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Carbonyl Hypofluorite-A Density Functional Theoretical Study

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Calculations on FOC(O)OF are reported at the B3LYP/6-311+G(2df)//B3LYP/6-31+G(d)+ZPC level of theory. The molecule is predicted to exist as a mixture of rotamers. The lowest-energy rotamer, the syn−anti, is predicted to be planar. The syn−syn rotamer appears to be conformationally floppy; a nonplanar (C_2) form, with O−F bonds rotated from the CO_3 plane by 16.4°, and a planar (C_{2v}) form are separated by only 0.01 kcal/mol. The anti−anti rotamer is predicted to be nonplanar (C_2 symmetry); the O−F bonds are rotated out of the CO_3 plane by 27.9°. Calculated barriers for interconversion of rotamers are less than 10 kcal/mol. We also calculate vibrational frequencies for the rotamers. The calculated O−F bond enthalpy is 30.2 kcal/mol.

Introduction

Species with O−F bonds have recently been of some interest in atmospheric chemistry, synthesis, and theory.[1] Recently Argüello et al.[2] described the synthesis, structure, vibrational spectrum, and calculations for fluoroformyl hypofluorite, FC(O)OF, a molecule first reported 30 years ago by Cauble and Cady.[3] We[4] reported calculations on a series of molecules FC(O)OF, FC(O)OOF, and FC(O)OOC(O)F. Structural studies and lower-level calculations had previously appeared for FC(O)OOC(O)F;[5] FC(O)OOF had merely been proposed as an impurity in the synthesis of FC(O)OF.[2a]

During the course of our earlier study, we recognized that the formula CF_2O_3 could also describe another hypofluorite: carbonyl hypofluorite, FOC(O)OF. This apparently unknown[6] species, an isomer of FC(O)OOF, is a logical target for further study. We report density-functional calculations on it here.

Methods

Calculations have used the GAUSSIAN94 program system.[7] Minima and transition states were fully optimized within the appropriate point group and frequencies were calculated at the B3LYP/6-31+G(d) level.[8] Default grid sizes were used throughout; a finer test grid produced the same energies.[9] Transition states were located using the default algorithm in GAUSSIAN94. Zero-point and heat-capacity corrections (298 K) are included without any scaling factor at the B3LYP/6-31+G(d) level. The standard "DFT" level is B3LYP/6-311+G(2df)//B3LYP/6-31+G(d) plus zero-point and heat-capacity corrections.

Hybrid density functional methods such as B3LYP have been shown to give results of near chemical quality with modest basis sets.[10] In addition, DFT appears to handle spin contamination better than Hartree−Fock (HF) theory does.[11] Two recent reports[1d,i] have demonstrated the utility of DFT in calculations on O−F bonded species.

Results and Discussion

Absolute energies (in hartrees) of species of interest are presented in Table 1. Relative energies are presented in Table 2. Structures of species of interest are given in Figure 1.

TABLE 1: Absolute Energies (hartrees) of Carbonyl Hypofluorite Species and Related Entities

	PG	state	B3LYP/ 6-311+G(2df)	ZPE[a,b]	C_p[b,c]	$\langle S^2\rangle$[d]
FOC(O)OF s−a(**1a**)	C_s	$^1A'$	−463.375 64	12.46	4.11	
FOC(O)OF s−s(**1b**)	C_2	^1A	−463.373 83	12.52	4.17	
FOC(O)OF a−a(**1c**)	C_2	^1A	−463.367 24	12.23	4.17	
FOC(O)OF(**TSab**)	C_1	^1A	−463.365 04	12.19	3.68	
FOC(O)OF(**TSac**)	C_1	^1A	−463.359 74	12.03	3.75	
OC(O)OF(**2′**)	C_s	$^2A'$	−363.563 04	9.79	3.45	0.76
OC(O)OF(**2″**)	C_s	$^2A''$	−363.544 35	9.51	3.38	0.78
OC(O)OF(**2TS**)	C_s	$^2A''$	−363.551 30	8.90	3.21	0.79
CO	$C_{\infty v}$	$^1\Sigma$	−113.354 49	3.15	2.07	
F	K	^2P	−99.761 65	0.00	1.48	0.75
OF	$C_{\infty v}$	$^2\Pi$	−174.940 38	1.58	2.49	0.75
CO_2	$D_{\infty h}$	$^1\Sigma_g^+$	−188.656 90	7.26	2.24	
F_2O	C_{2v}	$^1A_1$	−274.762 18	3.38	2.58	
FC(O)F	C_{2v}	$^1A_1$	−313.133 29	8.69	2.68	
FC(O)OOF	C_1	^1A	−463.422 03	12.66	4.15	
O_2	$D_{\infty h}$	$^3\Sigma_g^-$	−150.378 34	2.34	2.08	2.01

[a] Zero-point energy (kcal/mol). [b] Calculated at the B3LYP/6-31+G(d) level. [c] Heat capacity integrated from 0 to 298K (kcal/mol). [d] Spin-squared value for open-shell systems before spin projection.

TABLE 2: Relative Energies (kcal/mol) of Carbonyl Hypofluorite Species

	B3LYP/6-311+G(2df)	+ZPC[a]	+C_p[a]
FOC(O)OF s−a (**1a**)	0	0	0
FOC(O)OF s−s (**1b**)	1.1	1.2	1.2
FOC(O)OF a−a (**1c**)	5.3	5.0	5.1
FOC(O)OF (**TSab**)	6.7	6.4	6.0
FOC(O)OF (**TSac**)	10.0	9.5	9.2

[a] Zero-point and heat capacity corrections were calculated at the B3LYP/6-31+G(d) level and applied to B3LYP/6-311+G(2df) energies.

Our calculations on FOC(O)OF identify three minima, rotamers **1a**, **1b**, and **1c**, and two transition states, **TSab** and **TSac**, for their interconversion. In further discussion, we describe the stereochemistries of the rotamers in terms of the orientation of the fluorine atoms relative to the carbonyl oxygen (syn or anti).

The planar syn-anti rotamer **1a** is the lowest-energy species. The calculated syn and anti O−F bond distances in **1a** (and also in **1b** and **1c**) compare well with those in HOF, OF_2, SF_5OF, FC(O)OF, CF_3OF, and $CF_2(OF)_2$ (all between 1.41 and 1.45 Å)[2b,12] but not with that in FOOF (1.575 Å).[13] The corresponding C−O bond distances are almost identical with those found experimentally in the rotamers of FC(O)OF.[2b] The bond angles

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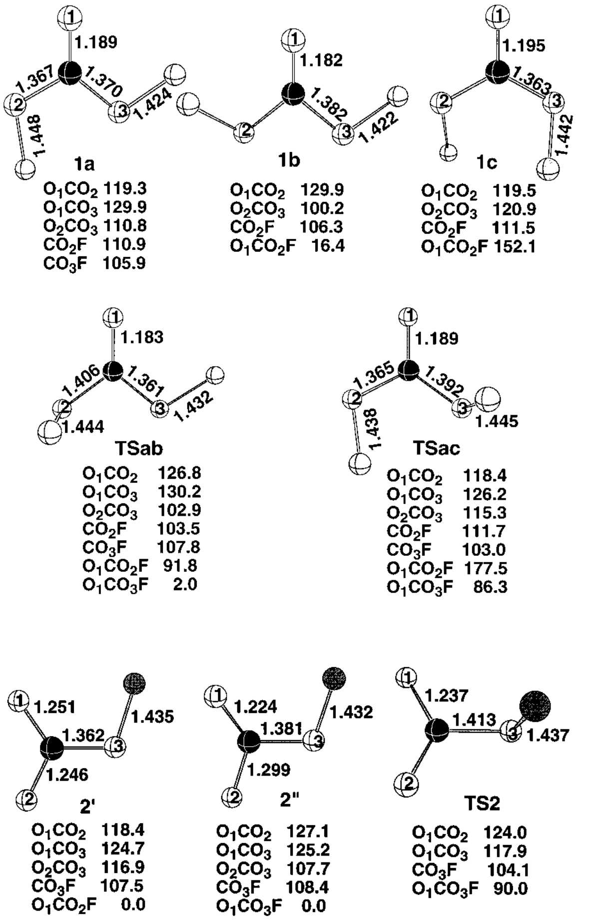

Figure 1. Structures of calculated species, with bond distances (Å) and bond and dihedral angles (deg) at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d)+ZPC level

around the central carbon in **1a** show significant distortions from the idealized 120°. We attribute this distortion to nonbonded repulsion between lone pairs on the syn fluorine atom and the carbonyl oxygen.

Calculations on planar forms of the syn–syn (**1b**) and anti–anti (**1c**) rotamers yield one imaginary vibrational frequency. These results indicate that the planar forms are not in fact minima. At the B3LYP/6-31+G(d)//B3LYP/6-31+G(d)+ZPC level of theory, the minima are 0.4 and 0.7 kcal/mol below the planar forms of **1b** and **1c**, respectively. These minima correspond to structures with C_2 symmetry in which the O–F bonds are conrotated out of the central CO_3 plane (16.4° in **1b** and 27.9° in **1c**). At the B3LYP/6-311+G(2df)//B3LYP/6-31+G(d) level, the minimum for **1c** is now 1.1 kcal/mol below the planar form, but the minimum for **1b** is now only 0.01 kcal/mol below the planar form. This implies that the potential surface for **1b** is very flat in the region around the planar geometry and that **1b** is rather floppy. At this level, **1b** is 1.2 kcal/mol above **1a**. Similarly, **1c** is 5.1 kcal/mol above **1a**. These results suggest that carbonyl hypofluorite would consist of a mixture of rotamers, dominated by **1a**.

The O=COF dihedral angles differ significantly from the experimental dihedral angle in FOOF and the predicted COOF dihedral angle in FC(O)OOF, both nearly 90°.[4,13] A natural population analysis[14] of **1a**–**1c** at the B3LYP/6-31+G(d) level reveals two dominant interactions: (1) carbonyl lone-pair donation into the adjacent σ^* C–O orbital and (2) C–O oxygen lone-pair donation into the adjacent π^* C=O orbital. Only the latter interaction is expected to play a role in the conformational preference of FOC(O)OF. This donation is maximum when the O–F bond is in the CO_3 plane and minimum when it is perpendicular. However, nonbonded O···F (syn) or F···F (anti) repulsion is also greatest when the O–F bond is in the CO_3 plane. Limited rotation of the O–F bonds out of the plane reduces the repulsion while not seriously disrupting donation. Thus, the dihedral angles reflect a compromise between these opposing effects, with donation being dominant in determining geometry.

Recently, Gobbato et al.[12e] have reported an electron diffraction study of the related molecule $CF_2(OF)_2$ along with calculations at several levels of theory. The lowest-energy conformer of this species is structurally analogous to **1c**; the OCOF dihedral angle is approximately 55°. They ascribe this dihedral angle to interactions between oxygen lone pairs and antibonding C–O and C–F σ^* orbitals.

We have located two transition states, **TSab** (for interconversion of **1a** and **1b**) and **TSac** (for interconversion of **1a** and **1c**). In each transition state, one O–F bond rotates out of the CO_3 "plane" by nearly 90°. The most interesting change in bond length is that for the C–O bond adjacent to the rotated O–F bond, which is some 0.02–0.03 Å longer than in the minima. Natural population analysis[14] of the donor–acceptor interactions in **TSab** and **TSac** indicates that the oxygen lone pair–π^* C=O interaction involving the rotated O–F bond is drastically reduced. This reduces the π character of the C–O bond and increases the bond length. **TSab** lies 6.0 kcal/mol above **1a**; **TSac** lies 9.2 kcal/mol above **1a**. These numbers are the predicted activation enthalpies for the interconversions **1a** → **1b** and **1a** → **1c**, respectively, as well as the barriers to rotation about the C–O bonds. These values are quite comparable to those determined for the rotamers of FC(O)OF[2] and calculated for FC(O)OOF[4] and should be accessible via NMR measurements, as were previously reported for FC(O)OF.[2a]

Calculated vibrational frequencies for the three rotamers appear in Table 3. Three of the modes may be cleanly assigned: the carbonyl stretch (the most intense fundamental in each spectrum, near 1900 cm^{-1}), the asymmetric O–C–O stretch, and the out-of-plane deformation of the central CO_3 group. Three other stretching modes, in the region near 1000 cm^{-1}, involve appreciable C–O and O–F stretching. We also note that the calculated spectra in the 1300–800 cm^{-1} region differ significantly for **1a** and **1b**; a variable-temperature infrared study in this region would serve to establish experimentally the presence and populations of these rotamers. Rotamer **1c** will be harder to detect, since its calculated spectrum is similar to that of **1a**. We should point out that the floppy nature of **1b** indicates that the torsions may be very anharmonic.

In determining the O–F bond energy in **1a**, we have also calculated the $FOCO_2$ radical. At our standard level, the ground state ($^2A'$, **2′**) is 11.4 kcal/mol lower in energy than the first excited state ($^2A''$, **2″**). In both states, the radical is predicted to be planar. The unpaired spin in **2′** is quite delocalized on the two carboxyl oxygens ($0.58e^-$, syn; $0.49e^-$, anti). The calculated rotational barrier about the C–O(F) bond (**2′** → **TS2**) is 6.4 kcal/mol.

The calculated O–F bond dissociation enthalpy (**1a** → **2′** + F) is 30.2 kcal/mol, well within the rather broad range of O–F bond energies (20–50 kcal/mol)[15,16] and almost identical with those calculated earlier for FC(O)OF and FC(O)OOF (28.7 and 30.8 kcal/mol, respectively).[4] Calculation of the C–O bond enthalpy (**1a** → FOCO + OF) has failed; geometry optimization of FOCO led instead to CO_2 and F. This result suggests that FOCO is not bound at the B3LYP/6-311+G(2df)//B3LYP/6-

TABLE 3: Calculated (B3LYP/6-31+G(d)) Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) for the Rotamers of FOC(O)OF

1a			1b			1c		
sym	assign	freq (int)	sym	assign	freq (int)	sym	assign	freq (int)
a′	$C{=}O$ str	1906 (315)	a	$C{=}O$ str	1948 (331)	a	$C{=}O$ str	1854 (284)
a′	OCO as	1225 (269)	b	OCO as	1133 (245)	b	OCO as	1267 (233)
a′	mixed[a]	1030 (22)	a	mixed[a]	1064 (4)	a	mixed[a]	970 (12)
a′	mixed[a]	946 (31)	b	mixed[a]	959 (129)	b	mixed[a]	926 (27)
a′	mixed[a]	883 (39)	a	mixed[a]	957 (14)	a	mixed[a]	842 (35)
a″	CO_3 oop	701 (29)	b	CO_3 oop	737 (18)	b	CO_3 oop	719 (43)
a′	bend	626 (19)	b	bend	670 (10)	a	bend	636 (9)
a′	bend	519 (2)	a	bend	458 (0)	b	bend	503 (7)
a′	bend	329 (9)	b	bend	336 (5)	b	bend	316 (12)
a′	bend	240 (1)	a	bend	266 (2)	a	bend	261 (0)
a″	bend	177 (0)	a	bend	121 (0)[b]	b	bend	134 (1)
a″	bend	131 (1)	b	bend	109 (0)[b]	a	bend	128 (1)

[a] These vibrations involve appreciable contributions from both C−O stretching and O−F stretching motions. [b] The lowest torsions for the planar form of this rotamer are 94 (imaginary) and 123 cm^{-1}, respectively.

31+G(d) level of theory. Su and Francisco[17] have recently reported ab initio calculations on this radical as an intermediate in the reaction between CO and OF. At their highest level of theory (UQCISD(T)/6-311+G(3df)//UQCISD/6-31G(d)+ΔZPE), *trans*-FOCO is bound, but the activation energy for its conversion to CO_2 and F is only 0.3 kcal/mol (the cis radical is not bound).[18] We calculate the enthalpy change for the process FOC(O)OF → CO_2 + F + OF as 9.0 kcal/mol.

We finally consider other possible reactions of carbonyl hypofluorite. The molecule is an isomer of fluoroformyl peroxyhypofluorite, FC(O)OOF. We predict that the enthalpy change for the isomerization (reaction 1)

$$\mathrm{FOC(O)OF} \rightarrow \mathrm{FC(O)OOF} \qquad (1)$$

is −28.9 kcal/mol (assuming lowest-energy rotamers). We have also calculated two decompositions (eqs 2 and 3).

$$\mathrm{FOC(O)OF} \rightarrow \mathrm{F_2O} + \mathrm{CO_2} \qquad (2)$$

$$\mathrm{FOC(O)OF} \rightarrow \mathrm{FC(O)F} + \mathrm{O_2} \qquad (3)$$

The enthalpy changes for these reactions are −28.4 and −86.1 kcal/mol, respectively. Although these reactions are energetically favorable, none of them appears to be mechanistically simple, and therefore, all may have substantial activation barriers. (The calculated[17] barrier for the isomerization of *trans*-FOCO to FC(O)O is 58.2 kcal/mol. The overall process is exothermic by at least 80 kcal/mol.) FOC(O)OF should be amenable to low-temperature studies if it can be prepared. It is therefore tempting to consider possible syntheses. Su and Francisco's calculations[17] suggest that FOCO decomposes too readily to be a plausible intermediate. Bond-energy data (ca. 20 kcal/mol for O−F vs 48 kcal/mol for O−O)[19] rule out FOOF as a precursor (thermal decomposition should lead to F and OOF instead of OF). Common condensed-phase routes to hypofluorites (fluorination of a peroxide[2] or CsF-catalyzed addition of F_2 across a $C{=}O$ bond[20]) are not applicable here; a reaction between F_2 and Cs_2CO_3 could be a possible condensed-phase alternative. We hope that the present theoretical study will encourage attempts at the synthesis of this challenging molecule.

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