# CAN FLUOROSYL HYDRIDE BE FORMED OR EVEN PREPARED?

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HFO and HClO (fluorosyl and chlorosyl hydrides) and isomeric molecules HOF and HOCl (hypofluorous and hypochlorous acids) have been studied theoretically. On the basis of non-empirical quantum chemical calculations (MP2, MP4 and CCD/6-311G**) geometry, energy and vibrational characteristics are analyzed and it is concluded that there is a poor chance to observe formation of HFO. Possibly, bombardment of HF in a solid matrix by $^{16}O$ could lead at very low temperature to HFO.

It was realized many years ago that the possibility of making predictions based on results obtained from theoretical tools represents an especially important aspect of theory in chemistry. This is particularly true for potentially unstable species and with characteristics which are important but not easily accessible. Various branches of contemporary theory are capable of offering valuable information. The role of quantum chemistry is especially worth mentioning. It is desirable, however, not to limit a prediction concerning a species which has not yet been synthesized to a statement whether that species possesses a minimum on the respective potential energy surface (P.E.S.), but also to predict some physical characteristics which can be later used in its identification, e.g., optical, electric, or magnetic characteristics. Finally, it is especially appreciated if a suggestion on its preparation can be offered on the basis of theory.

In this communication we deal with prospects of the preparation of the as yet unknown fluorosyl hydride ($I$, X = F), based mainly on the relative energies of stationary points on the P.E.S. This system belongs to a class of molecules having structure $I$. Stability of all the species included in formula $II$ (hypofluorous acid, etc.) is low, nevertheless at least in form of anions they are accessible in aqueous solutions. These species may be considered as halogenated water. (It is expedient to note that in connection with $I$ and $II$, X = F or Cl, sometimes erroneous nomenclature is used. Specifically, the HOF molecule is sometimes called fluorosyl hydride; the correct name is hypofluorous acid.)

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HXO                                    HOX

*I*, X = F, Cl, Br, I                        *II*, X = F, Cl, Br, I

(*Ia* = HFO, *Ib* = HClO)                   (*IIa* = HOF, *IIb* = HOCl)

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Hypofluorous acid has been prepared by the reaction of fluorine with liquid or solid water[1]. Hydrolysis of HOF leads[2] to $H_2O_2$. Its chemistry was summarized recently[3]. The IR spectrum of the $v_2$ and $v_3$ bands of $H^{16}OF$ (1 353 and 889 cm$^{-1}$). Its isotopically substituted derivatives have also been reported[4]. In connection with the investigation of the role of electron correlation on calculated equilibrium geometry and with the study of isomerization of extensive sets of molecules possessing two first-row atoms and a few hydrogen atoms, HOF and HFO were also treated[5,6]. The neutral and cationic forms of HOF were studied quantum chemically (MP2 level). In addition to the hypofluorous acid minimum, two additional high-lying structures were found[7]. The energy differences between these three isomers are significantly reduced when passing from the molecule to the cation. (See also ref.[8].) There is no experimental evidence concerning formation or even the existence of fluorosyl hydride, HFO. In the cited theoretical papers[5,6] fluorosyl hydride was studied and it was concluded[6] that HFO has either a shallow potential minimum or does not have a minimum at all.

The interaction of O $(^1D_2)$ with HCl leads to Cl, HCl, or ClO (refs[9,10]). Using a dynamic HOCl source, the UV spectrum of HOCl was measured and analyzed[11]. For the same molecule the high-resolution IR spectrum of the $v_2$ and $v_3$ band was studied[12]. Moreover, vibration-rotation spectra of deuterated species were measured and rotational constants obtained for $H^{16}O^{35}Cl$ and geometrical data tabulated for fluoro and chloro analogues of water[13]. An MP3 calculation and anharmonic force field is available for HOCl (ref.[14]). HOCl has also attracted attention because of its potential role as a reservoir for chlorine atoms in the stratosphere[15].

## RESULTS OF CALCULATIONS AND DISCUSSION

Energy, geometry and vibrational characteristics of fluorosyl hydride $(I, X = F)$ hypofluorous acid $(II, X = F)$ and of both the chlorine containing systems $(I, X = Cl$ and $II, X = Cl)$ are presented in Table I. For each of the four mentioned molecules three real vibrational frequencies have been obtained on the basis of the Wilson analysis, which means that those systems represent minima on the P.E.S. Moreover, it has turned out that cyclic species *III* represent saddle points, i.e. activated com-
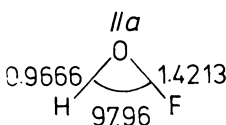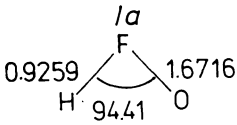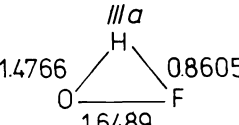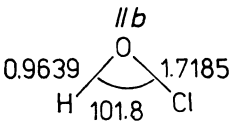
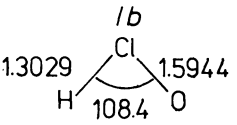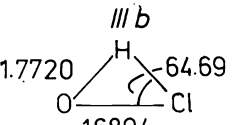<div align="center">

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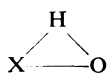
*IIIa*, X = F   *IIIb*, X = Cl

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plexes in the Eyring sense, connecting minima *I* and *II*. There is a very good agreement between calculated bond lengths and angles and those obtained experimentally as compiled by Deeley[13]. Geometric, vibrational and energetic characteristics suggest that fluorosyl hydride should be a very unstable molecule. The FO bond length in *IIa* $(1.412$ Å, $1$ Å $= 10^{-10}$ m$)$ is shorter than the bond lengths of single bonds between first-row atoms (e.g., the CC bond length, $1.54$ Å), while the FO bond in

TABLE I

MP2/6-311G** (full core) optimized geometries (Å and angles), vibrational frequencies (cm$^{-1}$) and infrared intensities (Km/mol) and MPN (or CCD)/6-311G**//MP2/6-311G** (frozen core) (au, unless stated otherwise)

| Characteristics | Geometry | | |
|---|---|---|---|
| | *IIa*<br>O<br>0.9666 / \ 1.4213<br>H  97.96  F | *Ia*<br>F<br>0.9259 / \ 1.6716<br>H  94.41  O | *IIIa*<br>H<br>1.4766 / \ 0.8605<br>O —— F<br>1.6489 |
| $-E^a$(MP2) | 175.25242 | 175.15103 | 175.14792 |
| $-E^b$(MP2) | 175.20009 | 175.09935 | 175.09619 |
| $-E^b$(MP3) | 175.20060 | 175.10898 | 175.10202 |
| $-E^b$(MP4) | 175.22163 | 175.12856 | 175.12100 |
| $-E^b$(CCD) | 175.20392 | 175.11568 | 175.10826 |
| $v$, cm$^{-1}$ | 966   1 411   3 833 | 451   612   4 067 | 878i   541   3 490 |
| int., Km/mol | 0.83   58.60   37.67 | 72.11   161.09   282.27 | —   —   — |
| ZPE, kcal/mol | 17.76 | 14.67 | 11.53 |
| | *IIb*<br>O<br>0.9639 / \ 1.7185<br>H  101.8  Cl | *Ib*<br>Cl<br>1.3029 / \ 1.5944<br>H  108.4  O | *IIIb*<br>H<br>1.7720 / \ 64.69<br>O —— Cl<br>1.6894 |
| $-E^a$(MP2) | 535.30317 | 535.19201 | 535.16637 |
| $-E^b$(MP2) | 535.23530 | 535.12400 | 535.09858 |
| $-E^b$(MP3) | 535.24758 | 535.13731 | 535.11502 |
| $-E^b$(MP4) | 535.26353 | 535.15487 | 535.13356 |
| $-E^b$(CCD) | 535.24982 | 535.13940 | 535.11677 |
| $v$, cm$^{-1}$ | 724   1 222   3 853 | 740   1 013   2 754 | 1 3061   612   2 925 |
| int., Km/mol | 4.25   39.94   69.82 | 32.15   1.13   10.77 | —   —   — |
| ZPE, kcal/mol | 16.58 | 12.89 | 10.11 |

[a] Full core; [b] frozen core.

fluorosyl hydride is predicted to be extremely long (1·67 Å), even 0·08 Å longer than the analogous calculated bond ClO in chlorosyl hydride. The FO bond length in *Ia* is longer than that in the activated complex *IIIa*, which is also unusual. Moreover, the length of the FH bond in *Ia* is very short (0·93 Å) and approaches the value in hydrogen fluoride (0·92 Å). In a sense, it is possible to view fluorosyl hydride as a molecule of hydrogen fluoride slightly perturbed by a singlet oxygen atom. This view also suggests a possible approach to the preparation of HFO: bombardment of hydrogen fluoride trapped in, e.g., an argon matrix by singlet oxygen atoms.



Fig. 1

Fragmentary reaction profiles for passing from HFO (*Ia*), HClO (*Ib*) to HOF (*IIa*), HOCl (*IIb*) via activated complexes (*IIIa*), (*IIIb*). Energies of the activated complexes were arbitrarily set equal zero. MP2/6--311G** characteristics in kcal/mol
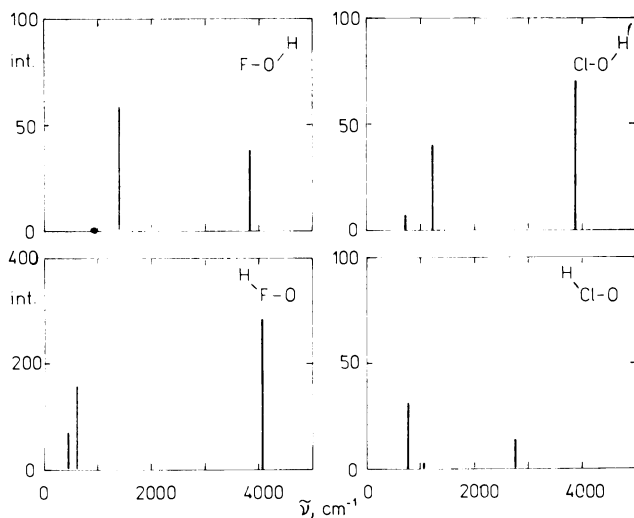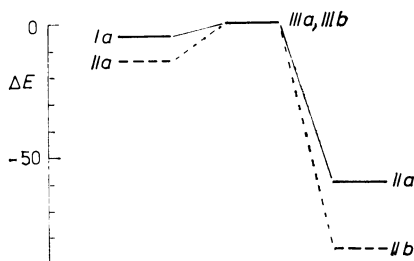


Fig. 2

Calculated infrared spectra of the studied molecules: MP2/6-311G** vibrational frequencies (cm⁻¹) and intensities (Km/mol)

Before passing to energy considerations, it is instructive to realize that the relative geometries of species *Ib*, *IIb* and *IIIb* differ significantly from those of the fluorine--containing species. The ClO bond length in hypochlorous acid (*IIb*) is 0·12 Å longer than that in chlorosyl hydride. Also the relative bond lengths of the OH and ClH bonds are opposite to the analogous bonds in the F-containing molecules. This permits one to consider *Ib* as if it were an associate of ·H⁻ with the chlorosyl cation and *IIb* as a hydroxyl radical weakly interacting with the Cl atom.

In Fig. 1 energy profiles of HFO and HClO species are presented. The total energies of HFO and HClO are arbitrarily set equal to zero. It is evident that *Ia* and *Ib* are thermodynamically unstable with respect to the isomers *IIa* and *IIb*. The energy barrier (CCD values) representing the source of kinetic stability is significantly higher for the chlorine containing case (14·2 kcal/mol, 1 kcal/mol = 4·184 kJ/mol) than for HFO. This $\Delta E^{+}$ value which is only 4·7 kcal/mol is reduced to 1·5 kcal/mol when passing to $\Delta H_0^{+}$ (inclusion of ZPE). Obviously, prospects for the preparation of HFO are not good.

From the comparison of calculated IR spectra of the isomeric species (HFO vs HOF and HClO vs HOCl) it seems that IR spectroscopy should be a valuable tool for distinguishing between the isomers (Fig. 2). A reasonable agreement between the observed[13] and calculated (Table I) values (724, 1 222, 3 853 vs 826, 1 370, 4 143 cm⁻¹) has been found for HOCl. A similar agreement is observed for the $v_2$ and $v_3$ bands of HOF (889, 1 353 vs 966, 1 411 cm⁻¹) (ref.[4] and Table I).

Finally the calculated MP4/6-31G*//6-31G* $\Delta E$ value (0·8 kcal/mol) is in good agreement with the observed[9] $\Delta H_0^{\circ}$ (0·9) for the following reaction:

$$O(^2P) + HCl \rightarrow OH + Cl(^2P) . \tag{1}$$
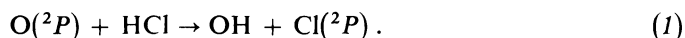
An analogous process with HF is associated with $\Delta E = 32·2$ kcal/mol. Also the following two processes, topical from the point of view of the potential preparation of HFO, are endoergic (MP4/6-31G*//6-31G* values and kcal/mol throughout):

$$O(^3P) + HF \rightarrow HFO , \quad \Delta E = 50·8 \tag{2}$$

$$O(^1D_2) + HF \rightarrow HFO , \quad \Delta E = 27·5 . \tag{3}$$
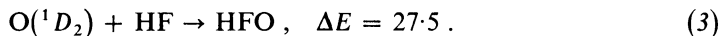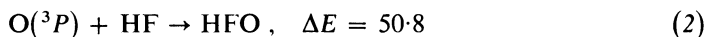
Let us conclude by saying that the prospects concerning even only formation of fluorosyl hydride are poor.

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