Journal of Fluorine Chemistry 131 (2010) 78–80

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Can PF_2OF exist?

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ARTICLE INFO

Article history:
Received 25 September 2009
Received in revised form 22 October 2009
Accepted 23 October 2009
Available online 4 November 2009

Keywords:
PF_2OF
G2 calculations
G3 calculations

ABSTRACT

G2 and G3 compound methods were used to explore the possibility that the covalent hypofluorite compound PF_2OF might exist as a stable compound. Calculations suggest that it may exist, making it a legitimate synthetic target. If it is isolable, it is likely to be very reactive, as the O–F bond is expected to be rather weak.

1. Introduction

Can PF_2OF exist? Its isomer phosphoryl fluoride, $PF_3 = O$, is well-known, with an enthalpy of formation of −1254.25 kJ/mol [1]. The bonding in phosphoryl fluoride is rationalized by invoking an expanded valence shell for the central phosphorus atom, and makes a common appearance in freshman chemistry sequences when covalent bonding is studied. However, the hypofluorite structure PF_2OF also satisfies valence requirements, and should be a reasonable covalent compound. A review of the literature using CAS SciFinder found no hits for a substance having formula PF_2OF with a hypofluorite structure.

While no stable ionic hypofluorite (OF^-) salts are known, a few covalent compounds have been isolated that contain an O–F moiety. HOF, FOF, FOOF, O_4F_2, O_2NOF, F_5SOF, FSO_2OF, CF_3OF, TeF_5OF and O_3ClOF have all been isolated long enough for at least some physical properties (appearance and melting and/or boiling points) have been determined; however, all are very reactive, even explosive [2]. Also known are CF_3OF, $CF_2(OF)_2$, CH_3OF [3], and $(CH_3)_3COF$ [4]; interestingly, this same group was able to isolate C_2D_5OF but not C_2H_5OF [5]. They hypothesized that ethyl hypofluorite spontaneously decomposed by HF elimination.

In 1965, Prager and Thompson isolated a series of organic –OF containing molecules, including CF_3CF_2OF, $CF_3CF_2CF_2OF$, $(CF_3)_2CFOF$, $(CF_3)_3COF$, $O_2NCF_2CF_2OF$, $ClCF_2CF_2OF$, Cl_2CFCF_2OF, and Cl_3CCF_2OF [6]. They indicate that these compounds are thermally stable at room temperature, some over a period of years, but are very strong oxidizing (fluorinating) agents. $CF_2(OF)_2$ was first isolated in 1967 [7], followed not long after by F_5SeOF [8]. Some fluoroperoxy compounds are also known, like CF_3OOF [9], and several acyl compounds, like $CF_3C(O)OF$ and $C_2F_5C(O)OF$ [10], $R(CF_2)_nC(O)OF$ (n = 4, 7–10) [11], and $CH_3C(O)OF$ [12], have been identified. Other hypofluorite compounds have been studied theoretically but not synthesized, like ONOF [13]. Thus, covalent hypofluorite is a well-established, if chemically reactive, functional group. It is unquestionable that if synthesized, PF_2OF will also be highly reactive. The question here is, is it isolable?

We have used the techniques of computational chemistry to try to address that question. We have used the G2 and G3 compound methods to determine optimized geometries and vibrational frequencies for PF_2OF, the latter being useful for identification purposes. We can compare the total energy of PF_2OF to that of $PF_3 = O$ to determine the relative thermodynamic stability of PF_2OF. We have also determined an energy barrier to isomerization to PF_3O. Finally, we have made estimates of the P–O and P–F bond strengths to get an indication of the reactivity of PF_2OF, which would address other aspects of its reactivity.

2. Computational details

The GAUSSIAN03 package [14] was used to perform G2 [15] and G3 [16] compound calculations, which are recognized as having a high energy accuracy. The methods were used as implemented in the program. Vibrational frequencies were scaled by 0.899, as recommended by NIST [17].

3. Results and discussion

Fig. 1 shows the optimized structure of PF_2OF. Bond distances are $r(P–F) = 1.590$ Å, $r(P–O) = 1.690$ Å, and $r(O–F) = 1.350$ Å; bond angles are $\alpha(FPF) = 98.2^\circ$, $\alpha(FPO) = 90.6^\circ$ and 99.7°, and

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doi:10.1016/j.jfluchem.2009.10.008

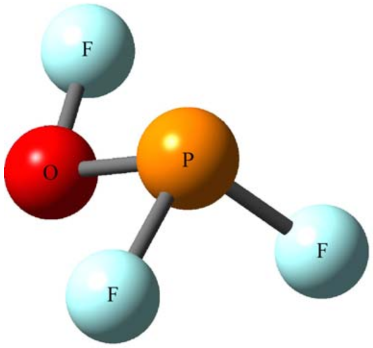

Fig. 1. Optimized geometry of PF_2OF.

$\alpha(POF) = 100.1^\circ$. The dihedral angle made by the O–F bond is 180° with respect to one of the P–F bonds, as if to adopt a perfect *trans* orientation.

Table 1 lists the scaled vibrational frequencies, calculated intensities, and approximate descriptions of the normal modes of vibration for PF_2OF. The lowest-energy vibration, at 83 cm^{-1}, is a twist of the O–F bond about the P–O bond, as if the O–F bond were undergoing hindered rotation. Should PF_2OF ever be isolated, the data in Table 1 should help provide identification.

Table 2 lists a variety of energies of species calculated by the G2 and G3 methods that should allow us to assess the potential for isolating PF_2OF. The enthalpies of PF_2OF and $PF_3 = O$ at 298.15 K were calculated in order to determine their relative energies, and the enthalpies of various fragments of PF_2OF were determined to estimate the covalent bond strengths in the title molecule, similar to the methods of Mó et al. [18] for determining bond energies.

The first Δ in Table 2 is the difference between the isomers: the G2 and G3 methods indicate that PF_2OF is 525–530 kJ/mol *higher* in energy than $PF_3 = O$. This still translates, however, into a calculated enthalpy of formation of −722 to −729 kJ/mol. Thus we predict that PF_2OF should be thermodynamically stable with respect to its constituent elements.

The second and third Δs in Table 2 are the enthalpy differences between the parent PF_2OF molecule and the two fragments listed immediately above each Δ. These enthalpies are used to estimate the bond energies of the O–F and P–O bonds, respectively. As expected, the P–O bond is relatively strong, while the O–F bond is relatively weak. It is the presence of the weak O–F bond that will likely introduce kinetic challenges to the isolation of PF_2OF. The O–F bond in FOOF has a bond energy of only ~75 kJ/mol; Greenwood and Earnshaw [2] mention that mass spectrometric, infrared, and electron spin resonance studies confirm the dissociation of FOOF into FOO and F radicals.

However, there do exist isolable species that have bond energies on the order of that predicted here for O–F. The N–N bond in N_2O_4 has a bond energy of 56.9 kJ/mol; the similar bond in N_2F_4 has a bond energy of about 88 kJ/mol [19].

While the optimization calculations confirm that PF_2OF lies in a potential energy well, there is the question of whether PF_2OF can exist without spontaneously rearranging to form its isomer, PF_3O, which is obviously more stable. To evaluate this possibility, we calculated the transition state of the unimolecular isomerization reaction

$$PF_2OF \rightarrow PF_3O$$

using the MP2(full)/6–31G(d) method and basis set. This computational combination was chosen because it is the final optimization method in the G2 method [14]. We were able to identify the transition state between the two isomers, which is shown in Fig. 2 on a relative energy level diagram. This structure was confirmed as a transition state by noting a single imaginary vibrational frequency at 812.9*i* cm^{-1}. Fig. 2 also shows that the potential energy barrier of PF_2OF to isomerization is approximately 168 kJ mol^{-1}. Insofar as this barrier is substantially larger than *RT* at normal temperatures, we can suggest that PF_2OF, if synthesized, is likely stable to isomerization. The weak calculated bond energy

Table 1
Calculated vibrations and absorption intensities of PF_2OF.

Frequency, cm^{-1}	Intensity, km/mol	Approx desc
82.7	0.7	FPOF twist
231.0	4.7	POF bend
319.5	4.8	PF_2 bend
361.8	10.3	FPOF wag
433.5	27.7	PF_2O umbrella
765.7	227.1	P–O stretch
862.2	196.0	P–F stretch
876.1	148.2	P–F stretch
1065.0	9.2	O–F stretch

Table 2
Enthalpies of various molecules and fragments used to assess the isolability of PF_2OF.[a]

	G2 method	G3 method
PF_3O	−715.46241 h	−715.96632 h
PF_2OF	−715.26220 h	−715.76350 h
Δ	+0.20021 h = 525.6 kJ/mol	+0.20282 h = 532.5 kJ/mol
$\Delta H_f[PF_2OF]$	−1254.25 + 525.6 = −728.6 kJ/mol	−1254.25 + 532.5 = −721.7 kJ/mol
PF_2O	−615.60579 h	−616.05815 h
F	−99.63045 h	−99.68184
Δ (O–F)	+0.02596 h = 68.2 kJ/mol	+0.02351 h = 61.7 kJ/mol
PF_2	−540.43414 h	−540.84080 h
OF	−174.69031 h	−174.79375 h
Δ (P–O)	+0.13775 h = 361.7 kJ/mol	+0.12895 h = 338.6 kJ/mol

[a] h = hartrees.

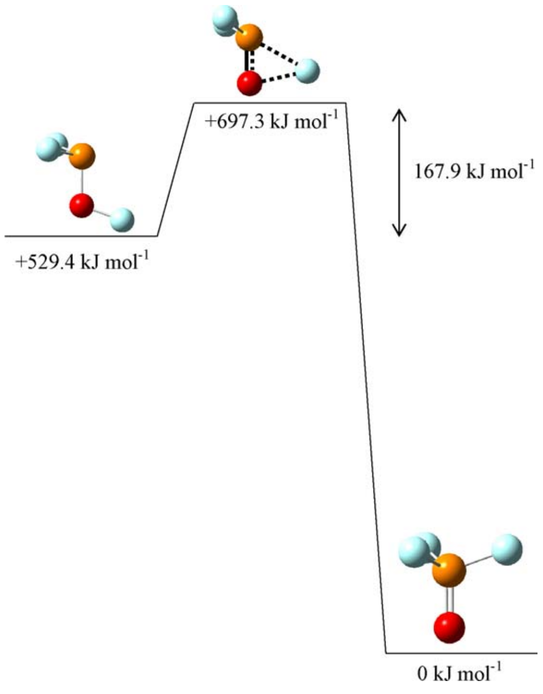

Fig. 2. Relative energies of PF_2OF, PF_3O, and the transition state found between them. The energy of PF_3O is arbitrarily set to zero. Because these energy values came from an MP2(full) calculation, the energy difference between PF_2OF and PF_3O are slightly different from that in Table 2.

of the O–F bond (see Table 2) suggests that the mode of reactivity of PF_2OF will be fluorine donation to another species (i.e. bimolecular decomposition) and that PF_2OF would be a strong fluorinating agent, on the order of FOOF.[1]

We conclude that it might be very possible to isolate PF_2OF under the right conditions, and have calculated some properties of this molecule that would aid in its identification. We look forward to a synthesis accepting the challenge.

Acknowledgements

The author thanks the Ohio Supercomputer Center for a grant of time with which to perform this work. Thanks to anonymous reviewers for helpful suggestions. Thanks also to several students in the summer session general chemistry course for inspiring this molecule.

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[1] One of the reviewers suggested that the actual pathway of decomposition would be bimolecular and would involve a P–O–F–P–O–F six-membered ring. All attempts to find a six-membered ring species as either a minimum-energy dimer or a transition state failed at the MP2(full)/6–31G(d) level. We believe that this is due, in part, to the preference to form a four-membered P–O–P–O ringed dimer. In all calculations, the O atom was predicted to have a more negative charge than the F atom attached to the O atom. This is likely caused by the rather high positively charged P atom, which in turn was caused by two rather negatively charged F atoms bonded directly to the P atom. We submit that if the weak O–F bond is the likely site of reaction, the decomposition of PF_2OF is inherently bimolecular (at least) in any case. We thank the reviewer for the comment.