ELSEVIER

Journal of Fluorine Chemistry 83 (1997) 27-30

JOURNAL OF FLUORINE CHEMISTRY

Reaction mechanisms of phosphorus fluorides: An ab initio study [1]

Alexander F. Janzen [a], Xiaobo Ou [a], Michael G. Sowa [b]

[a] *Department of Chemistry, University of Manitoba, Winnipeg, Man., R3T 2N2, Canada*
[b] *Institute for Biodiagnostics, National Research Council, 435 Ellice Ave., Winnipeg, Man., R3B 1Y6, Canada*

Received 9 July 1996; accepted 12 November 1996

Abstract

Reaction mechanisms of phosphorus fluorides may be analyzed on the basis of the coordination model of reaction mechanisms. Some of the intermediates and mechanistic details arising out of such an analysis have been investigated by ab initio molecular orbital calculations. The rapid equilibrium between five- and six-coordinate phosphorus fluorides, and exchange of axial and equatorial fluorines in PF_5, is investigated by calculating the structures of adducts of phosphorus pentafluoride, i.e. D–PF_5 where D = NH_3, H_2O, CH_3F, HF, PF_5 and PF_6^-. Bond cleavage in phosphorus fluorides is investigated by calculating the structure of a fluorine-bridged anion $P_2F_{11}^-$. A reaction pathway is proposed for the fluoride-catalyzed oxidation of phosphorus(III) to phosphorus(V) fluorides which involves the known species PF_3, PF_4^-, $PF_4^{\cdot}$ and PF_5. © Elsevier Science S.A.

Keywords: Phosphorus fluorides; Reaction mechanisms; Ab initio calculations

1. Introduction

Reaction mechanisms may be analyzed on the basis of the coordination model of reaction mechanisms [1]. This model emphasizes the discrete variables of coordination number and electron count, as well as the connectivity of atoms along a reaction pathway, and classifies the elementary steps of reactions as $+C$, $-C$, $+C^c$, $-C^c$. Reaction pathways may be tested by ab initio molecular orbital calculations, e.g. the mechanism of cleavage of Si–F and Si–C bonds in fluorosilicates [2], or oxidative fluorination of sulfur(IV) to sulfur(VI) compounds [3]. Other reaction pathways have been tested by kinetic simulation, e.g. the BF_3-base system [4]. Calculations have now been carried out for phosphorus fluorides, and these results are related to mechanistic details such as rapid equilibria between five- and six-coordinate phosphorus compounds, exchange of axial and equatorial fluorines in PF_5, the cleavage of P–F bonds in phosphorus compounds, and the mechanism of oxidation of phosphorus(III) to phosphorus(V) fluorides.

2. Results and discussion

In order to test the statement that trigonal bipyramidal molecules are among the most sensitive indicators of bond formation, $+C$, because of the change in symmetry and NMR spin pattern that accompanies the formation of six-coordinate adducts or intermediates [1], we studied the interaction of PF_5 with Lewis bases of widely differing basicity (Eq. (1)), and calculated the structures of adducts **1**–**6**.

$$PF_5 + D \underset{-C}{\overset{+C}{\rightleftharpoons}} D\text{–}PF_5 \qquad (1)$$

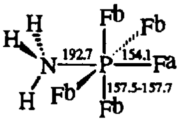
D = *1* NH_3; *2* H_2O; *3* CH_3F;
4 HF; *5* PF_5; *6* PF_6^-

As a six-coordinate adduct such as H_3N–PF_5 **1** is formed, the coordination number of phosphorus is increased from 5 to 6, and nitrogen from 3 to 4, i.e. $+C_{P(5)N(3)}$. Cleavage of a P–N bond in adduct **1** is denoted as $-C_{P(5)N(3)}$. If the calculated structures confirm that four basal fluorines in adducts **1**–**6** are essentially equivalent, then it is reasonable to assume that an equilibrium between five- and six-coordinate phosphorus species (Eq. (1)), can provide a pathway for the exchange of axial and equatorial fluorines in PF_5. Our criterion for evaluating the equivalence of four basal P–F^b bonds is based on a qualitative comparison of P–F^b bond lengths and $\angle F^aPF^b$ bond angles. Other means of estimating the distortion from D_{3h} or C_{4v} symmetry in phosphorus or silicon fluorides have been proposed by Holmes [5].

---

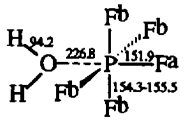
[2] Dedicated to Professor Alois Haas on the occasion of his 65th birthday.

PII S0022-1139(96)03566-X



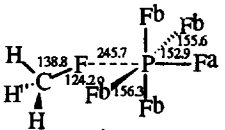
∠FaPFb = 93.3°

1 [6-311G*(2d,2p)]



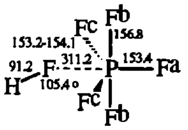
∠FaPFb = 97.7-99.6°

2 [6-311G*(2d,2p)]



∠FaPFb = 100.6-101.2°

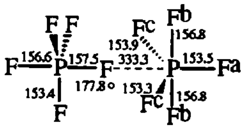
3 (6-31G**)



∠FaPFb = 91.0°

∠FaPFc = 116.8-117.0°

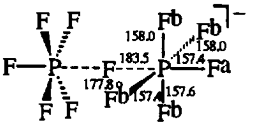
4 (6-31G**)



∠FaPFb = 90.4°

∠FaPFc = 118.8-118.9°

5 (6-31G*)



∠FaPFb = 94.0-94.3°

6 (6-31G*)

Of adducts **1–6**, only **1** is sufficiently inert to allow characterization by NMR and X-ray crystallography [6], but there is some indirect support for the existence of **2–6**. For example, adduct **2** has not been characterized, but the closely related adduct $Et_2O–F_5$ is stable below −65 °C [7]. Furthermore, the deprotonated anion F_5PO^{2-} [8], and related species F_5AsOH^- [9] and $H_2O–GeF_5^-$ [10], have been described in the literature. The adducts $H_3N–F_5$ **1** and $H_2O–PF_5$ **2** are reasonable intermediates of ammonolysis and hydrolysis reactions, respectively [6,7]. Adducts $CH_3F–PF_5$ **3** and $HF–PF_5$ **4** are unknown, but related adducts with somewhat stronger Lewis acids have been identified by NMR at low temperature, e.g. $CH_3F–AsF_5$ and $CH_3F–SbF_5$ [11]. Suggestions have been made that dimeric PF_5 **5** [12], or dimeric SiF_5^- [13], might contribute to axial–equatorial ligand exchange. NMR studies on the $PF_5–PF_6^-$ [14] and $PhPF_4–PhPF_5^-$ [15] systems confirm that rapid P–F bond cleavage occurs in these systems, and a bridged intermediate, e.g. $P_2F_{11}^-$ **6**, can account for the NMR results.

Calculations were carried out with several basis sets and they confirm that four basal fluorines in adduct $H_3N–PF_5$ **1** are essentially equivalent. With the 6-311G* (2d,2p) basis set, the four basal $P–F^b$ bond lengths in **1** are in the range 157.5–157.7 pm, and the four angles between the apical and basal fluorines, $\angle F^aPF^b$, are all 93.3°. With the 3-21G* basis set, very similar results were obtained, namely, four basal $P–F^b$ bond lengths in the range 158.1–158.2 pm, and four angles $\angle F^aPF^b$ in the range 94.5–94.6°. Calculations therefore show that all basal $P–F^b$ bonds in adduct **1** are essentially equivalent. These results may be compared with experimental $P–F^b$ bond lengths in the solid state, which are in the range 158.9–160.0 pm, and $\angle F^aPF^b$ in the range 90.8–92.3° [6].

The calculated lengths of the P–N bond in **1** are 192.7 pm [6-311G* (2d,2p)], 193.1 pm (3-21G*), and 195.1 pm (MINI-1). In the solid state, the experimental P–N bond length is 184.2 pm [6].

Calculations with the 6-311G* (2d,2p) basis set also show that adduct $H_2O–PF_5$ **2** has four essentially equivalent basal fluorines, with $P–F^b$ bond lengths in the range 154.3–155.5 pm, and bond angles $\angle F^aPF^b$ in the range 97.7–99.6°. It was suggested some time ago that the rapid formation and dissociation of adduct **2** can lead to exchange of axial and equatorial fluorines in PF_5 [7].

Adduct $CH_3F–PF_5$ **3** was selected to test the hypothesis that "inert" solvents may bring about axial–equatorial ligand exchange in PF_5 without participating in further chemical reactions [1]. Calculations with the 6-31G* basis set show four basal $P–F^b$ bond lengths in the range 155.6–156.3 pm, and $\angle F^aPF^b$ in the range 100.6–101.2°. These results strongly imply that axial and equatorial fluorines in PF_5 can be exchanged as a result of interaction with a solvent such as CH_3F. A similar conclusion is reached on the basis of 3-21G* calculations, which show four basal $P–F^b$ bond lengths in the range 155.9–157.4 pm, and four bond angles $\angle F^aPF^b$ in the range 97.0–98.0°.

It is uncertain from our calculation of **4** or **5** whether interaction with HF, or with another PF_5 molecule, leads to exchange of axial and equatorial fluorines in PF_5. Adduct **4** (6-31G**) shows a relatively large variation in $P–F^b$ and $P–F^c$ bond lengths in the range of 153.2–156.8 pm, and bond angles $\angle F^aPF^b$ and $\angle F^aPF^c$ in the range 91.0–117.0°. The long bond between HF and PF_5, namely, 311.2 pm (6-31G**), or 211.1 pm (3-21G*), implies that **4** is a very weakly bound adduct in which the PF_5 moiety is only slightly distorted. Similar comments can be made about the PF_5 dimer **5**, where calculation (6-31G*) shows relatively large variation in basal P–F bond lengths 153.3–156.8 pm, and $\angle F^aPF^b$ and $\angle F^aPF^c$ bond angles, 90.4–118.9°.

Calculation (6-31G*) of the fluorine-bridged anion $P_2F_{11}^-$ **6** shows four basal $P–F^b$ bond lengths in the range 157.4–158.0 pm, and $\angle F^aPF^b$ in the range 94.0–94.3°, indicating that **6** has essentially equivalent basal fluorines.

In summary, the calculations described above are in agreement with the view that axial and equatorial fluorines in PF_5 undergo intramolecular ligand exchange as a result of bond formation, +C, whenever PF_5 interacts with a donor molecule such as NH_3, OH_2, CH_3F and PF_6^-, to give adducts **1–3**,**6** (Eq. (1)). The calculated structures of adducts **4–5**, however, suggest that interaction with HF, or with another PF_5 molecule, probably does not bring about exchange of axial and equatorial fluorines in PF_5.

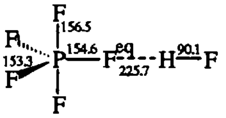
Turning to the question of bond cleavage, −C, in phosphorus fluorides, NMR studies show clearly that rapid bond cleavage occurs in the $PF_5–PF_6^-$ [14] and $PhPF_4–PhPF_5^-$ [15] systems. The calculated structure of intermediate **6** shows a substantially longer/weaker P···F bridging bond of 183.5 pm, as compared to the terminal P–F bond lengths of 157.4–158.0 pm. This calculated (6-31G*) bridge bond of

183.5 pm may be compared with a previous calculation of 183.1 pm [16]. An analogously bridged intermediate $Si_2F_{11}^{3-}$ can account for rapid intermolecular fluorine exchange in the SiF_5^-–SiF_6^{2-} system [13]. As the strength of the bridging bond increases in related anions such as $As_2F_{11}^-$ or $Sb_2F_{11}^-$, the bridged species can be identified in solution, or isolated [17].

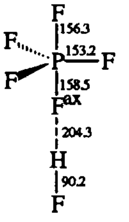
NMR experiments show that P–F coupling is retained in purified samples of PF_5, or when PF_5 is dissolved in solvents such as CH_3F [1]. Furthermore, PF_5 is a nonelectrolyte and has a small solubility in hydrogen fluoride [18]. Based on the calculated structures of **3–5**, only cleavage of the weakest/longest P–F bridge bond in **3–5** is expected, which leaves the original PF_5 molecule intact. For example, the calculated long/weak bridging P–F bond in **3**, namely, 245.7 pm (6-31G*) or 196.5 (3-21G*), may be compared to the shorter/stronger terminal P–F bonds of 152.9–156.3 pm (6-31G*), or 154.1–157.4 pm (3-21G*). Only a simple dissociation of adduct CH_3F–PF_5 **3** is thus expected, with no further chemical reaction, and this result is consistent with the known stability of PF_5 in hydrocarbon and halogenated solvents.

Similar arguments can be applied to **4** and **5** to account for the chemical stability of PF_5 in the presence of HF, or in the presence of other PF_5 molecules.

To test for the possibility that hydrogen bonding might lead to P–F bond cleavage, the calculation (6-31G**) of **7** and **8** was carried out. Other than a small lengthening of the axial or equatorial P–F bond, however, no significant changes are evident in the PF_5 moiety. The trigonal bipyramidal geometry of PF_5 is not significantly distorted, therefore, neither chemical reaction nor axial–equatorial fluorine exchange is expected as a result of the formation of hydrogen-bridged intermediates **7–8**.

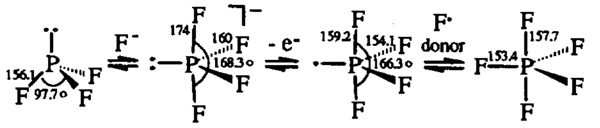


7 (6-31G**)



8 (6-31G**)

Finally, a mechanism of oxidation of phosphorus(III) to phosphorus(V) fluorides is proposed (Scheme 1) which is based on the mechanism of oxidation of sulfur(IV) to sulfur(VI) fluorides in the presence of fluoride ion [3]. The latter mechanism postulates initial attack of F^- on sulfur(IV) compounds, followed by oxidation to a fluorosulfur radical and, lastly, reaction with a suitable fluorine atom donor to give the sulfur(VI) product. The *N*–X–*L* notation of Perkins et al. [19] is used in Scheme 1 to specify the valence electron count (*N*) and coordination number (*L*) of phosphorus (X). Calculations for **9–12** were not carried out in this study because both calculated and experimental results have been reported by others [20–23].



8-P-3 10-P-4 9-P-4 10-P-5

9 [20] **10** [21] **11** [22] **12** [23]

Scheme 1. Proposed mechanism of oxidation of P(III) to P(V) fluorides in the presence of F^-.

The fact that F^- adds readily to PF_3 to give anion PF_4^-, in solution [21] or in the gas phase [24], is in agreement with the first step of the proposed mechanism (Scheme 1). In the absence of F^- (and PF_4^-), the mechanism of oxidation is presumably simplified to $PF_3 \rightarrow PF_4^{\cdot} \rightarrow PF_5$, as suggested for the free-radical addition of fluorine atoms to PF_3 [25]. In principle, there is a sharp distinction between an oxidation that occurs in the presence of F^-, and a free-radical oxidation that occurs in the absence of F^-, but this distinction may be difficult to observe in practice because of the inadvertent introduction of fluoride ion during the course of typical oxidative fluorinations. The finding that the rate of oxidative chlorination of PF_3 is photosensitive, but also catalyzed by glass surfaces [26], hints at experimental difficulties.

Scheme 1 does not identify the electron acceptor that converts anion PF_4^- **10** to radical $PF_4^{\cdot}$ **11**. However, for the related anion-to-radical oxidation of $PhSiF_5^{2-}$ to $PhSiF_5^- \cdot$, numerous one-electron acceptors can be used, including metal ions, halogen compounds, tetracyanoethylene, etc. [27].

The last step of Scheme 1 involves the interaction of $PF_4^{\cdot}$ with a fluorine atom donor to give the product PF_5. For typical oxidative fluorinating agents such as F_2, ClF or XeF_2, we postulate that rapid bond cleavage occurs as a result of the formation of intermediates F_4P–$F\cdots F\cdot$, F_4P–$F\cdots Cl\cdot$ or F_4P–$F\cdots XeF\cdot$, respectively. An explanation for the catalytic role of F^- is then apparent, because the presence of F^- allows bond cleavage of very weakly bound intermediates, e.g., F_4P–$F\cdots F\cdot \rightarrow PF_5 + F\cdot$, however, in the absence of F^- the oxidizing agents themselves must undergo bond cleavage to give radical intermediates, e.g. F–$F \rightarrow 2F\cdot$.

It is interesting to speculate whether the catalytic role of F^- (Scheme 1) applies to less electronegative anions such as Cl^-, and the X-ray structure of anion PCl_4^- provides some insight into this question. There are nonequivalent axial P–Cl bonds in PCl_4^-, 211.8 and 285.0 pm [28], and the substantial lengthening of one of the axial P–Cl bonds (285.0 pm) raises the possibility that the lifetime of anion PCl_4^- in solution might be relatively short, as compared to that of anion PF_4^-. This suggests that electronegative anions such as F^-, and perhaps HO^-, are suitable catalysts for oxidation of phosphorus(III) compounds, whereas larger and less electronegative anions such as Cl^- or Br^- are less effective. Without a catalyst, oxidation may follow a free-radical pathway and, indeed, radical $PCl_4^{\cdot}$ is a known species [29].

3. Methods

The GAUSSIAN 92 system of programs [30] was used for all ab initio molecular orbital calculations. Interacting molecules and ions were treated as one large system and were fully optimized with analytical gradient method at restricted Hartree–Fock level, using basis sets 3-21* and 6-31G*. Polarization basis sets, 6-31G**, with p orbitals for each hydrogen, were used for hydrogen-bond structures **4**, **7** and **8**, and triple split-valence orbital basis set 6-31G* (2d,2p) were used for structure **1** and **2**.

For the MINI-1 calculations, Huzinaga's minimal basis set [31] was used with the atomic scaling factors of Deisz [32]. Binding energies were determined by the supermolecule approach with the full counterpoise correction of Boys and Bernardi [33].

Acknowledgements

We thank the University of Manitoba for a graduate fellowship award (to X.O.) and for allotment of computer time. We thank Mr Rudy Sebastian for helpful discussions.

References

[1] A.F. Janzen, Coord. Chem. Rev. 130 (1994) 355.
[2] X. Ou, A.F. Janzen, Inorg. Chem., in press.
[3] (a) X. Ou, A.F. Janzen, Can. J. Chem., in press; (b) A.F. Janzen, X. Ou, J. Fluorine Chem. 71 (1995) 207.
[4] X. Ou, R. Wallace, A.F. Janzen, Can. J. Chem. 71 (1993) 51.
[5] R.R. Holmes, Chem. Rev. 90 (1990) 17.
[6] W. Storzer, D. Schomburg, G.-V. Röschenthaler, R. Schmutzler, Chem. Ber. 116 (1983) 367.
[7] J.A. Gibson, D.G. Ibbott, A.F. Janzen, Can. J. Chem. 51 (1973) 3203.
[8] M. Kant, M. Meisel, Z. Anorg. Allg. Chem. 620 (1994) 1937.
[9] L. Kolditz, W. Röhnsch, Z. Anorg. Allg. Chem. 293 (1957) 168.
[10] I. Wharf, M. Onyszchuk, Can. J. Chem. 48 (1970) 2250.
[11] J.-Y. Calves, R.J. Gillespie, J. Am. Chem. Soc. 99 (1977) 1788.
[12] J.I. Musher, Tetrahedron Lett. (1973) 1093.
[13] R.K. Marat, A.F. Janzen, Can. J. Chem. 55 (1977) 3845.
[14] S. Brownstein, J. Bornais, Can. J. Chem. 46 (1968) 225.
[15] C. Wang, A.F. Janzen, Can. J. Chem. 62 (1984) 1563.
[16] C. Kölmel, G. Palm, R. Ahlrichs, M. Bär, A.I. Boldyrev, Chem. Phys. Lett. 173 (1990) 151.
[17] (a) P.A.W. Dean, R.J. Gillespie, R. Hulme, D.A. Humphreys, J. Chem. Soc. A (1971) 341; (b) C.G. Davies, R.J. Gillespie, P.R. Ireland, J.M. Sowa, Can. J. Chem. 52 (1974) 2048.
[18] (a) A.F. Clifford, S. Kongpricha, J. Inorg. Nucl. Chem. 20 (1961) 147; (b) R. Gut, K. Gantschi, J. Inorg. Nucl. Chem. Suppl. (1976) 95.
[19] C.W. Perkins, J.C. Martin, A.J. Arduengo, W. Lau, A. Alegria, J.K. Kochi, J. Am. Chem. Soc. 102 (1980) 7753.
[20] Y. Kawashima, A.P. Cox, J. Mol. Spectrosc. 65 (1977) 319.
[21] K.O. Christe, D.A. Dixon, H.P.A. Mercier, J.C.P. Sanders, G.J. Schrobilgen, W.W. Wilson, J. Am. Chem. Soc. 116 (1994) 2850.
[22] C.J. Cramer, M.H. Lim, J. Phys. Chem. 98 (1994) 5024.
[23] K.W. Hansen, L.S. Bartell, Inorg. Chem. 4 (1965) 1775.
[24] T.C. Rhyne, J.G. Dillard, Inorg. Chem. 10 (1971) 730.
[25] I.B. Goldberg, H.R. Crowe, D. Pilipovich, Chem. Phys. Lett. 33 (1975) 347.
[26] J.N. Wilson, J. Am. Chem. Soc. 80 (1958) 1338.
[27] K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Kurita, M. Murata, M. Kumada, Organometallics 1 (1982) 355.
[28] K.B. Dillon, A.W.G. Platt, A. Schmidpeter, F. Zwaschka, W.S. Sheldrick, Z. Anorg. Allg. Chem. 488 (1982) 7.
[29] (a) G.L. Gutsev, Chem. Phys. 179 (1994) 325; (b) G.F. Kokoszka, F.E. Brinckman, J. Am. Chem. Soc. 92 (1970) 1199.
[30] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, J.A. Pople, GAUSSIAN 92, Revision C, Gaussian, Pittsburgh, PA, 1992.
[31] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, Gaussian Basis Sets for Molecular Calculations, Elsevier, Amsterdam, 1984.
[32] M.W. Schmidt, J.A. Boatz, K.K. Baldridge, S. Koseki, M.S. Gordon S.T. Elbert, B. Lam, GAMESS, QCPE Bull. 7 (1987) 115.
[33] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.