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STUDY OF HYPERCONJUGATION IN TRIFLUORAMINE OXIDE AND RELATED MOLECULES
USING CORE AND VALENCE IONIZATION POTENTIALS

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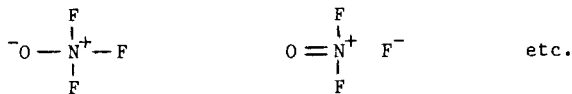
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SUMMARY

The oxygen, nitrogen and fluorine core binding energies of ONF_3 have been redetermined. The data indicate strong hyperconjugation, with N-O π -bonding and weak N-F σ -bonding. The core and valence ionization potentials together indicate that the HOMO of ONF_3 (derived mainly from the O p π orbitals) is weakly antibonding. This result is consistent with other data if it is assumed that the latter orbital has considerable fluorine lone pair character and that the orbital derived mainly from the N-F σ orbitals (at lower energy) has considerable N-O π character. The core and valence ionization potentials of OPF_3 and OPCl_3 indicate that the oxygen "lone pair" orbitals of these molecules are at lower energies than the corresponding hypothetical nonbonding oxygen p orbitals. These results imply significant participation of phosphorus 3d π orbitals in the P-O bonds.

INTRODUCTION

Several of the molecular properties of trifluoramine oxide suggest N-O π -bonding and N-F σ -antibonding, corresponding to hyperconjugation of the following type [1].



For example, the N-O bond length, 1.16 Å, is 0.26 Å shorter than the distance usually ascribed to an N-O single bond, and the N-F bond length, 1.43 Å, is 0.06 Å longer than that of NF₃ [2]. The weighted average N-O stretching frequency of ONF₃ is intermediate between the corresponding values of ONF and NO₂F [3].

Hyperconjugation in ONF₃ would be expected to have a marked effect on the 6e molecular orbitals, which would be, in the absence of π interactions between the oxygen atom and the rest of the molecule, simply a nonbonding pair of oxygen pπ orbitals. An *ab initio* MO study of ONF₃ by Olsen and Howell [4] suggests that the 6e orbitals are significantly delocalized, with π bonding character in the N-O region and weak σ antibonding character in the N-F regions. The first band in the ultraviolet photoelectron spectrum of ONF₃, which has been assigned to these orbitals, shows considerable vibrational fine structure and thus is consistent with significant delocalization [5].

The ionization potential of the 6e orbitals, by itself, gives little information about the bonding or antibonding character of the orbitals. Even a comparison of the ionization potential with the first ionization potential of the H₂O molecule (which corresponds to ionization of a strictly nonbonding, localized oxygen pπ orbital) is of little value because, on going from H₂O to ONF₃, one does not know the extent to which the ionization potential changes due to changes in electrostatic potential (atomic charges) and electronic relaxation energy. However, it has been shown that both of these effects can be approximately accounted for by using the difference in the oxygen 1s binding energy between H₂O and ONF₃ [6]. The available binding energy data, when applied in this way lead to the conclusion that the 6e orbitals of ONF₃ are weakly antibonding or nonbonding relative to hypothetical localized oxygen 2p orbitals in ONF₃. Because this conclusion is apparently at odds with the other experimental and theoretical data, and because the nitrogen and fluorine core binding energies of ONF₃ (which are also relevant to this problem of hyperconjugation) have not been carefully determined, [7,8] we decided to completely redetermine the X-ray photoelectron spectrum of ONF₃ and to make a comparative study of the UPS and XPS spectra of ONF₃ and similar molecules.

QUALITATIVE TREATMENT OF CORE BINDING ENERGIES

In Table 1 we have listed pertinent core binding energies for the molecules considered in this study. The core binding energies listed for ONF_3 are newly determined. The N 1s and O 1s values for ONF_3 are practically identical to our previously reported values, but the F 1s value is 1.02 eV lower than the previously reported value.

TABLE 1
Core binding energies^a

Compound	E_B , eV		
	O 1s	N 1s or P 2p _{3/2}	F 1s or Cl 2p _{3/2}
NF_3		414.2	694.45
ONF_3	541.96 ^b	417.00 ^b	694.25 ^b
$\text{ON}(\text{CH}_3)_3$	537.7		
PF_3		141.78	694.09
OPF_3	539.1	143.0	695.6
PCl_3		139.75	206.42
OPCl_3	537.97	141.02	207.33
$\text{P}(\text{CH}_3)_3$		135.93	
$\text{OP}(\text{CH}_3)_3$	536.05	137.80	
OVCl_3	538.90		206.10
H_2O	539.8		
HF			694.22
HCl			207.39

^a Except where noted, binding energies are from the table in ref. 8.

^b This work.

Useful information can be obtained from a simple qualitative consideration of the core binding energies. First, let us compare NF_3 and ONF_3 with PF_3 and OPF_3 . Because phosphorus is less electronegative than nitrogen, one would ordinarily expect a given set of ligand atoms to be more negatively charged when bonded to a phosphorus atom than when bonded to a nitrogen atom. This prediction is clearly borne out by the fact that the fluorine 1s binding energy of PF_3 is 0.36 eV lower than that of NF_3 .

However, the data for ONF_3 and OPF_3 are not consistent. Although the oxygen 1s binding energy of OPF_3 is 2.86 eV lower than that of ONF_3 , the fluorine 1s binding energy of OPF_3 is 1.35 eV greater than that of ONF_3 . We believe the latter data strongly support the concept of hyperconjugation in ONF_3 . Because of delocalization of the oxygen $p\pi$ orbital of ONF_3 , the electron density of the oxygen atom is very much lower, and that of the fluorine atoms is higher, than in the case of OPF_3 , where there is relatively little π interaction between the oxygen atom and the rest of the molecule.

In the case of $\text{ON}(\text{CH}_3)_3$, hyperconjugation of the type found in ONF_3 is unimportant, and the oxygen 1s binding energy is, as expected, relatively low.

QUANTITATIVE TREATMENT OF CORE AND VALENCE IONIZATION POTENTIALS

In Table 2 we have listed the vertical ionization potentials of the oxygen and halogen 'lone pair' orbitals. In the case of the OMX_3 molecules, the oxygen 'lone pair' orbitals are the orbitals of e symmetry derived from the degenerate $p\pi$ -type orbitals of the oxygen atoms. The lone pair orbital of H_2O is the nonbonding $p\pi$ orbital perpendicular to the molecular plane. In the case of the halogen lone pair orbitals of the MX_3 and OMX_3 molecules, we have listed the ionization potentials of the orbitals of a_2 symmetry which have pure halogen p orbital character and which have no net overlap with any other orbitals. The halogen lone pair orbitals of HF and HCl are the degenerate nonbonding $p\pi$ orbitals.

In Table 2 we have also listed the localized orbital ionization potential (LOIP) values, i.e. the ionization potentials, calculated using core binding energies, for the orbitals in hypothetical localized (nonbonding) states. These LOIP values were calculated assuming that the HOMOs of H_2O , HF, and HCl are strictly nonbonding and that their ionization potentials are true LOIPs. It was also assumed that differences in LOIP values between compounds are eight-tenths of the corresponding differences in core binding energy [9,10]. The latter assumption has considerable experimental and theoretical justification [6,9]. It should be pointed out that all the conclusions of this paper would be essentially unchanged if the factor of 0.8 were changed by 0.1.

TABLE 2

Valence shell vertical ionization potentials, in eV

Compound	Oxygen 'lone pairs'		Halogen 'lone pairs'	
	IP ^a	LOIP	IP ^a	LOIP
NF ₃			16.15	16.2
ONF ₃	14.11	14.3	15.54	16.1
ON(CH ₃) ₃	8.43 ^b	10.9		
PF ₃			15.89	16.0
OPF ₃	13.52	12.1	17.09	17.2
PCl ₃			11.70 ^c	11.96
OPCl ₃	12.13	11.2	12.52	12.69
OP(CH ₃) ₃	9.9 ^b	9.6		
OVCl ₃	~12.9 ^d	~12.0	11.84 ^d	11.71
H ₂ O	12.61 ^e	(12.61)		
HF			16.06 ^f	(16.06)
HCl			12.75 ^f	(12.75)

^a Except where noted, ionization potentials and assignments from ref. 5.

^b S. Elbel, H. tom Dieck, J. Chem. Soc. Dalton (1976) 1757. ^c J. L. Berkosky, F. O. Ellison, T. H. Lee, J. W. Rabalais, J. Chem. Phys. (1973) 59, 5342. ^d P. Burroughs, S. Evans, A. Hamnett, A. F. Orchard, N. V. Richardson, J. Chem. Soc. Faraday II (1974) 70, 1895. ^e C. R. Brundle, D. W. Turner, Proc. Roy. Soc., Ser. A (1968) 307, 27. ^f D. C. Frost, C. A. McDowell, D. A. Vroom, J. Chem. Phys. (1967) 46, 4255.

It will be noted that the ionization potentials of the strictly nonbonding a_2 halogen lone pair orbitals of the OMX_3 and MX_3 molecules are very close to the LOIP values calculated using the core and valence ionization potentials of these molecules and the reference molecules, HF and HCl. If we omit the data for ONF₃, the average deviation between the ionization potentials and the calculated LOIP values is only ± 0.13 eV, a gratifying confirmation of the validity of the method for calculating LOIP values. The relatively large deviation of 0.47 eV in the case of ONF₃ is probably not much greater than the uncertainty of the experimental ionization potential. The band centered at 15.54 eV in the UV photoelectron spectrum of ONF₃ has a half-width of about 1.1 eV and has been assigned to both the e and a_2 orbitals associated with the fluorine $p\pi$

orbitals [5]. It is quite conceivable that the a_2 orbital (which by symmetry is strictly nonbonding) has an ionization potential near 16.0 eV and that the e orbital (which could interact repulsively with other filled e orbitals) has an ionization potential such that the weighted average ionization potential is 15.54 eV.

Now let us consider the oxygen 'lone pair' orbitals. In each of the OMX_3 compounds, the oxygen atom has a degenerate pair of $p\pi$ orbitals which can conceivably interact with the bonding and antibonding M-X σ orbitals of the same symmetry.

In the case of ONF_3 , the oxygen lone pair ionization potential is just slightly lower than the LOIP value, indicating that the energy of the HOMO is slightly above that of a hypothetical nonbonding oxygen p orbital. We believe the only reasonable explanation of this result is that the oxygen $p\pi$ orbitals interact slightly more with the N-F σ orbitals than with the N-F σ^* orbitals, as suggested by the qualitative energy level diagram of Fig. 1. The N-F σ^* level is raised and the N-F σ level is lowered as a consequence of interactions with the O $p\pi$ orbitals, but there is relatively little net change in the energy of the O $p\pi$ orbitals. The lowest orbitals, derived mainly from the N-F σ orbitals, acquire considerable N-O π -bonding character and lose some of their N-F σ bonding character. The oxygen 'lone pair' orbitals (the HOMO) also become quite delocalized; they acquire considerable fluorine lone pair character. Because of the weak antibonding character of the HOMO, the vibrational fine structure associated with its ionization is understandable.

The data in Table 2 for $ON(CH_3)_3$ indicate that the oxygen 'lone pair' level is 2.5 eV higher than the hypothetical nonbonding O $p\pi$ level. This result can be interpreted as follows. Because the electronegativity of carbon is much less than that of fluorine, the N-C σ levels of $ON(CH_3)_3$ lie higher than those of ONF_3 . Hence the O $p\pi$ orbitals of $ON(CH_3)_3$ interact principally with the N-C σ -bonding orbitals (as shown schematically in Fig. 2), and the resulting oxygen 'lone pair' level is raised relative to the hypothetical nonbonding O $p\pi$ level. The relatively long N-O bond of $ON(CH_3)_3$, 1.39 Å, [11] is consistent with little net π -bonding character.

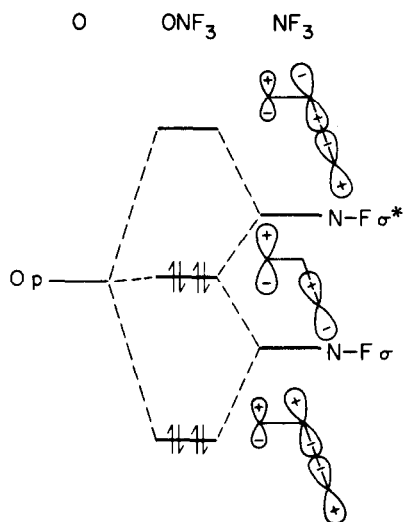


Fig. 1. Qualitative molecular orbital energy level diagram for ONF₃.

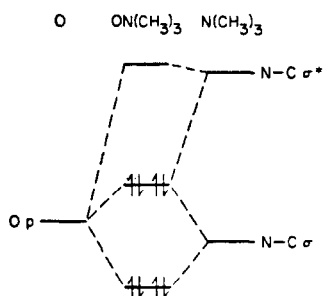


Fig. 2. Qualitative molecular orbital energy level diagram for ON(CH₃)₃.

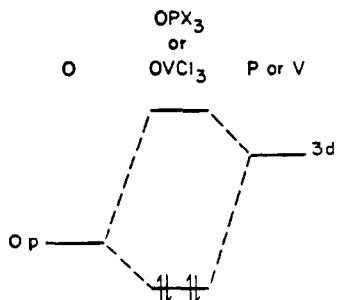


Fig. 3. Qualitative molecular orbital energy level diagram for OPX₃ or OVCl₃.

From Table 2 we see that the oxygen 'lone pair' levels of OPF_3 , OPCl_3 , $\text{OP}(\text{CH}_3)_3$ and OVCl_3 lie below the corresponding hypothetical nonbonding $0\text{ p}\pi$ levels. Because the electronegativities of phosphorus and vanadium are much lower than that of nitrogen, the $\text{M-X } \sigma^*$ orbital levels of the MX_3 groups in these OMX_3 molecules lie higher, relative to the corresponding $0\text{ p}\pi$ levels, than in the case of ONF_3 . Hence the lowering of the oxygen lone pair orbital levels in these OMX_3 molecules cannot be a consequence of hyperconjugation. We are forced to the conclusion that the principal interaction of the $0\text{ p}\pi$ orbitals in these molecules is with the empty $3d$ orbitals of phosphorus and vanadium, as indicated qualitatively in Fig. 3. The data of Table 2 show that the $(0\text{ p}\pi)\text{-(P d}\pi)$ interaction decreases on going from OPF_3 to OPCl_3 to $\text{OP}(\text{CH}_3)_3$, presumably as a consequence of the decrease in charge on the phosphorus atom and the concomitant increase in diffusivity of the $3d$ orbitals.

EXPERIMENTAL

The core binding energies of gaseous ONF_3 were determined at room temperature using the spectrometer and procedures described previously [12]. The trifluoramine oxide was obtained from the Allied Chemical Corporation. Its infrared spectrum agreed very closely with the published spectrum, [3] including peaks attributed to impurities. Inasmuch as the $\text{N } 1s$ spectrum showed no evidence of other peaks (except that due to the N_2 calibrant), we conclude that the sample contained no significant amount of nitrogen-containing impurities. (All other N compounds would have $\text{N } 1s$ binding energies at least 2.5 eV lower than that of ONF_3 .) The estimated uncertainties in the $\text{N } 1s$, $0\text{ } 1s$, and $\text{F } 1s$ binding energies, and the corresponding FWHM values in eV are, respectively: ± 0.05 (1.46), ± 0.02 (2.33), and ± 0.03 (1.77).

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