

Structure and Spectra of the 1:1 Addition Compound of 1,4-Dioxane and Oxalyl Fluoride

G. Möller, M. M. Olmstead, and D. S. Tinti*

Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received July 23, 1986

Abstract: The crystal structure and Raman and optical spectra of a solid 1:1 addition complex between 1,4-dioxane and oxalyl fluoride are reported. The structure consists of infinite chains of alternating dioxane and oxalyl fluoride molecules, with the oxygens of dioxane situated symmetrically above and below the plane of the oxalyl fluoride molecule. The structure and spectroscopic results are discussed in terms of Hartree–Fock calculations on a model system consisting of two waters and one oxalyl fluoride.

A variety of solid addition complexes between ethers and halogen-containing molecules are known. Based largely on structural determinations, the interactions between the components in these complexes are generally interpreted in terms of charge-transfer bonding between the ether oxygen (donor) and the halogen (acceptor), with the interaction strength increasing in the order $\text{Cl} < \text{Br} < \text{I}$.¹ Examples of this class are the solid complexes of 1,4-dioxane with oxalyl chloride and oxalyl bromide. Their isomorphous structures contain chains of alternating dioxane and oxalyl halide molecules linked by apparent weak bonds between the oxygen atoms of dioxane and the halogen atoms of the acid halide.² A solid complex is also known between dioxane and dinitrogen tetroxide, the latter being isoelectronic with oxalyl fluoride. Its structure again consists of chains of alternating moieties, but their relative orientations are grossly different than in the preceding systems.³ The weak bonding interaction now apparently occurs between the oxygen atoms of dioxane and the nitrogen atoms of dinitrogen tetroxide. Prompted by the foregoing results and our interest in comparing the electronic structure of the oxalyl halides,⁴ we undertook to prepare and characterize the addition complex of 1,4-dioxane and oxalyl fluoride. We report herein its X-ray crystal structure and its Raman and optical spectra.

Experimental Section

Oxalyl fluoride (Columbia) was subjected to freeze–pump–thaw cycles in its lecture bottle to remove trace volatiles before use. The 1,4-dioxane (Aldrich, Gold Label) and pentane (Aldrich) were carefully dried and stored over sodium pellets under a nitrogen atmosphere.

The solid complex between oxalyl fluoride and 1,4-dioxane formed readily with various preparation schemes. For example, the mixing together of roughly equal molar amounts of oxalyl fluoride and dioxane by cryopumping in a vacuum system led to the immediate formation of the polycrystalline product upon warming to room temperature. The complex was also prepared by a variation of the method described by Varvoglis⁵ for the corresponding complexes of oxalyl chloride and bromide. Namely, under a dry nitrogen atmosphere a pentane solution of dioxane was added dropwise to a flask of pentane through which oxalyl fluoride was being bubbled. Crystalline needles of the complex formed at the tip of the dropper and could be harvested. With continued addition of dioxane, crystals of the complex would also precipitate from the pentane solution in the flask. The best crystals were obtained by slowly cooling a near-saturated pentane solution of the complex. The latter crystals were used for all of the results reported herein.

Samples for optical and Raman spectroscopic study were prepared by transferring in a drybox some crystals into quartz ampules, which were subsequently sealed off on a vacuum line under a helium atmosphere. The instrumentation used for obtaining low-temperature emission and excitation spectra has been described previously.⁴ Raman spectra at

Table I. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^b
F	−0.2658 (12)	0.48977 (11)	0.6371 (10)	81 (4)
O(1)	0.2776 (12)	0.8499 (12)	0.8399 (11)	77 (4)
O(2)	−0.1123 (11)	0.6984 (10)	0.4363 (10)	53 (4)
C(1)	0.4253 (20)	1.0872 (16)	0.8558 (15)	75 (6)
C(2)	0.3211 (22)	0.8519 (18)	1.0640 (17)	96 (8)
C(3)	−0.1032 (19)	0.5539 (20)	0.5162 (8)	64 (7)

^a Estimated standard deviations are given in parentheses. ^b $U(\text{eq}) = (U_{11} + U_{22} + U_{33})/3$.

ambient temperature were excited by the 488-nm line of an argon ion laser and recorded with a Spex Ramalab spectrometer.

Results and Discussion

1. Crystal Structure. A parallelepiped of approximate dimensions $0.1 \times 0.15 \times 0.25 \text{ mm}^3$ was selected from a pentane recrystallization for data collection with a Syntex P2₁ X-ray diffractometer. The crystal was coated with a hydrocarbon oil to reduce sublimation losses and reaction with atmospheric water during handling and cooled to $\approx 140 \text{ K}$ by a modified LT-1 low-temperature apparatus on the diffractometer. The crystal data at 140 K with the estimated standard deviations in parentheses are as follows: formula $\text{C}_2\text{F}_2\text{O}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$; triclinic; $a = 5.503 (7) \text{ \AA}$, $b = 6.388 (7) \text{ \AA}$, $c = 6.518 (7) \text{ \AA}$; $\alpha = 111.81 (9)^\circ$, $\beta = 91.20 (10)^\circ$, $\gamma = 108.87 (8)^\circ$; $V = 198.7 (4) \text{ \AA}^3$; $d(\text{calcd}) = 1.49 \text{ g cm}^{-3}$; $Z = 1$; space group $P\bar{1}$; $\mu(\text{MoK}\alpha) = 1.5 \text{ cm}^{-1}$; range of absorption correction factors 1.01–1.03. Absorption corrections were not applied. A total of 911 reflections were collected in the range $0 < 2\theta \leq 55^\circ$, of which 496 ($I > 2\sigma(I)$) were used to solve and refine the structure. The structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included in the refinement at calculated positions assuming a C–H bond distance of 0.96 \AA and idealized angles. At convergence, $R = 0.123$, $R_w = 0.089$, $w = 1/\sigma^2(F_o)$, $\text{GOF} = 9.65$, and there are 55 parameters.⁶ The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table I, with the atom numbering scheme shown in Figure 1.

The structure is shown in Figure 2 and consists of infinite chains of alternating oxalyl fluoride and dioxane molecules along $[111]$. Both moieties are at centrosymmetric positions with the oxalyl fluoride molecules having a trans planar conformation and the dioxane molecules in the chair form. However, the thermal parameters found in the refinement are quite large, leading to rather large uncertainties in the bond distances and valence angles of oxalyl fluoride and dioxane in the complex. The latter are given in Table II, together with comparison values for the complexes of oxalyl chloride and bromide with dioxane² and for oxalyl

(1) Hassel, O.; Rømming, Chr. *Q. Rev., Chem. Soc.* **1962**, *16*, 1.

(2) Damm, E.; Hassel, O.; Rømming, Chr. *Acta Chem. Scand.* **1965**, *19*, 1159.

(3) Groth, P.; Hassel, O. *Proc. Chem. Soc., London* **1962**, 379. Groth, P.; Hassel, O. *Acta Chem. Scand.* **1965**, *19*, 120.

(4) Möller, G.; Tinti, D. S. *Mol. Phys.* **1985**, *54*, 541.

(5) Varvoglis, G. *An. Prakt. Akad. Athenon* **1938**, *13*, 641. Varvoglis, G. *An. Ber. Dtsch. Chem. Ges.* **1938**, *17B*, 32.

(6) Scattering factors were taken from: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. Crystallographic programs used were SHELXTL, version 4.1, obtained from Nicolet Instruments and installed on a Data General Eclipse computer.

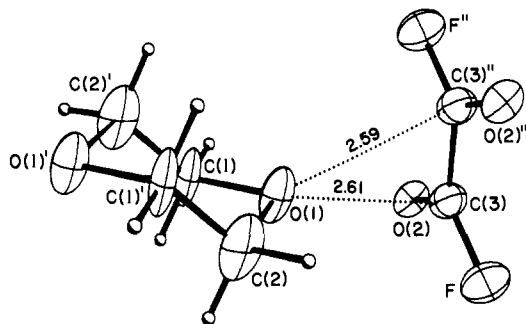


Figure 1. Computer-generated drawing of the addition complex of 1,4-dioxane and oxalyl fluoride showing the atom numbering scheme and anisotropic thermal ellipsoids at the 20% probability level. Hydrogen atoms are shown at an arbitrary size. Symmetry positions: primed atoms, $1-x, 2-y, 1-z$; doubled primed atoms, $1-x, 1-y, 1-z$. The estimated standard deviations for the distances (in Å) shown are ± 0.02 Å.

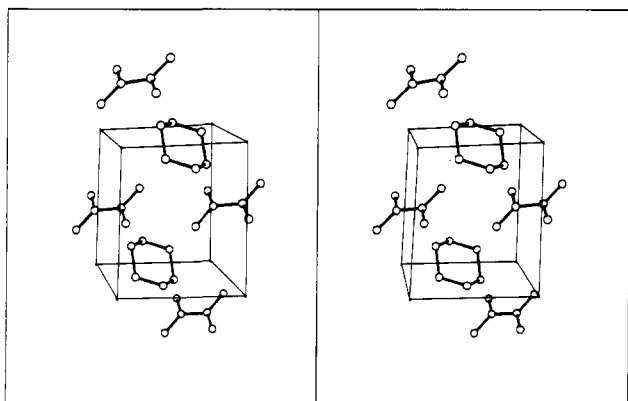


Figure 2. Stereoview of the packing in the crystal of the addition complex of 1,4-dioxane and oxalyl fluoride viewed along the b direction.

Table II. Bond Lengths (Å) and Angles (deg) for Trans Oxalyl Halides and 1,4-Dioxane

	gas ^a	fluoride complex ^b	chloride complex ^c	bromide complex ^c
Oxalyl Halide				
C-C	1.536	1.489 (26)	1.58	1.50
C-O	1.180	1.230 (17)	1.15	1.12
C-X	1.329	1.274 (13)	1.73	1.96
\angle CCO	126.0	122.4 (13)	125	133
\angle CCX	109.8	115.0 (16)	109	108
\angle OCX	124.2	122.6 (11)	123	118
Dioxane				
C-C	1.523	1.356 (16)	1.49	1.62
C-O	1.423	1.432 (12)	1.48	1.39
\angle CCO	109.2	110.2 (11)	112	108
		113.9 (10)	113	118
\angle COC	112.4	106.7 (6)	120	118

^a Reference 7 for oxalyl fluoride; ref 8 for dioxane. ^b This work, with estimated standard deviations in parentheses. ^c Calculated from data in ref 2.

fluoride⁷ and dioxane⁸ in the gas phase.

The comparison of the geometrical parameters for oxalyl fluoride in the complex and in the gas phase emphasizes a possible problem with the refinement. Namely, the C-O and C-F distances and the CCO and CCF angles are more similar in the complex than expected. This suggests a possible disorder in the crystal that interchanges the oxygen and fluorine atoms of oxalyl fluoride. A likely disorder would involve "rotation" of the oxalyl fluoride molecule by 180° about its C-C bond, which retains the trans conformation. An alternate possibility involving the trapping

Table III. Comparison of the Raman Bands (cm^{-1}) of Oxalyl Fluoride in Its Neat Crystal and Dioxane Complex

dioxane complex		neat crystal		assignment (C_{2h}) ^a
ν	int ^b	ν	int ^b	
418	w	420	m	$\nu_5(\text{ag})$, FCO rock
		513	w	$\nu_4(\text{ag})$, FCO bend
		595	vw	$\nu_8(\text{bg})$, FCO bend
772	m	799	m	
804	m	812	s	$\nu_3(\text{ag})$, CC stretch
		838	w	$2\nu_5 = 840$
1270	m	1290	w	$\nu_2(\text{ag})$, CF stretch
1873	s	1866	s	$\nu_1(\text{ag})$, CO stretch
1886	m	1874	m	

^a Reference 17. ^b Abbreviations: s, strong; m, medium; w, weak; and v, very.

of a significant amount of the cis conformation during crystal growth seems less likely. The difficulties in handling the highly reactive crystals precluded a definite analysis of this problem.

The significant features of the structure involve the intermolecular distances and relative orientations of the dioxane and oxalyl fluoride moieties. The oxygen of dioxane is essentially symmetrically located above the oxalyl fluoride plane. The distances from the dioxane oxygen to the oxalyl fluoride atoms are O...F, 3.02 and 3.04 Å; O...C, 2.59 and 2.61 Å; and O...O, 3.00 and 3.09 Å. The mean O...C distance of 2.60 Å is significantly smaller than the sum of the van der Waals radii (≈ 3.1 Å) and, thus, is indicative of appreciable intermolecular interaction. The COC plane of the ether atoms in dioxane is furthermore roughly perpendicular to the plane of the oxalyl fluoride molecule (88.8°) and to its C-C bond (78.0°).

This structure, and the implied intermolecular interaction, is much different than the structures of the corresponding 1:1 complexes of dioxane with oxalyl chloride and oxalyl bromide.² The structures of the latter complexes are isomorphous ($P2_1/c$, $Z = 2$) and consist of chains of alternating dioxane and nearly planar oxalyl halide molecules, both moieties at centrosymmetric positions. However, the nearest intermolecular contacts occur between the dioxane oxygen and the halogen (X) atoms along a near linear arrangement O...X-C. The intermolecular O...X distances are 3.18 and 3.21 Å in the oxalyl chloride and bromide complexes, respectively, which are only slightly less than the van der Waals contact distances (≈ 3.3 and 3.4 Å, respectively).

Two additional complexes related to the present system are known. The more similar is the solid complex formed between dinitrogen tetroxide and 1,4-dioxane, which is both isostructural and isoelectronic with the present system.³ The intermolecular distances between an oxygen of the dioxane and the two nitrogens are 2.90 and 2.76 Å, compared to ≈ 3.0 Å for van der Waals contact. The second complex involves the addition of the fluoride ion to oxalyl fluoride, forming the $C_2F_3O_2^-$ anion. A recent infrared study of this product ion in a matrix has suggested that its structure involves a symmetric fluoride bridge wherein the fluoride ion sits above the oxalyl fluoride plane and interacts with both carbon atoms.⁹

The feature common to the preceding two complexes and the present system is the near-symmetric interaction between an electron-rich center (the oxygen of dioxane or the fluoride ion) and the central atoms of a 34 valence electron system ($C_2F_2O_2$ or N_2O_4) of the general type A_2Y_4 . The latter systems are unusual in several regards. For example, members of the class exhibit different geometries, with both planar and perpendicular conformations known, which is rather atypical among members of an isoelectronic series.¹⁰ The A-A bond in the class is also often unusually long and weak,^{10,11} most notably in N_2O_4 , which readily dissociates into NO_2 . However, the C-C bond length in oxalate

(7) Hedberg, K., private communication. See also: Friesen, D. T. *Dis. Abstr. Int.*, **B 1981**, 41, 3458.

(8) Davis, M.; Hassel, O. *Acta Chem. Scand.* **1963**, 17, 1181.

(9) Ault, B. S. *Inorg. Chem.* **1986**, 25, 1013.

(10) Clark, T.; Schleyer, P. v. R. *J. Comput. Chem.* **1981**, 2, 20 and references therein.

(11) Brown, R. D.; Harcourt, R. D. *Aust. J. Chem.* **1963**, 16, 737.

Table IV. Calculated Structures^a and Energies^b for Oxalyl Fluoride, Water, and a Model Complex

	C ₂ F ₂ O ₂ (C _{2h})			C ₂ F ₂ O ₂ ·2H ₂ O (C _{2h})		
	STO-3G	4-31G	6-31G	STO-3G	4-31G	6-31G
C-C	1.566	1.500	1.503	1.566	1.493	1.484
C-O	1.212	1.177	1.180	1.212	1.178	1.181
C-F	1.350	1.341	1.348	1.351	1.347	1.353
∠CCO	125.0	126.1	126.2	125.4	127.3	127.3
∠CCF	112.5	110.8	110.9	112.3	110.3	110.4
-E	418.5272	423.7098	424.1405			

	H ₂ O (C _{2v})			C ₂ F ₂ O ₂ ·2H ₂ O (C _{2h})		
	STO-3G	4-31G	6-31G	STO-3G	4-31G	6-31G
O-H	0.989	0.950	0.950	0.988	0.950	0.950
∠HOH	100.1	111.2	111.6	100.6	112.4	112.5
-E	74.9659	75.9086	75.9854			
C...O				2.719	2.593	2.566
-E				568.4699	575.5765	576.1439
ΔE ^c				-0.0110	-0.0495	-0.0327
Δq ^d				0.0073	0.0258	0.0425

^aDistances in Å and angles in deg. ^bEnergies in hartrees (1 hartree = 627.5 kcal/mol). ^cΔE = E(complex) - E(C₂F₂O₂) - 2E(H₂O). ^dΔq = q(H₂O) - q(H₂O) in complex, where q is the sum of the total atomic charges, i.e., q(H₂O) = 10 exactly.

anion (1.57 Å),¹² oxalyl bromide (1.56 Å),¹³ oxalyl chloride (1.53 Å),¹³ oxalic acid (1.54 Å),¹⁴ and dimethyl oxalate (1.53 Å)¹⁵ is also somewhat longer than expected for sp² hybridized carbon atoms. The data for the oxalate compounds have been discussed by Küppers.¹⁶ A suggested explanation for the lengthening of the central A-A bond in these systems involves mixing between the nonbonding orbitals on the Y atoms and the central sigma orbitals.^{11,16} The C-C bond length of oxalyl fluoride in the complex is 1.49 Å, less than that of the other derivatives of oxalic acid and more in line with expectations, although in the gas its length is 1.54 Å and again rather long.

2. Raman Spectrum. The Raman spectrum of the complex was obtained to investigate if the intermolecular interactions were sufficiently large to cause observable perturbations of the intramolecular vibrational modes of the oxalyl fluoride moiety. The spectrum at ≤1500 cm⁻¹ was dominated by bands of the dioxane due to the relatively poor scattering associated with the oxalyl fluoride. However, by comparison with the spectra of solid oxalyl fluoride¹⁷ and liquid dioxane, the stronger bands due to the oxalyl fluoride in the spectrum of the complex could be identified. The results are summarized in Table III, which compares the oxalyl fluoride bands in the complex and in the neat crystal. The neat crystal results and the assignments are taken from the vibrational study of oxalyl fluoride by Durig et al.,¹⁷ incorporating a recently suggested minor assignment change.⁴ Durig et al. concluded from their studies that oxalyl fluoride in the solid phase exists as the trans planar conformer.

The frequencies and relative intensities of the Raman active modes of oxalyl fluoride in the neat crystal and in the complex are similar, as expected for an identical trans conformation for oxalyl fluoride in the two systems. Doublets are seen at ≈800 (ν₃, C-C stretch) and ≈1870 cm⁻¹ (ν₁, C-O stretch) in both systems. For the neat crystal Durig et al. invoked factor group splitting to explain the former and assigned the weaker member of the latter to a combination band. However, the crystal structure of the complex precludes factor group splittings, so that at least for the complex an alternate assignment is required for the lower frequency doublet. We assume that the bands at 772 and 804 cm⁻¹ in the complex represent the fundamental ν₃ and some other intramolecular mode, but the assignment of the latter is unclear.

Aside from the preceding, the largest observed shift occurs for the C-F stretching mode, ν₂, at ≈1270 cm⁻¹ and amounts to only 20 cm⁻¹. The shifts for the remaining observed bands are ≤10 cm⁻¹.

3. Optical Spectra. Contrary to the Raman spectrum, the optical spectra of the complex are clearly perturbed relative to neat oxalyl fluoride. The results are shown in Figure 3, which compares the emission and (uncorrected) photoexcitation spectra at 4.2 K of the complex and neat oxalyl fluoride. The spectra of the neat solid, which have been presented and assigned previously,⁴ involve the ¹A_u and ³A_u nπ* excited states. Its emission spectrum is phosphorescence from the ³A_u state of a shallow oxalyl fluoride trap, while the excitation spectrum corresponds to the ³A_u-¹A_g and ¹A_u-¹A_g transitions of oxalyl fluoride in the bulk solid. The respective origins occur at 316.0 and 296.2 nm.

We assume that similar assignments apply for the complex, so that the origins of the ³A_u-¹A_g and ¹A_u-¹A_g transitions, determined from the peaks of the excitation spectrum, are shifted to 371 and 340 nm, respectively. The ^{1,3}A_u states of oxalyl fluoride in the complex thus show red shifts of ≈4500 cm⁻¹ relative to the neat solid⁴ and ≈3000 cm⁻¹ relative to the pure gas.¹⁸ These are rather large shifts and may be associated with oxalyl fluoride traps and the possible disorder in the solid complex. However, the assignments appear justified by the general similarities to neat oxalyl fluoride; for example, the phosphorescence lifetimes (≈0.7 ms), the dominant activity in the phosphorescence spectra of a progression in a ≈1850-cm⁻¹ mode, assigned to the symmetric carbonyl stretching frequency ν₁, and the ¹A_u-³A_u splittings (≈2300 cm⁻¹).

4. Calculations. The interactions in the complex were investigated in a series of calculations using standard, restricted Hartree-Fock theory and the GAUSSIAN 82¹⁹ series of programs. A system consisting of two water molecules and one oxalyl fluoride molecule with an idealized C_{2h} symmetry similar to the dioxane complex was chosen as a model. A full geometry optimization was performed for water (C_{2v}) and trans planar oxalyl fluoride (C_{2h}), and a limited optimization for the model complex was performed wherein the waters were maintained perpendicular to the oxalyl fluoride and to its C-C bond. Calculations were performed for three basis sets (STO-3G, 4-31G, and 6-31G),²⁰ with the results summarized in Table IV.

A local minimum was found for the model complex with an average O(water)···C distance for the three basis sets of 2.63 Å,

(12) Reed, D. A.; Olmstead, M. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 938.

(13) Groth, P.; Hassel, O. *Acta Chem. Scand.* **1962**, *16*, 2311. Hjortaa, K. E. *Acta Chem. Scand.* **1967**, *21*, 1579.

(14) Delaplane, R. G.; Ibers, J. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *25*, 2423.

(15) Dougill, M. W.; Jeffrey, G. A. *Acta Crystallogr.* **1953**, *6*, 831.

(16) Küppers, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *29*, 318.

(17) Durig, J. R.; Brown, S. C.; Hannum, S. E. *J. Chem. Phys.* **1971**, *54*, 4428.

(18) Balfour, W. J.; King, G. W. *J. Mol. Spectrosc.* **1968**, *25*, 130.

(19) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Flueger, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

(20) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

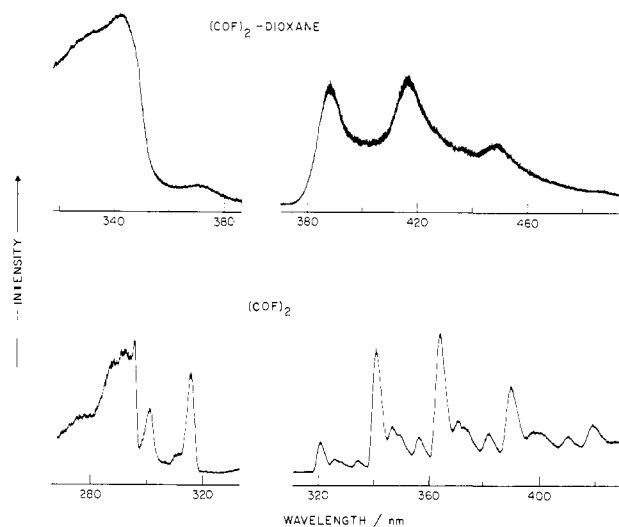


Figure 3. Phosphorescence emission and uncorrected photoexcitation spectra at 4.2 K of neat oxalyl fluoride and its complex with 1,4-dioxane.

in good agreement with the mean O(dioxane)···C distance of 2.60 Å found in the dioxane complex. At the optimized geometries, the energy of the model complex was lower than the sum of the energies of its moieties by 7–30 kcal/mol, depending on the basis set, which exceeds the expected difference in the zero-point energies. The geometries of the water and oxalyl fluoride at the

optimized geometry for the model complex remained essentially unchanged from those of the free molecules. The agreement between the calculated and experimental geometries for oxalyl fluoride is poor for the data obtained from the dioxane complex but reasonable for the gas-phase data, which again suggest some disorder in the crystals of the complex.

The interaction between the waters and the oxalyl fluoride can be loosely described as “charge-transfer” bonding, wherein each water donates charge to the oxalyl fluoride (an average of 0.025 e for the three basis sets). The largest change that results within the oxalyl fluoride is a redistribution of the $2p\pi$ orbital populations. The gross $2p\pi$ orbital populations of the carbons decrease while those of the oxygens, and to a lesser extent the fluorines, increase relative to uncomplexed oxalyl fluoride. Concomitantly, the Mulliken overlap population for the π orbitals of the carbons is reduced in the complex (0.0097 vs. 0.0087 in STO-3G). The largest overlap population between the waters and the oxalyl fluoride involves the $2p\pi$ orbitals of the carbons and the parallel $2p_z$ orbitals on the oxygens of the waters (0.0007 in STO-3G).

Calculations were not done for any excited states. However, the changes in the HOMO and LUMO energies suggest that the ${}^1,{}^3A_u \rightarrow {}^1A_g$ transitions of oxalyl fluoride would blue shift upon complexation, contrary to the observed results. Presumably, the excited states are somehow stabilized by the interactions, or the observed spectra are not due to bulk oxalyl fluoride in the crystal.

Acknowledgment. We thank Professor W. H. Fink for making available the GAUSSIAN 82 programs and Z. Darakjian for aid in their use.

The Reaction of Nitriles and Fe^+ in the Gas Phase. A Case of Remote Functionalization

Carlito B. Lebrilla, Christian Schulze, and Helmut Schwarz*

Contribution from the Institut für Organische Chemie, Technische Universität Berlin, D-1000 Berlin 12, FRG. Received July 24, 1986

Abstract: The gas-phase reaction of bare Fe^+ atoms with linear alkyl nitriles generates “end-on” complexes (**1**) which, depending on geometrical constraints, specifically interact with remote C–H bonds. Based on chain length effect studies and the investigation of labeled precursors, a mechanism is suggested which accounts for the chemospecificity observed for the loss of H_2 and C_2H_4 from RCN/Fe^+ complexes. This mechanism does not follow the analogous reaction of Fe^+ with alkenes and alkynes but involves an initial C–H insertion of the remote CH bonds followed by a C–C insertion.

The selective functionalization of C–H bonds remains one of the major focuses of catalytic and organic chemistry. In solution chemistry, high selectivity is often obtained by the presence of activating groups which induce the reactivity of the neighboring C–H bonds by, for example, polarizing the bond, thus making the hydrogen more acidic, or by generally weakening the C–H bond.¹ In the reactions of metals, both in the gas phase and in the bulk phase, activation of the neighboring C–H groups is accomplished selectively by initial complexation of the functional group and the metal.^{2,3,4} Hence, allylic activation has widely been

observed both in heterogeneous catalysis and in the gas phase with a variety of metals. Conversely, the functionalization of *remote* C–H bonds, i.e., several carbon atoms away from the functional group, remains a challenge. Such reactions are nonetheless

(1) Several basic organic chemistry books exist on the functionalization of activated C–H bonds. Some examples: (a) March, J. *Advanced Organic Chemistry—Reactions, Mechanisms, and Structure*; Wiley: New York, 1985. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1981.

(2) (a) Lebrilla, C. B.; Maier, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 1606. (b) Rooney, J. J. *J. Catal.* **1983**, *2*, 53. (c) Burwell, R. L., Jr.; Shim, B. C. C.; Rowlinson, H. C. *J. Am. Chem. Soc.* **1953**, *79*, 5142.

(3) (a) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (c) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484. (e) Tsaropoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085. (f) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (g) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

(4) (a) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Chem. Soc.* **1984**, *106*, 4307. (b) Schulze, C.; Steinrück, N.; Weiske, T.; Schwarz, H.; Gross, M. L., unpublished results. (c) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236.