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Synthesis and Stability of N–O–F Compounds from a MINDO Molecular Orbital Perspective[1]

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The MINDO semiempirical molecular orbital scheme has been fit to several calibration compounds and then used both to develop structures as well as to calculate the energetics of all six of the now known N–O–F compounds as well as a number of related postulated molecules. Where data are available, agreement with experiment for both structures and energetics is excellent even though no input data on the compounds were used in the calculations. Thus, rather confident comment on the expected thermodynamic stability of each postulated compound is possible. These results then serve as an indicator among the compounds of the probable relative synthetic success prior to embarking upon complex experimental programs. Even so, it is unlikely that any of these compounds would be interesting oxidizers because of their low endothermicity.

I. Introduction

The family of N–O–F compounds has a special importance due both to the basic interest in their bonding and energetic characteristics and to their possible use as oxidizers or additives in propulsion applications. Although a large number of N–O–F compounds can be postulated, at present only six compounds have been synthesized and positively identified.[2] Reasonable synthesis procedures are complex, usually involving combined plasma or pyrolysis and cryogenic operations, and hence some overall assessment of the relative probabilities of success is desirable before mounting an extensive experimental program. Although too late to guide a large amount of experimentation already accomplished, recent developments in molecular orbital theory now allow such an assessment.

We have used the MINDO[3] semiempirical molecular orbital method to calculate the heats of formation and ionization potentials of both the known and many postulated N–O–F compounds and to predict the relative stabilities of these postulated compounds. Several MO–SCF approximations have been used to calculate molecular structure by searching out the energy minimum as a function of geometry, but extensive computer time is, of course, essential for complex molecules, and results have not been encouraging either. As an approximation to such a procedure, we have found the structure of lowest energy from a series of reasonable structure developed using a table of "standard bond lengths." The resulting best MINDO structures have been compared with qualitative expectations from the double-quartet bonding notions of Linnett[4] and from the bonding suggestions involving electron sharing in antibonding orbitals of Spratley and Pimentel.[5] The MO-based procedure yielded much the better agreement with nature. This accuracy, combined with simplicity, rapidity, and rather wide applicability,[3,6,7] suggests the increasing utility of semiempirical MO schemes in both the qualitative and quantitative systematizing of molecular structure.

II. Calibration

Following Baird and Dewar,[3] we have developed standard bond lengths for the several bonds and bond orders that occur in N–O–F compounds by selecting values close to the experimental values of a number of well-characterized calibration compounds. For example, the data on all compounds containing an assignable first-order N–F bond vary little from a bond length of 1.37 Å, so this value was selected. There is an obvious *ad hoc* element in this specification, for clearly we are categorizing all of the nuances of N–N bonds that are given by nature into only four types, all N–O bonds into only three types, and O–O, N–F, and O–F bonds into only two types. Previously reported standard bond lengths were also used where available.[8] The resulting standard bond length assignments are summarized in Table I.

In the MINDO approximation,[3,6] a version of the INDO approximation modified for quantitative utility in energetic calculations, the one-center repulsion integrals are written in terms of the Slater–Condon parameters which, along with the one-center attraction integrals, are input data and are listed in the program as a block data subroutine. The MINDO approximation for the one-electron resonance integral is

$$\beta_{\mu\nu} = S_{\mu\nu}(I_\mu + I_\nu)(\beta_{AB}{}^{I} + \beta_{AB}{}^{II}/R_{AB}{}^2) \qquad (1)$$

ϕ_μ and ϕ_ν are atomic orbitals of atoms A and B, respectively, I_μ and I_ν are the corresponding valence-state ionization potentials, $S_{\mu\nu}$ is the overlap integral, R_{AB} is the internuclear separation of the atoms, and $\beta_{AB}{}^{I}$ and $\beta_{AB}{}^{II}$ are empirical parameters evaluated for the A–B bond. The MINDO method is calibrated for a family of compounds by determining the β values that yield correct heats of formation for a series of calibration compounds. The two β parameters for O–F bonds were obtained by calibration with respect to

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[1] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under Grant No. AFOSR-71-2109.

[2] P. A. Sessa and H. A. McGee, Jr., *Inorg. Chem.*, **10**, 2066 (1971).

[3] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.*, **50**, 1275 (1969), and a continuing series of papers. We gratefully acknowledge the kindness of Professor Dewar in providing us with listings and helpful comments. The program used here was obtained from the Quantum Chemistry Program Exchange, Chemistry Department, University of Indiana, Bloomington, Ind., and was designated MINDO 4. The heat of formation of the fluorine atom in that program was changed to 15.45 kcal/mol rather than 18.86 kcal/mol: V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, **51**, 4230 (1969).

[4] J. W. Linnett, *J. Amer. Chem. Soc.*, **83**, 2643 (1961); J. W. Linnett, "The Electronic Structure of Molecules," Wiley, New York, N. Y., 1964.

[5] R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **88**, 2394 (1966).

[6] G. Klopman and B. O'Leary, "All Valence Electrons S.C.F. Calculations," Springer-Verlag, New York, N. Y., 1970.

[7] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[8] N. C. Baird, M. J. S. Dewar, and R. Sustmann, *J. Chem. Phys.*, **50**, 1275 (1969).

TABLE I

STANDARD BOND LENGTHS FOR N–O–F COMPOUNDS

Bond	Bond order (approx)	Std bond length, Å	Bond	Bond order (approx)	Std bond length, Å	Bond	Bond order (approx)	Std bond length, Å
O—F	1	1.415	N—F	1	1.37	N---N	$^1/_2$	1.63
O---F	$^1/_2$	1.575	N---F	$^1/_2$	1.466	O—H	1	0.96
N≡O	$2^1/_2$	1.13	N≡N	3	1.098[a]	N—H	1	1.012[a]
N=O	2	1.20	N=N	2	1.24	O=O	2	1.22
N—O	1	1.44	N—N	1	1.45[a]	O—O	1	1.48[a]

[a] Standard bond lengths determined in ref 8.

TABLE II

BOND CHARACTERIZATION PARAMETERS

Bond	$\beta_{AB}{}^{I}$	$\beta_{AB}{}^{II}$	Bond	$\beta_{AB}{}^{I}$	$\beta_{AB}{}^{II}$	Bond	$\beta_{AB}{}^{I}$	$\beta_{AB}{}^{II}$
O–F	0.292	0.03055	N–O	0.22	0.074	N–F	0.2307	0.051
N–N	0.2089[a]	0.109[a]	O–O	0.3226[a]	0.00[a]	N–H	0.2214[a]	0.00[a]

[a] Bond characterization parameters determined in ref 8.

TABLE III

GEOMETRIES AND ENERGETICS OF CALIBRATION COMPOUNDS[a]

Compd	Calcd std geometry (exptl)	Calcd ΔH_f, kcal/mol (exptl)	Calcd I, eV (exptl)
OF_2	O–F 1.415 Å (1.412 Å), FOF 109.5° (103°)	5.90 (5.86)	15.53 (13.7)
O_2F_2	O–F 1.575 Å (1.575 Å), O–O 1.22 Å (1.217 Å), OOF 109.5° (109.5°), dihed 90° (87.5°)	4.77 (4.73)	14.91
HNO	N–H 1.012 Å (1.062 Å), N–O 1.20 Å (1.211 Å), HNO 109.5° (108.5°)	26.78 (24.7)	11.7
HO′NO	O′–H, 0.96 Å (0.98 Å*), O–N 1.44 Å (1.46 Å*), N–O′ 1.13 Å (1.20 Å*), HO′N 90° (105°), ONO′ 109.5° (118°)	−17.59 (−18.58)	11.69
$HO'NO_2$	N–O′ 1.44 Å (1.44 Å), N–O 1.20 Å (1.203 Å*), O′–H 0.96 Å (0.96 Å*), HO′N 90° (90°*), ONO 134° (137.8°)	−34.32 (−32.1)	12.88
$O'NNO_2$	N–N 1.63 Å (1.864 Å), N–O 1.20 Å (1.202 Å), N–O′ 1.13 Å (1.142 Å), ONO 134° (130°), O′NN 109.5° (105.1°)	17.48 (19.8)	11.74
O_2NNO_2	N–N 1.63 Å (1.75 Å), N–O 1.20 Å (1.18 Å), ONO 134° (133.7°)	−0.548 (2.17)	12.43
NF_3	N–F 1.37 Å (1.371 Å), FNF 109.5° (102.5°)	−31.90 (−31.75)	15.61 (13.00)
FNO	N–F 1.466 Å (1.52 Å) N–O 1.13 Å (1.13 Å), FNO 109.5° (110°)	−19.224 (−15.80)	13.64

[a] Geometries: mostly from "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1965; starred values are reported therein as estimated; O_2F_2 from R. H. Jackson, *J. Chem. Soc.*, 4585 (1962); N_2O_3 from A. H. Brittain, A. P. Cox, and R. L. Kuczkowski, *Trans. Faraday Soc.*, **65**, 1963 (1969). Heats of formation: "JANAF Thermodynamic Data," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1965; 1st Addendum, 1966; 2nd Addendum, 1967; OF_2 from R. C. King and G. T. Armstrong, *J. Res. Nat. Bur. Stand., Sect. A*, **72**, 113 (1968); O_2F_2 from A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, *J. Amer. Chem. Soc.*, **81**, 6398 (1959); HNO from J. L. Holmes, *Proc. Chem. Soc., London*, 75 (1962); HNO_2 from P. G. Ashmore and B. J. Tyler, *J. Chem. Soc.*, 1017 (1961); HNO_3 from *Nat. Bur. Stand. (U. S.), Circ.*, **No. 500** (1952); NF_3 from L. C. Walker, *J. Phys. Chem.*, **71**, 361 (1967); FNO from H. S. Johnston and H. T. Bertin, Jr., *J. Amer. Chem. Soc.*, **81**, 6402 (1959). Ionization potentials: OF_2 from V. H. Dibeler, R. M. Reese, and D. E. Mann, *J. Chem. Phys.*, **27**, 176 (1957); NF_3 from V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969).

OF_2 and O_2F_2; these values for N–O bonds were obtained by calibration and optimization with respect to HNO, HNO_2, HNO_3, N_2O_3, and N_2O_4; and the β^{I} and β^{II} values for N–F bonds were obtained by calibration with respect to NF_3 and FNO. These β values are given in Table II which includes the previously reported values[8] that were also used in this work.

The fit to the heats of formation of the nine calibration compounds is summarized in Table II along with the standard and experimental geometries. Inferences as to the overall quality of the calibration are then apparent. Standard bond angles have been taken to be 109.5°, and the ONO angle in the $-NO_2$ group has been set equal to 134°. The standard geometry selections rather accurately portray the experimental values. Note, however, that the standard N–N bond lengths in N_2O_3 and N_2O_4 are the same and much smaller than their experimental values. Also the standard bond length of N–O′ in HNO_2 of 1.13 Å is rather less than the estimated experimental value of 1.20 Å. The final fit to the heats of formation of the nine calibration compounds is reasonably good, but in the two cases where it is possible to compare ionization potentials, NF_3 and OF_2, we find the MINDO values to be much larger than experiment. The only other possible ionization potential comparison is with N_2F_4 where the agreement is perfect (see Table IV).

III. Utilization

After having made standard bond length assignments, what can we now use as a guide in assembling these building blocks to construct known as well as any postulated N–O–F compounds? And does the guide yield molecular structures consistent with experiment for those N–O–F molecules on which structural information has been reported?

Useful systematizing of bonding observations dates from Lewis, but no generally comprehensive and accurate scheme has yet appeared. With an SCF–MO theory such as INDO or CNDO, it is possible to search out the energy minimum with respect to molecular geometry and to hence calculate the equilibrium struc-

TABLE IV

STRUCTURE AND ENERGETIC CHARACTERIZATION OF N–O–F AND N–F COMPOUNDS[a]

Compd	Calcd std geometry (exptl)	Calcd ΔH_f, kcal/mol (exptl)	Calcd I, eV (exptl)
FNO_2 (planar)	F–N 1.466 Å (1.46 Å), N–O 1.20 Å (1.18 Å), ONO 134° (136°)	−31.48 (−25.8 to −33.8)	14.65 (13.15)
$FO'NO_2$ (planar)	F–O′ 1.415 Å (1.42 Å), O′–N 1.44 Å (1.39 Å), N–O 1.20 Å (1.29 Å), FO′N 109.5° (105°), ONO 134° (125°)	1.5 (2.5)	13.82
ONF_3	O–N 1.13 Å (1.15 Å), N–F 1.466 Å (1.48 Å), tetrahed (tetrahed)	−33.31 (−34.1)	15.83 (13.26)
$ONNF_2$ (planar)	O–N 1.13 Å, N–N 1.45 Å, N–F 1.37 Å, FNF 109.5°, ONN 109.5°	18.21 (18.9)	12.82
O_2NNF_2 (nonplanar)	O–N 1.20 Å, N–N 1.45 Å, N–F 1.37 Å, ONO 134°, FNF 109.5°, dihed 90°	−14.67 (0.0)	13.44
FNNF (chair)	F–N 1.37 Å (1.371 Å), N–N 1.24 Å (1.25 Å), NNF 109.5° (115°)	19.45 (19.4)	13.68
F_2NNF_2 (nonplanar)	F–N 1.37 Å (1.371 Å), N–N 1.45 Å (1.47 Å), FNF 109.5° (108°), NNF 109.5° (104°), dihed 90° (65°)	−2.81 (−5.0)	12.06 (12.04)

[a] Geometries: FNO_2 from A. C. Legon and D. J. Millen, *J. Chem. Soc., A*, 1736 (1968); $FONO_2$ from R. H. Miller, D. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23,** 223 (1967); ONF_3 from E. C. Curtis, D. Pilipovich, and H. W. Moberly, *J. Chem. Phys.*, **46,** 2905 (1967); FNNF and F_2NNF_2 from "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1965. Heats of formation: FNO_2 from P. A. Sessa and H. A. McGee, Jr., *Inorg. Chem.*, **10,** 2066 (1971); $FONO_2$ same as for FNO_2 and recalculated from F. A. Johnson and C. B. Colburn, *ibid.*, **2,** 24 (1963); ONF_3 from R. Bougon, J. Chatelet, J. P. Desmonlin, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **266,** 1761 (1968); $ONNF_2$ recalculated from data of F. A. Johnson and C. B. Colburn, *Inorg. Chem.*, **2,** 24 (1963); O_2NNF_2 from P. A. Sessa and H. A. McGee, Jr., *ibid.*, **10,** 2066 (1971); FNNF from "JANAF Thermodynamic Data," 1st Addendum, D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1966; F_2NNF_2 from L. C. Walker, *J. Phys. Chem.*, **71,** 361 (1967). Ionization potentials: FNO_2 from P. A. Sessa and H. A. McGee, Jr., *Inorg. Chem.*, **10,** 2066 (1971); ONF_3 from V. H. Dibeler and J. A. Walker, *ibid.*, **8,** 1728 (1969); N_2F_4 from J. T. Herron and V. H. Dibeler, *J. Chem. Phys.*, **33,** 1595 (1960).

ture. This has been successfully accomplished for a number of small molecules, but calculations require extensive computer time and results are inaccurate for molecules of chemically useful or meaningful complexity. As an approximation, we have used our standard bond lengths, tetrahedral angles, and fixed values for both the O–N–O angle in $-NO_2$ and for dihedral angles, to define a small number of "reasonable" structures. By calculating the energy of each such structure, the MINDO scheme itself becomes the final arbiter in arriving at the "best" structure.[9]

As examples of the efficacy of this proposal, let us examine the known N–F and N–O–F compounds. The results appear in Table IV wherein one can compare the MINDO selected "standard" structure with the experimental structure. The agreement is generally good. The MINDO calculation either failed to converge at all or gave higher energies for all standard structures other than the best one tabulated in Table IV. Recalling that no input data of any sort on these known N–O–F compounds were used in these calculations, the heats of formation reported in Table IV are in good agreement with experiment with the exception of O_2NNF_2. And the experimental data on that compound are somewhat uncertain due to uncertainties in the ionization potential of NO_2.[2,10] In other words, we have simultaneously selected a structure and calculated a heat of formation, both in good agreement with experiment and with no input data of any sort on the compound in question. In the very few cases where comparison is possible, the calculated ionization potentials are too high with the exception of N_2F_4 where the agreement is perfect.

It is interesting to compare these numerically specified structures with the predictions of two qualitative guides that have received attention in systematizing the structure and behavior of many H–N–O–F compounds. These are the bonding theory ideas of Linnett[4] (L) and of Spratley and Pimentel[5] (S&P). The utility of each is as a qualitative guide and in general understanding, for neither allows any numerical assignments nor computations.

Linnett deemphasized the importance of the Lewis type of electron pairing but rather considered the octet as consisting of two groups of four electrons, a double quartet, with each group having opposite spin. Using this idea with several simple rules based upon spin correlation, charge correlation, and formal charge limitations, one can readily develop many possible structures for a molecule, but the selection of the most probable structure is not always unambiguous.

On the other hand, according to the Spratley and Pimentel bonding notions, a bond can be formed between an antibonding π^* orbital and an atom sharing an electron with this orbital. The bond becomes weaker with increasing electronegativity of the atom. One then may argue, for example, that in the questionable compound FONO the highly electron-attracting OF will form a weak bond with the electron in the antibonding orbital of NO $(\sigma_z)^2(\pi_x)^2(\pi_y)^2(\pi_x{}^*)$.[1] The weak F–N bond in FNO (see Table IV) is similarly understood, and so on.

The standard structure of FNO is the same as that suggested by both L and S&P ideas, while those of FNO_2 and $FONO_2$ were among several ambiguous structures from L, but each was clearly suggested by S&P. On the other hand, the correct structure of ONF_3 was suggested by neither theory, yet the MINDO-selected structure and the heat of formation of the molecule are both in excellent agreement with experiment. Similarly, neither L nor S&P correctly suggested the structure of $ONNF_2$; L gave a reasonable picture of O_2NNF_2, but S&P did not, and both N_2F_2 and N_2F_4 were correctly suggested by normal Lewis-type valence rules.

The accuracy of the MO approach when contrasted with either Linnett or Spratley and Pimentel qualitative

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(9) With molecules of the complexity of those studied here, processing times on the IBM 370 Model 155 were typically of the order of 1 min or so.

(10) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26** (1969).

theory is not surprising in view of the antibonding orbitals, half-filled orbitals, multiple bonding, and other complexities of this family of compounds.

IV. Extension to Hypothetical Molecules

With inferences from the structures of known compounds (Table IV), we have postulated structures for a series of presently unknown molecules as is summarized in Table V. Bond angles were again always taken to be tetrahedral. Other possible structures constructed from the table of standard bond lengths were found to yield either unreasonable energies or to fail to converge to any value at all. In those few cases where more than one structure yielded a reasonable energy, the lowest energy structure was selected. For example, in the case of ONO′F, L theory suggests a long and weak O′–F bond as a tenuous best choice among several distinctly different structures while S&P theory suggests a long and weak N–O′ bond. The corresponding standard structures from Table I yielded heats of formation of 22.3 and 7.59 kcal/mol, respectively. Thus, the lowest energy standard structure that was adopted also corresponded to the qualitative S&P ideas. Possible molecules that were unreasonable by this sort of analysis were discarded. For example, it is not possible to construct a satisfactory structure for any member of the series $FO(O_2)_nNO$ that was proposed by Spratley and Pimentel other than for $n = 0$. The lowest energy structure of $FO(O_2)_1NO$ yielded a heat of formation of 93.63 kcal/mol which makes this molecule exceedingly unlikely (see following discussion), whereas if one uses the structure suggested by Spratley and Pimentel, the molecule becomes energetically even more unlikely. For FOONO, F_2NONF_2, $F_2NO_2NF_2$, and ONNFNFNO, the selected structures were in keeping with suggestions from both S&P and L theory. The selected structures for $NF_2(OF)$, $NF(OF)_2$, and $N(OF)_3$, were again among several very different possibilities, but with no means of clear selection among them, that were obtained from L theory. The structures were allowable by S&P bonding notions but were certainly not obvious constructions. All structures of $NF_2(O_2F)$, $NF(O_2F)_2$, and $N(O_2F)_3$ other than those selected were energetically unreasonable on the basis of MINDO calculations, including suggestions from both L and S&P theory.

Table V

Structures of Postulated N–O–F Compounds for MINDO Energetic Calculations[a]

Compd	Geometry, Å
ONO′F	O–N 1.13, N–O′ 1.44, O′–F 1.415
FOONO′	F–O 1.575, O–O 1.22, O–N 1.44, N–O′ 1.13
F_2NONF_2	N–F 1.37, N–O 1.44
$F_2NO_2NF_2$	N–F 1.37, N–O 1.44, O–O 1.48
ONNFNFNO (trans)	N–F 1.37, N–O 1.13, N–N 1.45
$F_nN(OF)_{3-n}$ ($n = 0$–3)	N–F 1.37, N–O 1.20, O–F 1.575
$F_nN(O_2F)_{3-n}$ ($n = 0$–3)	N–F 1.37, N–O 1.44, O–O 1.48, O–F 1.415

[a] All angles were assumed to be tetrahedral.

Table VI

Energetics of Postulated N–O–F Compounds

Compd	Heat of formn, kcal/mol			I, eV	Stability[a]	
	MINDO	$\Sigma\Delta H_{fp1}$	$\Sigma\Delta H_{fp2}$		MINDO	Linnett
FONO	7.59	23.8	−25.8	13.09	m	m
FO_2NO	−31.1	27.7	−15.8	12.87	m	m
F_2NONF_2	21.69	2.6	−47.6	14.70	u	u
$F_2NO_2NF_2$	37.12	−11.8	−57.6	12.79	u	u
ONNFNFNO	78.8	43.2	−31.6	10.97	u	m
$F_2N(OF)$	−20.48	10.0	−34.1	14.80	m	m
$FN(OF)_2$	−9.87	−25.8	−31.8	14.33	u	m
$N(OF)_3$	6.56	2.5	−19.9	14.04	u	m
$F_2N(O_2F)$	7.88	14.6	−31.8	14.57	m	u
$FN(O_2F)_2$	74.02	22.3	−31.8	14.15	u	u
$N(O_2F)_3$	140.1	133.0	−31.8	13.8	u	u

[a] Key: m, marginally stable; u, unstable.

The MINDO-calculated heats of formation of these several postulated N–O–F compounds are summarized in Table VI.

V. Discussion

There are a number of useful guides in chemistry which however cannot be supported as a statement of principle. The so-called "principle of maximum bonding" of Woodward and Hoffmann is a good example as is the Thomsen–Berthelot principle. This later "principle" states that the heat evolved in a reaction is a measure of the tendency of that reaction to proceed.[11] Let us employ this idea to provide at least a hint of the possible stable existence of our postulated compounds before mounting what will surely be a complex synthesis program. This analysis will also provide an indication of the relative stability of the group of eleven compounds. Interestingly, these very reactive N–O–F compounds will likely be kinetically stable only at very low temperatures where $T\Delta S$ may be small and ΔH thus closer to ΔG.

The total heats of formation of decomposition products resulting from two different kinds of decomposition pathways of the parent compound are given in Table VI. Here ΔH_{fp1} and ΔH_{fp2} are the lowest total ΔH_f of products with no rearrangement and with rearrangement, respectively. A summary of some possible decomposition pathways for all eleven compounds appears in Table VII, and the heat of formation data required for these calculations of ΔH_{fp1} and ΔH_{fp2} are summarized in Table VIII.

With the Thomsen–Berthelot principle, a compound should be thermodynamically stable if its heat of formation is lower than ΔH_{fp1}, and the resulting conclusion for each compound appears in Table VI together with a similar stability conclusion drawn from L theory for comparison. Most interestingly and significantly, both of these tests of stability were uniformly positive for all of the presently known N–O–F compounds of Table IV.

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(11) H. S. Taylor, "A Treatise on Physical Chemistry," Van Nostrand, New York, N. Y., 1925, p 43.

TABLE VII

SOME POSSIBLE INITIAL DECOMPOSITION PROCESSES OF SEVERAL POSTULATED N–O–F COMPOUNDS

Process	$\Sigma \Delta H_f$(product), kcal/mol
$FONO \rightarrow FO + NO$	53.6
$\rightarrow F + NO_2$	23.8[a]
$\rightarrow FNO + O$	43.8
$\rightarrow FNO_2$	−25.8[b]
$FO_2NO \rightarrow FO_2 + NO$	27.7[a]
$\rightarrow OF + NO_2$	39.9
$\rightarrow O_2 + FNO$	−15.8[b]
$\rightarrow NO_3F$	2.5
$F_2NONF_2 \rightarrow NF_2 + ONF_2$	2.6[a]
$\rightarrow NF_3 + FNO$	−47.6[b]
$\rightarrow 2F_2 + N_2O$	19.6
$\rightarrow ONF_3 + NF$	40.4
$F_2NO_2NF_2 \rightarrow 2NF_2 + O_2$	17.0
$\rightarrow 2ONF_2$	−11.8[a]
$\rightarrow NF_3 + FNO_2$	−57.6[b]
$\rightarrow FNO + ONF_3$	−49.9
$ONNFNFNO \rightarrow 2NO + N_2F_2$	62.6
$\rightarrow 2NO + N_2 + F_2$	43.2[a]
$\rightarrow 2N_2O + F_2$	39.2
$\rightarrow 2FNO + N_2$	−31.6[b]
$F_2NOF \rightarrow F + ONF_2$	10.0[a]
$\rightarrow NF_2 + OF$	40.5
$\rightarrow FNO + F_2$	−15.8
$\rightarrow ONF_3$	−34.1[b]
$FN(OF)_2 \rightarrow FNO_2 + F_2$	−25.8[a]
$\rightarrow FNO + OF_2$	−10.0
$\rightarrow NO_2 + 3F$	55.6
$FN(OF)_2 \rightarrow NF + 2OF$	138.5
$\rightarrow ONOF + F_2$	7.6
$\rightarrow NF_3 + O_2$	−31.8[b]
$N(OF)_3 \rightarrow NO_3F + F_2$	2.5[a]
$\rightarrow FNO_2 + OF_2$	−19.9[b]
$\rightarrow ONOF + OF_2$	13.5
$\rightarrow FNO + 2OF$	48.2
$F_2N(O_2F) \rightarrow NF_2 + O_2F$	14.6[a]
$\rightarrow FNO + F + OF$	32.1
$\rightarrow NF_3 + O_2$	−31.8[b]
$\rightarrow FNO + OF_2$	−9.9
$\rightarrow ONF_3 + O$	25.5
$\rightarrow FNO_2 + F_2$	−31.5
$\rightarrow ONOF + F_2$	7.6
$FN(O_2F)_2 \rightarrow NF + 2O_2F$	86.7
$\rightarrow FNO_2 + 2OF$	38.2
$\rightarrow FNO + OF + O_2F$	22.3[a]
$\rightarrow NF_3 + 2O_2$	−31.8[b]
$\rightarrow FNO_2 + O_2 + F_2$	−25.8
$\rightarrow ONOF + O_2F_2$	12.3
$\rightarrow FNO_3 + OF_2$	8.4
$N(O_2F)_3 \rightarrow NO_3 + 3OF$	113.0[a]
$\rightarrow ONOF + 2O_2F$	19.8
$\rightarrow NF_3 + 3O_2$	−31.8[b]
$\rightarrow FNO + 2O_2 + OF_2$	−9.9
$\rightarrow FNO_2 + 2O_2F$	−19.3

[a] Lowest $\Sigma \Delta H_f$ (product) without rearrangement. [b] Lowest $\Sigma \Delta H_f$ (product) with rearrangement.

TABLE VIII

HEATS OF FORMATION OF N–O–F DECOMPOSITION PRODUCTS AT 298°K[a]

Species	Exptl ΔH_f, kcal/mol	Species	Exptl ΔH_f, kcal/mol	Species	Exptl ΔH_f, kcal/mol
N	113	OF	32	O_2F	6.1
O	59.6	NF	74.5	NF_2	8.5
F	15.9	NO_2	7.9	N_2O	19.6
NO	21.6	NO_3	17.0	NF_2O	−5.9

[a] D. R. Stull, Ed., "JANAF Thermodynamic Data," Dow Chemical Co., Midland, Mich., 1965; 1st Addendum, 1966; 2nd Addendum, 1967; F from V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, **51**, 4230 (1969); OF recalculated from P. A. G. O'Hare and A. C. Wahl, *ibid.*, **53**, 2469 (1970); NF and NF_2O from V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969); O_2F recalculated from value given by JANAF tables using the above value of $\Delta H_{f,298}$(F); NF_2 from L. C. Walker, *J. Phys. Chem.*, **71**, 361 (1967).

Linnett theory predicts the compounds FONO, FO_2NO, ONNFNFNO, $F_2N(OF)$, $FN(OF)_2$, and $N(OF)_3$ to be marginally stable and other postulated N–O–F compounds to be unstable, while conclusions from these MINDO calculations yield only FONO, FO_2NO, $F_2N(OF)$, and $F_2N(O_2F)$ as being thermodynamically stable. It is encouraging to note that Schumacher[12] has recently obtained experimental evidence for the existence of FONO.

So, in conclusion, we have successfully calibrated and applied the MINDO molecular orbital method to all known N–F and N–O–F compounds to obtain structures and heats of formation in good agreement with experiment. The construction of molecules from the developed table of standard bond lengths has yielded structures in good agreement with experiment and far superior to those of other recent proposed techniques. These results, together with successful applications to many other families of compounds,[3,7,13] make the semiempirical MO–SCF approach now appear to be the method of choice in rapidly calculating both structures and energetics.[7] The theoretical approximations and calibration procedures will improve making the semiempirical technique even more effective from the viewpoint of chemical utility.

We have predicted the energetics and thermodynamic stability of some postulated N–O–F compounds, but only FONO, FO_2NO, $F_2N(OF)$, and $F_2N(O_2F)$ are likely to be stable, and FONO has been recently claimed. Even so it is unlikely that any of these compounds would be interesting oxidizers because of their low endothermicity.

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(12) H. J. Schumacher, private communication; P. J. Bruna, J. E. Sicre, and H. J. Schumacher, *Chem. Commun.*, 1542 (1970).

(13) P. S. Ganguli, L. P. Gordon, and H. A. McGee, Jr., *J. Chem. Phys.*, **53**, 782 (1970).