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Geometries and Energies of Complexes between Formaldehyde and First- and Second-Row Cations. A Theoretical Study

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Complexes between formaldehyde and a set of first- and second-row cations, Li^+, BeH^+, BH_2^+, CH_3^+, Na^+, MgH^+, AlH_2^+, and SiH_3^+, have been explored by ab initio molecular orbital theory. Geometries and partial searches of the potential energy surfaces employed the 3-21G split-valence basis set. Interaction energies, calculated with the larger polarized basis (6-31G*), are smallest for the ionic complexes involving Na^+ and Li^+ (29.0 and 40.1 kcal/mol), are intermediate for the other second-row cations, MgH^+, AlH_2^+, and SiH_3^+ (54–60 kcal/mol) as well as CH_3^+ (66.5 kcal/mol), and are largest for BH_2^+ (71.3 kcal/mol) and BeH^+ (91.8 kcal/mol). The minimum energy geometries for most of the complexes, unlike protonated formaldehyde ($HO{=}CH_2^+$), had linear M–O–C arrangements. The exceptions, $CH_3OCH_2^+$ ($\angle COC = 128.0°$), $SiH_3OCH_2^+$ ($\angle SiOC = 148.9°$), and planar $BH_2OCH_2^+$ ($\angle BOC = 131.4°$), involve more electronegative elements and less polar, directed covalent bonds. However, the most stable BH_2^+ complex is perpendicular $BH_2OCH_2^+$ with a linear, allene structure where the formally vacant BH_2 orbital can interact with the lone-pair p orbital on oxygen. The linear preferences in other cases are attributed to the large electronegativity differences between oxygen and the metallic elements; hence, other metals should behave similarly. The potential energy surfaces are rather flat around the minima, and in-plane coordination at angles 30° from the optimum costs only a few kilocalories per mole. Hence, the metal cation coordination could also be effective at nonoptimum geometries. The implications with regard to the attachment of lanthanide shift reagents to carbonyl groups are considered.

Introduction

Complexes between carbonyl compounds and Lewis acids play a fundamental role in organic and biochemical reactions.[1] For example, protonation of carbonyl groups is known to precede and to facilitate nucleophilic addition in acidic media.[2,3] Methylated formaldehyde, more familiar as the methoxymethyl cation, is stable enough to be isolated in the solid state and is used as an initiator in cationic polymerizations.[4] Reactions of carbonyl functions are catalyzed by complexation with ions like Li^+ and Na^+ as well as by other metal cations; in many instances, the stereoselectivity is drastically altered as well.[5] The interaction between carbonyl groups and lanthanide complexes provides a handle for structural investigations using shift reagents.[6] The role of cation binding to carbonyl oxygen atoms in influencing polypeptide and protein conformations has been well documented.[7]

Not surprisingly, considerable experimental and theoretical efforts have been expended to characterize the structure and energies of carbonyl–Lewis acid complexes and also to understand the origin of their interaction.[8–19] However, most of the reported studies have considered only H^+, CH_3^+, Li^+, and Na^+ as the Lewis acids. Gas-phase binding energies for formaldehyde with H^+, CH_3^+, and Li^+ have been measured.[8] Protonated and methylated formaldehyde have been studied by NMR techniques under stable ion conditions.[9] For the latter, a geometrical isomerization has been observed whose barrier agrees well with the computed barrier (ab initio, 4-31G basis set) for an inversion process. A similar inversion barrier has been calculated for CH_2OH^+ (intervention of proton exchange prevents an NMR experimental verification).[9,10] On the other hand, linear coordination geometries are indicated to be the minima for the Li^+ and Na^+ complexes on the basis of MO calculations.[11]

The preferred geometries of complexes between formaldehyde and metal cations and the potential energy surfaces are the result of a complex interplay of electrostatic and orbital interactions and hence provide valuable information regarding the nature of these complexes. Several energy-partitioning schemes have been proposed and applied to complexes with H^+ and Li^+.[15–19] The interaction energies were broken down into physically understandable quantities like charge transfer,

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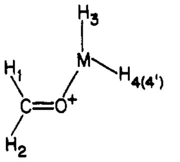
Table I. 3-21G Optimized Geometries (C_s Symmetry) of $CH_2{=}O^+{-}M$ Complexes



	bond lengths, Å						bond angles, deg				
M	H_1-C	H_2-C	C-O	M-O	M-H_3	M-H_4	H_1-C-O	H_2-C-O	C-O-M	O-M-H_3	O-M-H_4
none	1.083	*a*	1.207				122.5	*a*			
H	1.072	1.075	1.252	0.983			116.1	122.4	123.2		
Li	1.077	*a*	1.225	1.728			121.2	*a*	180		
BeH	1.076	*a*	1.240	1.514	1.313		120.0	*a*	180	180	
BH_2 (planar)	1.074	1.077	1.253	1.503	1.164	1.125	117.6	121.3	131.4	114.7	113.4
BH_2 (perp)	1.075	*a*	1.237	1.447	1.170	*b*	119.5	*a*	180	114.3	*b*
CH_3	1.073	1.076	1.239	1.525	1.078	1.025^c	117.5	121.8	128.0	108.3	115.9
Na	1.078	*a*	1.221	2.075			121.6	*a*	180		
MgH	1.077	*a*	1.231	1.892	1.684		120.8	*a*	180	180	
AlH_2 (planar)	1.076	*a*	1.234	1.833	1.564	*b*	120.4	*a*	180	109.4	*b*
AlH_2 (perp)	1.076	*a*	1.233	1.816	1.564	*b*	120.4	*a*	180	108.1	*b*
SiH_3	1.074	1.077	1.237	1.811	1.468	1.462^d	118.8	121.6	148.9	103.3	112.5

[a] By symmetry equivalent to the value for H_1. [b] By symmetry equivalent to the value for H_3. [c] H_4 and H_4' are equivalent by symmetry; H_4-C-H_4' = 112.4°. [d] H_4 and H_4' are equivalent by symmetry; H_4-C-H_4' = 116.4°.

Table II. Energies of Lewis Acid–Formaldehyde Complexes and Reference Species (hartrees)

$H_2C{=}OM^+$ complex, M^+ =	cation (M^+) energy (6-31G*//3-21G)^a	STO-3G//STO-3G	3-21G//3-21G^b	6-31G*//3-21G^b
none (formaldehyde)		−112.35435^a	−113.22182^a	−113.86528
H^+	0	−112.70702^a	−113.51414^a	−114.15437
Li^+	−7.23554^c	−119.60702^a	−120.49356^a	−121.16481
BeH^+	−14.84954^c	−127.23272	−128.15555	−128.86114
BH_2^+ (planar)	−25.47080^c	−137.70674	−138.67309	
BH_2^+ (perp)		−137.70674	−138.67793	−139.44974
CH_3^+	−39.23064^c	−151.30892	−152.35092	−153.20192
Na^+	−161.65929^d	−272.19288	−273.95623	−275.57086
MgH^+	−199.88493	−309.97147	−312.08718	−313.83900
AlH_2^+ (planar)	−242.76252	−352.43266	−354.76894	
AlH_2^+ (perp)		−352.43438	−354.77382	−356.71418
SiH_3^+	−290.32881	−399.56526	−402.13285	−404.28897

[a] Most of the reference values at STO-3G//STO-3G and at 3-21G//3-21G along with the geometries are available in ref 30. [b] The 3-21G optimized geometries given in Table I were used. [c] Value at 6-31G*//6-31G* from ref 30. [d] Reference 11e.

polarization, exchange energies, etc. These studies have been of significant value in understanding the origin of noncovalent interactions, although a certain degree of arbitrariness is implicit in each partitioning scheme.

An alternative procedure is adopted in the present study. A series of first- and second-row Lewis acids interacting with formaldehyde is considered at a uniform level of theory of reasonable accuracy. The electronegativities and the number of available acceptor orbitals as well as their energies vary significantly in this series. Therefore, an analysis of the potential energy surfaces of these complexes provides valuable insight into the nature of their interactions. Our results should also have significant implications for the interaction of carbonyl compounds with other electropositive groups, e.g., in structural investigations using lanthanide shift reagents.[6,12,13]

Table III. 3-21G Calculated Energies of Cation–Formaldehyde Complexes for Various C–O–M Angles (hartrees)^a

cation	120°	150°	180°
H^+	−113.51388	−113.50218	−113.49000
Li^+	−120.47774	−120.49025	−120.49356^b
BeH^+	−128.13879	−128.15239	−128.15555^b
BH_2^+ (planar)	−138.66984	−138.66882	−138.66167
BH_2^+ (perp)	−138.66355	−138.67648	−138.67793^b
CH_3^+ (syn)^c	−152.34892	−152.34245	−152.33072
Na^+	−273.94237	−273.95316	−273.95623^b
MgH^+	−312.06993	−312.08352	−312.08718^b
AlH_2^+ (planar)	−354.75843	−354.76802	−354.76894^b
AlH_2^+ (perp)	−354.75301	−354.76950	−354.77382^b
SiH_3^+ (syn)^c	−402.12400	−402.13284	−402.13146

[a] Each C–O–M angle was fixed at the indicated values, and the entire complex was restricted to C_s symmetry. All other bond angles and bond lengths were optimized. [b] Minimum-energy geometries, defined in Table I. [c] The dihedral angles HCOC or HSiOC were 0° for the in-plane hydrogens.

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Table IV. 3-21G Relative Energies of Formaldehyde–Cation Complexes for Different C–O–M Angles (kcal/mol)

M^+	180°	150°	120°	optimum angle[a]
H^+	15.2	7.5	0.2	0.0 (116.1°)
Li^+	0.0	2.1	9.9	
BeH^+	0.0	2.0	10.5	
BH_2^+ (planar)[b]	7.2	2.7	2.0	0.0 (131.4°)
BH_2^+ (perp)[b]	0.0	0.9	9.0	
CH_3^+	12.7	5.3	1.3	0.0 (128.0°)
Na^+	0.0	1.9	8.7	
MgH^+	0.0	2.3	10.8	
AlH_2^+ (planar)[c]	0.0	0.6	6.6	
AlH_2^+ (perp)[c]	0.0	2.7	13.1	
SiH_3^+	0.9	0.01	5.6	0.0 (148.9°)

[a] The optimum angle (if not 180°) is given in parentheses. [b] The best planar structure (nonlinear) is less stable than the best perpendicular structure (linear) by 3.0 kcal/mol. [c] The best planar structure is less stable than the best perpendicular structure (both linear) by 3.1 kcal/mol.

Table V. Complexation Energies between Lewis Acids and Formaldehyde (kcal/mol)[a]

Lewis acid	STO-3G	3-21G// 3-21G	6-31G*// 3-21G	exptl	best calcd
H^+	221.3	183.5	181.4	171–176[b]	172.6[c]
Li^+	73.6	53.1[d]	40.1[d]	36[e]	35.5[f]
BeH^+	134.0	108.8	91.8		
BH_2^+	111.4	86.3	71.3		
CH_3^+	109.8	75.1	66.5	78 ± 1[g]	[g]
Na^+	33.8	38.1	29.0		
MgH^+		70.2	55.7		
AlH_2^+	63.9	67.4	54.2		
SiH_3^+	77.7	70.7	59.5		

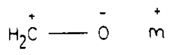
[a] Based on the equation $H_2C{=}OM^+ \rightarrow H_2C{=}O + M^+$. [b] See: Walker, R.; Franklin, J. L. *Int. J. Mass. Spectrom. Ion Phys.* 1980, *36*, 85. [c] Reference 19. [d] Reference 11e. [e] Reference 8. [f] Reference 11f. [g] See ref 9 and literature cited.

Computational Details

Ab initio calculations have been carried out on complexes between formaldehyde and the series of Lewis acids, M: H^+, Li^+ BeH^+, BH_2^+, CH_3^+, Na^+, MgH^+, AlH_2^+, and SiH_3^+.[20] Two conformations, planar and perpendicular, were considered for BH_2^+ and AlH_2^+ groups to probe the importance of orbital interactions in two orthogonal planes. Geometry optimizations were first carried out with the minimal STO-3G basis set, but the results proved to be unreliable for the systems with second-row atoms. We now recognize that the STO-3G basis set for sodium is unsatisfactory,[20g] and this compromises some conclusions we reached earlier.[21] Hence, we discuss here geometries obtained with the split-valence 3-21G basis set.[20] The potential energy surfaces (Tables III and IV), were calculated by optimizing all geometrical parameters for different C–O–M angles, with C_s symmetry constraint. The fully optimized geometries are given in Table I, and the corresponding energies are provided in Table II. Single-point calculations using the polarization 6-31G* basis set should afford more reliable energies, and these are also given in Table II. The 6-31G*//3-21G complexation energies between formaldehyde and the various Lewis acids are compared with available experimental and higher level theoretical values in Table V.

Results and Discussion

In agreement with previous calculations and available experimental results,[9–11,16] both CH_2OH^+ and $CH_2OCH_3^+$ are calculated to have bent geometries with significant barriers to inversion at oxygen, while the lithium complex, CH_2OLi^+, is indicated to prefer linear coordination. Previous discussions on the nature of oxygen base-Lewis acid interactions have been based mainly on these results.[15,16,18,19] There is general agreement that the interactions of H^+ and CH_3^+ with formaldehyde are mainly covalent in character. If corresponding complexes are regarded as methyl cations substituted by OH and OCH_3 groups, the bent geometry at the oxygen atoms is expected by analogy with water, alcohols, and ethers. The complex with Li^+, on the other hand, is predominantly ion-dipolar in nature.[15,16,18] Significant stabilization results by polarization of the carbonyl dipole. Such polarization is more effective along the C=O axis. Similarly, LiOH, Li_2O, and $LiOCH_3$ have linear geometries.[22] The ionic formulation **1** helps in understanding this effect.



$$\overset{+}{H_2C} —— \overset{-}{O} \quad \overset{+}{m}$$

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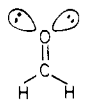

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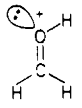

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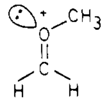

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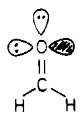

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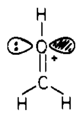

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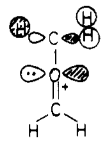

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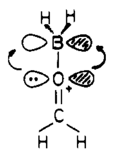

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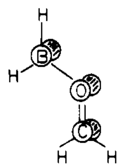

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While these are satisfactory explanations, they are not adequate to rationalize all the results in this study. However, an analysis in terms of molecular orbitals is uniformly successful in accounting for the calculated inversion potential energy surfaces.

The two oxygen lone pairs of formaldehyde are often represented by localized sp^2-hybridized orbitals, **2**. As pointed out inter alia by Jorgensen and Salem,[23] such "rabbit ear" representations do reflect the electron density. On this basis, it is easy to understand why acids like H^+ and CH_3^+, with a single low-lying vacant orbital, prefer bent arrangements, **3** and **4**. Such acids form bonds by attachment to one of the sp^2 lone pairs.

However, when the energy of the lone-pair orbitals in formaldehyde is important, representation **2** is inadequate. For

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(20) The GAUSSIAN 70 and GAUSSIAN 76 series of programs were used with some modifications: (a) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QCPE* **1973**, *13*, 236. (b) Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1979**, *13*, 368. (c) The STO-3G basis set: Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (d) The 3-21G basis set for first-row elements: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (e) The 3-21G basis set for second-row elements: Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (f) The 6-31G* basis set: Harihan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (g) Unpublished results in Erlangen.

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(23) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

example, the photoelectron spectrum indicates the lone-pair orbitals of formaldehyde to be different, and to be separated by ca. 5 eV.[24] As shown in **5**, one of these orbitals is sp hybridized and lies along the C=O axis. This sp lone pair actually lies below the π C=O orbital in energy. The HOMO, the lone-pair orbital with p character, lies perpendicular to the C=O axis. Formula **5**, rather than **2**, affords a better understanding of the nature of the interaction of a wide variety of Lewis acids with formaldehyde, although both are equivalent representations of the basis orbitals.

Consider protonated and methylated formaldehyde in linear arrangements, **6** and **7**. The sp-hybridized bonds to oxygen are strong, but the remaining lone pair is forced into a p orbital that is high in energy. Bending to give **3** and **4**, respectively, allows s character to mix into this lone-pair orbital, and the energy is significantly lowered. Consequently, **3** and **4** are preferred over **6** and **7**.

Stabilization of the linear form is found when a vacant p orbital is present on the atom attached to oxygen. Consider **6** and **7** again. The OH hydrogen in **6** has no orbital to interact with the lone pair. The methyl group in **7** does have an antibonding orbital of the proper symmetry for interaction with the lone-pair orbital. This interaction, although weak, contributes to the lower **4**–**7** energy difference (relative to **3**–**6**). A perpendicular BH_2 substitutent, **8**, is quite different. In the conformation shown in **8**, the vacant p orbital interacts strongly with the lone pair on oxygen. As this interaction is best when the lone pair is in a p orbital, the linear C=O—B arrangement, **8**, is favored. The preferred geometry is easy to understand, since **8** is isoelectronic and isostructural with allene (**9**). The dication $(CH_2OCH_2)^{2+}$ is also isoelectronic with allene, and it too prefers a linear geometry.[25]

If the BH_2 group is turned 90°, so that all atoms lie in the molecular plane, a bent structure, **10**, is favored. The vacant boron p orbital, as shown, now interacts with the C=O π orbital, but this interaction is substantially independent of the C—O—B angle. Both **10** and **8** are indicated to be minima on the potential energy surface, with **8** favored by 3 kcal/mol at the 3-21G level.

Although the SiH_3 group also prefers a bent conformation, the distortion from linearity and the resulting stabilization are much less than for methyl. The 3-21G basis set does not include d orbitals on silicon, and the lone-pair stabilizing effect can be attributed to interaction with relatively low-lying SiH_3 antibonding orbitals of appropriate symmetry (π^* SiH_3). The greater electronegativity of carbon, relative to silicon, also contributes to the difference in behavior.[26] Silicon and boron have comparable electronegativities, however, and the behavior of the SiH_3 and planar BH_2 complexes are qualitatively similar (table IV). A PRDDO calculational study indicates the acetone complex with SiH_3^+ to be nonlinear, but the bending also is less than in the CH_3^+ complex.[27]

Unlike $H_2C{=}O{-}BH_2^+$, both perpendicular and planar AlH_2 arrangements in $H_2C{=}O{-}AlH_2^+$ favor linear C–O–M geometries. The Al–O electronegativity difference is larger than for B–O, and this leads to the angle widening.[26] Planar $H_2C{=}O{-}BH_2^+$ (**10**), like $H_2C{=}OH^+$ (**3**), is best when bent; the electronegativity of boron is similar to that of hydrogen, and the bonds to oxygen are more covalent and less ionic in character than Al–O bonds. While the orbital overlap of oxygen with second-row atoms is less than with first-row atoms, an orbital contribution to the linear preference of the perpendicular conformation of AlH_2 is indicated by the data in Table IV. The 120–180° energy difference is twice as large for perpendicular $H_2C{=}O{-}AlH_2^+$ than for the planar form.

All the remaining electropositive groups investigated, Li^+, BeH^+, Na^+, and MgH^+, prefer linear C–O–M geometries. Although all these groups possess vacant p orbitals that could interact either with the oxygen lone-pair orbital (as in **8**) or with the carbonyl orbital (as in **10**), the large metal–oxygen electronegativity difference plays the dominant role in determining the minimum energy structure. Similar effects are responsible for the in-plane bisected geometries typically observed for the solid-state complexes of metal cations with ethers when no restraints are present.[28]

Acid–Formaldehyde Interaction Energies

A few of the interaction energies calculated in this study are available from experiment or through prior higher level calculations.[11,19] The data provided in Table V afford a check on the reliability of our calculations. The proton and methyl cation affinities are overestimated at the 3-21G level, while the 6-31G* values are in better agreement with experiment. The smaller basis set does not provide a good description of the oxygen lone pairs; this is improved when polarization functions are added.[29] The Li^+ interaction energy is still calculated to be too large at both levels, the 3-21G value being about 40% in error. Errors on species that have not yet been experimentally examined are expected to be comparable to those indicated in Table V.

Conclusions

Our calculations on a series of formaldehyde–Lewis acid complexes indicate that both bent and linear coordinations are possible, depending on the nature of the Lewis acid. A bent geometry is preferred if the major interaction is a charge transfer from the carbonyl oxygen to a σ type acceptor orbital on the Lewis acid. A linear geometry results if a π type acceptor orbital is available on the Lewis acid that can interact with the lone-pair p orbital of the carbonyl oxygen. If electrostatic interactions predominate, linear coordination is again preferred. The results also demonstrate that a linear geometry does not preclude significant charge-transfer interaction between the carbonyl group and the Lewis acid. In particular, the C_{2v} minimum energy geometry for the lithium complex is probably due to dominant ion–dipole interaction, but participation of acceptor p orbitals on lithium may also contribute. While the energy differences between linear and 120° structures is consistently large (usually 7–10 kcal/mol), distortions of up to 30° from the optimum geometry usually require only 2 kcal/mol or less. Consequently, strong interactions between carbonyl oxygen and metal cations are to be expected even when steric or other restraints preclude the optimum coordination geometry. The directionality of the interaction between carbonyl groups and Lewis acids has profound consequences in structural studies of ketones using lanthanide shift reagents. It has often been assumed that a lanthanide shift

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(29) Addition of diffuse functions on oxygen to the basis set are now known to bring a further improvement in accuracy. See: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

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reagent would coordinate to either of two equivalent lone pairs of electrons on the carbonyl oxygen (cf. structures **2**–**4**).[12] Spectroscopic results corresponding to a time average of these two complexes were expected, and this has been labeled the *two-site* model. However, some of us have found that results for $Eu(fod)_3$ complexes of symmetrical ketones are consistent only with a *linear* complex having a C═O—Eu angle of 180° (*one-site* model; cf. structures **5**–**7**).[13] Since lanthanide ions are highly electropositive and possess vacant d or f orbitals having the requisite symmetry, they may adopt a linear geometry in their complexes with ketones. Our results suggest that the *one-site* model[13] may not just be a computational convenience but rather may be a proper description of the actual complex.

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Note Added in Proof. Scatter plot analysis of X-ray data involving hydrogen-bonding interactions to a variety of oxygen functional groups reveals a statistical preference for the conventional lone-pair directions involving ketones (Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018). X-ray structures of an Ag^+–acetophenone complex (Crist, D. R.; Hsieh, Z.-H.; Quicksall, C. O.; Sun, M. K. *J. Org. Chem.* **1984**, *49*, 2478) and of a $[LiBr{\cdot}2(acetone)]_2$ complex (Seebach, D. Proceedings, 27th Welch Conference in Chemical Research, 1983, in press) also indicate nonlinear $C{=}O{-}M^+$ interactions. More data of this type are needed before reliable conclusions can be drawn about the shape of the potential energy surface.

Registry No. $CH_2{=}O$, 50-00-0; $CH_2{=}O{-}H^+$, 18682-95-6; $CH_2{=}O{-}Li^+$, 53259-65-7; $CH_2{=}O{-}BeH^+$, 91744-02-4; $CH_2{=}O{-}BH_2^+$, 91744-03-5; $CH_2{=}O{-}CH_3^+$, 41879-84-9; $CH_2{=}O{-}Na^+$, 57450-19-8; $CH_2{=}O{-}MgH^+$, 91744-04-6; $CH_2{=}O{-}AlH_2^+$, 91744-05-7; $CH_2{=}O{-}SiH_3^+$, 91744-06-8.

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X-ray Photoelectron Spectroscopic Study of Sulfur–Nitrogen–Fluorine Compounds

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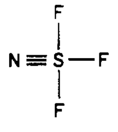
The gas-phase core binding energies of NSF, NSF_3, and several compounds of the types NSF_2R and F_2SNR have been determined. Qualitative interpretation of the data shows that $N(p\pi)\rightarrow S(d\pi)$ bonding is probably important in the NSF_2R compounds and in NSF_3, that the bonding of the sulfur atom in NSF is similar to that in SO_2, and that the nitrogen atom of NSF_3 is more negatively charged than that of NSF (in spite of a stronger N–S bond in NSF_3). Quantitative interpretation of the data for NSF and NSF_3, together with literature valence ionization potentials, shows that the HOMO of each molecule has principally nitrogen 2p character and is stabilized by interaction with a higher lying sulfur 3d orbital. The approximate atomic orbital contributions to the other molecular orbitals of these molecules are deduced.

We have obtained the gas-phase X-ray photoelectron spectra of the compounds[2] shown in Chart I in order to attempt clarification of the π bonding in the compounds. The structures in Chart I are Lewis octet structures, which imply the use of only s and p valence orbitals. The indicated charges are merely *formal charges*, i.e., the charges that the atoms would have if bonding electrons were equally shared between bonded atoms. It is of particular interest to determine whether $p\pi \rightarrow d\pi$ bonding is involved, i.e., to determine whether structures such as

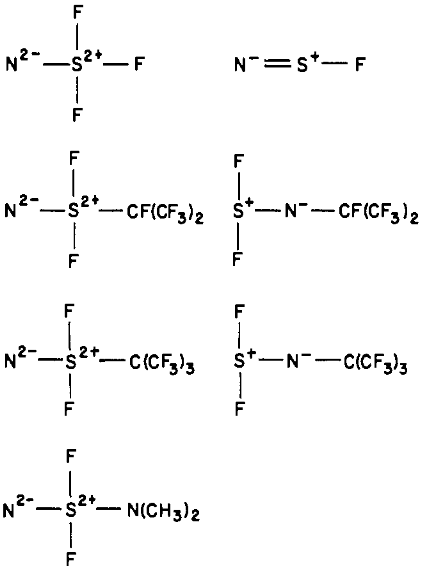


$$N{\equiv}SF_3$$

must be considered.

Qualitative Interpretation of Core Binding Energies

The core binding energy data for the compounds of Chart I are given in Table I.



$$N^{2-}{-}S^{2+}F_3 \qquad N^-{=}S^+{-}F$$
$$N^{2-}{-}S^{2+}F_2{-}CF(CF_3)_2 \qquad F_2S^+{-}N^-{-}CF(CF_3)_2$$
$$N^{2-}{-}S^{2+}F_2{-}C(CF_3)_3 \qquad F_2S^+{-}N^-{-}C(CF_3)_3$$
$$N^{2-}{-}S^{2+}F_2{-}N(CH_3)_2$$

Sulfur. It can be seen that replacement of a fluorine atom in NSF_3 by the $C(CF_3)_3$ or $N(CH_3)_2$ group causes a decrease in the sulfur $2p_{3/2}$ binding energy in qualitative accord with the relative electronegativities of the groups. As expected, replacement by the $CF(CF_3)_2$ group causes a decrease similar to that of the $C(CF_3)_3$ group, but inexplicably the $CF(CF_3)_2$ group causes a greater decrease than the $C(CF_3)_3$ group. Of course, removal of two fluorine atoms from NSF_3 to form NSF would be exected to cause a marked drop in the sulfur binding energy, and the observed drop of 2.96 eV is entirely

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(2) For a review of these compounds, see: Glemser, O.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 883.

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