond structure of H_2O_2, there are two alternative structures suggested in the first and third columns of Figure 3. Because of the relatively strong bond of the ClO radical, 63 kcal/mole,[20] the new structure seems to be quite likely.



5

Conclusions

We see that the [p–π^*]σ and [s–π^*]σ bond proposal at last provides a link that connects the diverse bonding in the related molecules in Table I. Thus it removes, in part, a profound weakness of the classical valence rules; though these rules may predict the formulas, they often are impotent in anticipating the structures and relative stabilities of newly discovered molecules. Finally, it offers an answer to the startling differences represented among the bonding properties of free radicals, as exemplified most vividly by the contrast between the 112 kcal/mole dimerization energy of the CN free radical[21] and the 4 kcal/mole dimerization energy of NO.[8] Electron sharing in bonding π orbitals, as between two CN radicals, forms a new bond and tends to strengthen the parent molecule bonds. Electron sharing in antibonding π^* orbitals, as between two NO radicals, forms a new bond but at the expense of weakened parent molecule bonds, which reduces the stability of the product molecule.

Acknowledgment. Funds in support of this research were provided by the Office of Naval Research which is gratefully acknowledged.

---

(14) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

(15) A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, *ibid.*, **81**, 6398 (1959).

(16) A. D. Kirshenbaum and A. G. Streng, *J. Chem. Phys.*, **35**, 1440 (1961).

(17) A. V. Grosse, A. G. Streng, and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **83**, 1004 (1961).

(18) Grosse, *et al.*, also anticipated a sequence of fluorine–oxygen compounds as they proposed[17] the possible existence of compounds O_5F_2, O_6F_2, and "cyclic O_5 and O_6 polymers." Their basis for this expectation differs significantly from that used here. Since their prediction predates the discovery of the O_2F_2 structure, they emphasized the *similarity* of the –O–O– and –O–F bonds in O_2F_2 and O_3F_3, as suggested by the bond strengths, 61 and 50 kcal, which they derive from the O_2F_2 and O_3F_2 heats of formation. Thus the thermodynamic argument gives no clue to the structure of O_2F_2 nor to the patterns of weak and strong bonds pictured in Figures 3 and 4.

(19) R. D. Spratley, J. J. Turner, and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2063 (1966).

(20) G. Herzberg and D. A. Ramsay, *Discussions Faraday Soc.*, **9**, 80 (1950).

(21) C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).