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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

New Perfluoroalkylphosphonic and Bis(perfluoroalkyl)phosphinic Acids and Their Precursors

Tariq Mahmood and Jean'ne M. Shreeve*

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Some new routes to the previously known acids $(R_f)_2P(O)OH$ and $R_fP(O)(OH)_2$ ($R_f = CF_3$, n-C_4F_9) as well as to the new acids $(C_2F_5)_2P(O)OH$ and $C_2F_5P(O)(OH)_2$ are reported. In addition, several mixed chloro(perfluoroalkyl)phosphorus(III) and -(V) compounds have been synthesized as reaction precursors, including $(C_2F_5)_2PCl_3$, $C_2F_5PCl_4$, $(C_2F_5)_2PCl$, $C_2F_5PCl_2$, $(C_2F_5)_2P(O)Cl$, and $C_2F_5P(O)Cl_2$. Under certain conditions, when chlorophosphines are oxidized with an excess of NO_2, acid anhydrides result, e.g., $(C_2F_5)_2P(O)OP(O)(C_2F_5)_2$ and c-$(C_2F_5PO_2)_3$.

Only a few (perfluoroalkyl)- or bis(perfluoroalkyl)phosphorus(V) acids, e.g., the monobasic phosphinic acids $(CF_3)_2P(O)OH$, $(C_3H_7)_2P(O)OH{\cdot}H_2O$, and $(n\text{-}C_4F_9)_2P(O)OH$ and the dibasic phosphonic acids $CF_3P(O)(OH)_2$, $C_3F_7P(O)(OH)_2$, and $C_4F_9P(O)(OH)_2$, have been reported and characterized.[1-8] Since it was thought that these (perfluoroalkyl)phosphorus(V) acids might have potential as electrolytes with good cell characteristics for use in fuel cells, it was appropriate to attempt to synthesize a larger number of these types of compounds as well as to improve upon the yields of products obtained by using previous methods or to develop more effective pathways.

Thus, we would like to report the missing member of these homologous series, $(C_2F_5)_2P(O)OH$ and $C_2F_5P(O)(OH)_2$. Several new chlorobis(perfluoroalkyl)- and dichloro(perfluoroalkyl)phosphine oxides, as well as trichlorobis(perfluoroalkyl)- and tetrachloro(perfluoroalkyl)phosphoranes, have been prepared as precursors to their respective acids or acid anhydrides.

Results and Discussion

Iodobis(trifluoromethyl)phosphine, $(CF_3)_2PI$, iodobis(pentafluoroethyl)phosphine, $(C_2F_5)_2PI$, diiodo(trifluoromethyl)phosphine, $(CF_3)PI_2$, diiodo(pentafluoroethyl)phosphine, $(C_2F_5)PI_2$, and tris(trifluoromethyl)phosphine, $(CF_3)_3P$, were prepared by the literature method[9-11] in which white phosphorus was reacted with R_fI ($R_f = CF_3$, C_2F_5).

$$P_4 + R_fI \xrightarrow[36\ h]{220\ ^\circ C} (R_f)_3P + (R_f)_2PI + R_fPI_2$$

When $R_f = CF_3$, all three products were obtained. However, when $R_f = C_2F_5$, none of the tris compound, $(C_2F_5)_3P$, was obtained. The relative amounts of the respective phosphines formed are a function of the stoichiometry used. A large excess of white phosphorus at 220 °C increased the yield of the diiodophosphine, whereas if the perfluoroalkyl iodide was in large excess, the yield of the monoiodophosphine improved. All of the iodophosphines were light-sensitive and must be handled accordingly. Both $(C_2F_5)PI_2$ and $(C_2F_5)_2PI$ were synthesized previously but characterized only by their infrared spectra.[10] We have completed that characterization by recording the ^{19}F and ^{31}P NMR spectra and the positive CI mass spectra.

Iodobis(pentafluoroethyl)phosphine and diiodo(pentafluoroethyl)phosphine were converted quantitatively to the chloro and dichloro compounds, respectively, by condensing each one onto freshly prepared and dried AgCl and by allowing the reaction to proceed for 15 days in the dark.[10] Liquid antimony trichloride has been used to chlorinate $C_2F_5PI_2$.[12] However, a superior yield is obtained with AgCl. Conversion of the iodophosphines to chlorophosphines was necessary due to the ease with which iodine was formed with oxidizing agents with the former compounds. The subsequent oxidation of these chlorophosphines with NO_2[13] gave not only the simple acid(V) chloride but also the acid anhydride. For example, chlorobis(pentafluoroethyl)phosphine (I) with NO_2 at −20 °C gave the chlorobis(pentafluoroethyl)phosphine oxide as the major product and a nonvolatile product, $(C_2F_5)_2P(O)OP(O)(C_2F_5)_2$ (II).

$$\underset{1}{(C_2F_5)_2PCl} + \underset{0.99}{NO_2} \xrightarrow{-20\ ^\circ C} \underset{I\ (90\%)}{(C_2F_5)_2P(O)Cl} + \underset{II}{(C_2F_5)_2P(O)OP(O)(C_2F_5)_2} + NOCl$$

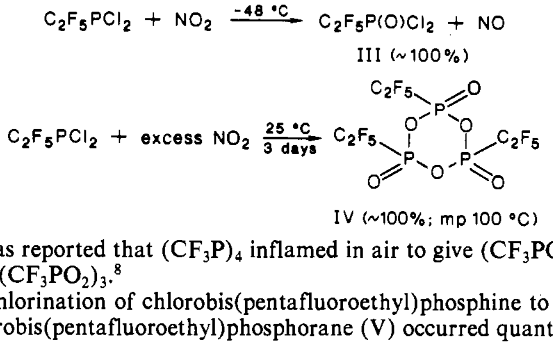
However, with excess NO_2, II was formed in high yield.

$$(C_2F_5)_2PCl + \text{excess } NO_2 \xrightarrow[3\ days]{25\ ^\circ C} \text{II } (80\%) + \text{I} + NOCl$$

The tetrakis(trifluoromethyl) diphosphate, $(CF_3)_2P(O)OP(O)(CF_3)_2$, was reported previously,[14,15] but it was characterized by ^{19}F NMR spectral measurements only.

The fact that both products, I and II, were formed at −20 °C supports the assumption that nitrogen dioxide abstracted chlorine from $(C_2F_5)_2PCl$ to give NOCl during the oxidation process.

When nitrogen dioxide was reacted with dichloro(pentafluoroethyl)phosphine at −48 °C, quantitative conversion to the phosphine oxide, III, occurred. Earlier workers reported that nitrogen dioxide with dichloro(trifluoromethyl)phosphine at 25 °C gave the corresponding phosphine oxide in a smooth reaction.[13] However, in our work an excess of nitrogen dioxide gave a cyclic anhydride, $(C_2F_5PO_2)_3$ (IV), at 25 °C.



It was reported that $(CF_3P)_4$ inflamed in air to give $(CF_3PO_2)_4$ and $(CF_3PO_2)_3$.[8]

Chlorination of chlorobis(pentafluoroethyl)phosphine to trichlorobis(pentafluoroethyl)phosphorane (V) occurred quantita-

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tively when the reaction mixture was warmed slowly from −78 to +25 °C. V is a stable liquid at 25 °C

$$(C_2F_5)_2PCl + Cl_2 \xrightarrow[10\ h]{-78\ to\ +25\ ^\circ C} \underset{V\ (\sim 100\%)}{(C_2F_5)_2PCl_3}$$

as is $(CF_3)_2PCl_3$.[2] Chlorination of $C_2F_5PCl_2$ over the range −120 to −10 °C gave tetrachloro(pentafluoroethyl)phoshorane (VI), which decomposes slowly at 25 °C with the decomposition incomplete after 72 h.

$$C_2F_5PCl_2 + Cl_2 \xrightarrow[10\ h]{-120\ to\ -10\ ^\circ C} \underset{VI}{C_2F_5PCl_4} + \underset{tr}{C_2F_5P(O)Cl_2}$$

$$VI \xrightarrow[72\ h,\ Pyrex]{25\ ^\circ C} C_2F_5Cl + PCl_3 + C_2F_5PCl_4 + C_2F_5P(O)Cl_2$$

The small amounts of $C_2F_5P(O)Cl_2$ found arose from hydrolysis of $C_2F_5PCl_4$ by traces of water in the system. On the other hand, CF_3PCl_4 was reported to be stable toward small amounts of water[8] but unstable at ambient temperatures to form CF_3Cl, CF_3PCl_2, PCl_5, and PCl_3.[16]

Bis(pentafluoroethyl)phosphinic acid (VII), which is a nonvolatile liquid, was formed in ~100% yield from the hydrolysis of I, II, or V.[8]

$$I,\ II,\ or\ V + H_2O \xrightarrow[10\ h]{25\ ^\circ C} \underset{VII}{(C_2F_5)_2P(O)OH} + HCl$$

Pentafluoroethylphosphonic acid (VIII) is a solid that sublimes at 70 °C (0.1 torr). It was synthesized by the oxidative hydrolysis of iodobis(pentafluoroethyl)phosphine or hydrolysis of III or VI.

$$(C_2F_5)_2PI + H_2O \xrightarrow[30\%]{H_2O_2}$$

$$\underset{VIII}{C_2F_5P(O)(OH)_{2aq}} + C_2F_2I\uparrow \xrightarrow[(2)\ sublime\ (70\ ^\circ C,\ 1\ mm)]{(1)\ freeze\text{-}dry} VIII_s$$

$$III\ or\ VI + 2H_2O \xrightarrow{25\ ^\circ C} VIII_s + 2HCl$$

When a mixture of tris(perfluorobutyl)phosphine oxide and tris(perfluorobutyl)difluorophosphorane (~95:5) was reacted with water at 44 °C, an essentially quantitative yield of the nonvolatile liquid, bis(perfluorobutyl)phosphonic acid (IX) was formed.

$$\underset{0.95}{(C_4F_9)_3PO} + \underset{0.05}{(C_4F_9)_3PF_2} + \underset{1}{H_2O} \xrightarrow[36\ h]{44\ ^\circ C}$$

$$\underset{IX}{(C_4F_9)_2P(O)OH} + C_4F_9H + HF$$

This hydrolysis method, which is much simpler than the literature method,[2] enabled the almost quantitative formation of $(CF_3)_2P(O)OH$ (X) from $(CF_3)_3PO + H_2O$ at 60 °C. However, when an excess of water was added to a mixture of $(C_4F_9)_3PO$ and $(C_4F_9)_3PF_2$ (~30:70), a very exothermic reaction occurred at 25 °C. After all the volatile materials (excess H_2O, C_4F_9H, HF) were removed under vacuum, a solid that could be sublimed at 70 °C (0.1 mm) remained. This was shown to be $(C_4F_9)_2P(O)(OH)\cdot H_2O$ (XI).

Hydrolyses of the monobasic acids $(R_f)_2P(O)OH$ ($R_f = CF_3$, C_2F_5, C_4F_9) at higher temperatures gave the corresponding dibasic acids $R_fP(O)(OH)_2$ that were obtained in nearly quantitative yield after freeze-drying.

$$(R_f)_2P(O)OH + excess\ H_2O \xrightarrow[36h]{T} R_fP(O)(OH)_2 + R_fH$$

$$R_f = CF_3,\ C_2F_5 \qquad T = 100\ ^\circ C$$

$$R_f = C_4F_9\ (XII) \qquad T = 150\ ^\circ C$$

Previous workers[2] employed aqueous NaOH to hydrolyze $(CF_3)_2P(O)OH$ to give $CF_3P(O)(ONa)_2$ + fluoroform. However, as the temperature of the aqueous hydrolysis continued to increase, the final carbon–phosphorus bond was severed and phosphoric acid resulted. On the basis of the hydrolyses data reported here, it is unlikely, given the current fuel cell technology, that these particular acids will be of practical value.

$$R_fP(O)(OH)_2 + H_2O \xrightarrow{T} R_fH + H_3PO_4$$

$$R_f = CF_3,\ C_4F_9 \qquad T = 180\ ^\circ C$$

$$R_f = C_2F_5 \qquad T = 195\ ^\circ C$$

Thus, we have developed facile routes to the perfluoroalkylphosphinic and -phosphonic acids that should be extendable to a very large number of substituted phosphorus(V) acids.

Experimental Section

Materials. Commercially available reagents were used as received: NO_2 (Air Products); Cl_2 (Linde); CF_3I and C_2F_5I (PCR); $(C_4F_9)_3PO$ and $(C_4F_9)_3PF_2$ (3M). Phosphorus was dried in absolute methanol prior to use. The iodophosphines were protected from light by wrapping the glass containers with aluminum foil.

General Procedures. A conventional Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac thermocouple gauges was used for the manipulation of volatile materials. Trap-to-trap distillation was employed to separate components in volatile mixtures. Reactions between −80 and +75 °C were carried out in 25-mL or 250-mL round-bottomed Pyrex flasks that were equipped with Kontes Teflon stopcocks. Reactions requiring temperatures greater than 100 °C were run in 75-mL Hoke stainless-steel reactors that were equipped with Hoke valves. Infrared spectra were obtained on a Perkin-Elmer 599B or a Perkin-Elmer 1710 FT spectrometer by using a 10-cm cell equipped with KBr windows. ^{19}F, ^{31}P, and ^{1}H NMR spectra were recorded by a JEOL FX 90Q FT NMR spectrometer with CCl_3F or H_3PO_4 as external reference and $CDCl_3$ or $(CD_3)_2SO$ as internal reference and solvent. Negative values were assigned to signals upfield from the reference. Mass spectra were recorded with a VG HS7070 mass spectrometer. In all cases where chlorine atoms were present, appropriate chlorine isotope ratios were observed. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, FRG.

Reaction of Phosphorus with C_2F_5I. Pentafluoroethyl iodide (15 g, 61 mmol) was heated with white phosphorus (15 g, 120.9 mmol) in a 75-mL Hoke stainless-steel reactor at 220–230 °C for 36 h.[4,5] Upon trap-to-trap distillation, pale yellow $C_2F_5PI_2$ was stopped in a trap at −10 °C, and $(C_2F_5)_2PI$ in a trap at −45 °C. For $C_2F_5PI_2$, the ^{19}F NMR spectrum had two resonance peaks at ϕ −77.16 (t of d) ($J_{CF_3-P} = 14.65$ Hz, $J_{CF_3-CF_2} = 2.93$ Hz) and at ϕ −104.9 (q of d) ($J_{CF_2-P} = 29.3$ Hz) assigned to CF_3 and CF_2, respectively. The ^{31}P NMR spectrum had a peak at δ 65.69 (q of t). The CI^+ mass spectrum contained a molecular ion at *m/e* 405 ($M^+ + H$) 19.5% and at *m/e* 404 (M^+) 88.6%, as well as peaks at *m/e* 385 ($C_2F_4PI_2$) 23.8%, 285 (PI_2^+) 100%, 277 ($C_2F_5PI^+$) 5.3%, 150 ($C_2F_5P^+$) 1.0%, 127 (I^+) 36.9%, 119 ($C_2F_5^+$) 4.9%, 69 (CF_3^+) 31.5%, and 51 (CHF_2^+) 1.6%. For $(C_2F_5)_2PI$, the ^{19}F NMR showed a multiplet (CF_3) centered at ϕ −79.2 ($J_{CF_3-P} = 14.65$ Hz) and a multiplet (CF_2) at ϕ −110.0. The ^{31}P NMR spectrum was a multiplet centered at δ 12.38. The CI^+ mass spectrum had a molecular ion at *m/e* 397 (M^++H) 6.8% and 396 (M^+) 61.6%, as well as peaks at *m/e* 376 ($C_4F_9PI^+$) 5.6%, 277 ($C_2F_5PI^+$) 13.6%, 269 ($C_4F_{10}P^+$) 1.8%, 239 ($C_2F_3PI^+$) 7.6%, 208 (CF_2PI^+) 2.3%, 177 (FPI^+, CF_2I^+) 100%, 158 (PI^+) 10.6%, 131 ($C_2F_4P^+$) 20.3%, 128 (HI^+) 3.8%, 127 (I^+) 21.3%, 119 ($C_2F_5^+$) 46.9%, 81 (CF_2P^+) 4.3%, and 69 (CF_3^+) 95.5%.

Reaction of AgCl with $C_2F_5PI_2$ and $(C_2F_5)_2PI$. The literature method was employed.[5] Diiodo(pentafluoroethyl)phosphine (14.0 g, 10 mmol) or iodobis(pentafluoroethyl)phosphine (3.96 g, 10 mmol) was transferred into a reaction vessel that contained dry AgCl (5 g) and that was equipped with a Kontes Teflon stopcock. The mixture was stored for 15 days in the dark. Then trap-to-trap distillation allowed the isolation of either dichloro(pentafluoroethyl)phosphine or chlorobis(pentafluoroethyl)phosphine at −70 °C in ~100% yield. The ^{19}F NMR spectrum of $C_2F_5PCl_2$ showed a peak at ϕ −78.5 (CF_3, t of d) ($J_{CF_3-P} = 14.65$ Hz, $J_{CF_3-CF_2} = 2.32$ Hz) and a peak at ϕ −122.5 (CF_2, q of d) ($J_{CF_2-P} = 68.36$ Hz). The ^{31}P NMR spectrum contained a peak at δ 141.7 (q of t). The CI^+ mass spectrum has molecular ions at *m/e* 221 ($C_2F_5P^{35}Cl_2H^+$) 2.2% and 220 ($C_2F_5P^{35}Cl_2^+$) 14.9%, as well as peaks at *m/e* 201 ($C_2F_4P^{35}Cl_2^+$) 3.1%, 185 ($C_2F_5P^{35}Cl^+$) 3.3%, 151 ($CF_2P^{35}Cl_2^+$) 3.6%, 120 ($C_2F_5H^+$) 10.8%, 119 ($C_2F_5^+$) 6.4%, 116 ($CF_2P^{35}Cl^+$) 1.9%, 101 ($P^{35}Cl_2^+$) 100%, 100 ($C_2F_4^+$) 27.3%, 85 (CF_2Cl^+, $PClF^+$) 58.1%, 81 (CF_2P^+) 2.7%, 69 (CF_3^+) 35.7%, and 66 (PCl^+) 13.3%.

The ^{19}F NMR spectrum for $(C_2F_5)_2PCl$ had doublets at ϕ −81.63 (CF_3) ($J_{CF_3-P} = 14.56$ Hz) and at ϕ −117.2 (CF_2) ($J_{CF_2-P} = 58.59$ Hz). The ^{31}P NMR spectrum showed a pentet of septets centered at δ 61.17. The CI^+ mass spectrum has molecular ions at *m/e* 306 and 304 (11.8,

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35.2%), as well as peaks at *m/e* 286 ($C_4F_9PClH^+$), 1.5%, 285 ($C_4F_9PCl^+$) 4.8%, 185 ($C_2F_5PCl^+$) 5.7%, 166 ($C_2F_4PCl^+$) 7.9%, 147 ($C_2F_3PCl^+$) 12.7%, 131 ($C_2F_4P^+$) 13.3%, 119 ($C_2F_5^+$) 77.3%, 100 ($C_2F_4^+$, CF_3P^+) 23.6%, 85 ($FPCl^+$, CF_2Cl^+) 100%, 69 (CF_3^+) 85.7%, and 51 (CF_2H^+) 2.2%.

Reaction of NO_2 with $(C_2F_5)_2PCl$. Nitrogen dioxide (0.23 g, 5 mmol) and $(C_2F_5)_2PCl$ (1.52 g, 5 mmol) were condensed into a reaction vessel at −196 °C. The vessel was placed in a slush bath at −78 °C and allowed to warm slowly to −20 °C. Trap-to-trap distillation from −20 °C gave $(C_2F_5)_2P(O)Cl$ (I) in a trap at −55 °C. Its vapor pressure is ~12 torr at 25 °C. The ^{19}F NMR spectrum had a peak at ϕ −79.34 (CF_3, t of d) ($J_{CF_3-P} = 3.05$ Hz, $J_{CF_3-CF_2} = 0.54$ Hz) and a multiplet at ϕ −121.0 (CF_2). The ^{31}P NMR spectrum was a pentet at δ 21.4 ($J_{P-CF_2} = 97.06$ Hz. The infrared spectrum had bands at 1328 vs, 1301 vs, 1237 s, 1161 s, 994 s, 950 m, 756 m, 630 m, 596 vs, and 489 s cm^{-1}. The CI$^+$ mass spectrum has a molecular ion at *m/e* 321 ($M^+ + H$) 100%, as well as peaks at *m/e* 201 ($C_2F_5POCl^+$) 1.4%, 119 ($C_2F_5^+$) 67%, 100 ($C_2F_4^+$) 76.8%, 85 (CF_2Cl^+) 99.9%, and 69 (CF_3^+) 50.7%.

In a trap at −196 °C, NOCl was found. The infrared spectrum contained peaks at 1819 vs, 1786 vs, 606 s, and 580 s cm^{-1}.

The nonvolatile material that remained in the reaction vessel was $(C_2F_5)_2P(O)OP(O)(C_2F_5)_2$ (II). The ^{19}F NMR spectrum had a singlet at ϕ −81.4 (CF_3) and a doublet centered at ϕ −126.3 (CF_2) ($J_{CF_2-P} = 73.24$ Hz). The ^{31}P NMR spectrum had a pentet centered at δ −0.3. The CI$^+$ mass spectrum had a molecular ion at *m/e* 587 and 586 ($M^+ + H$, M^+) 1.9% and 20.4%, as well as peaks at *m/e* 567 ($C_8F_{19}P_2O_3$) 4.7%, 467 ($C_6F_{15}P_2O_3^+$) 3.3%, 398 ($C_5F_{12}P_2O_3^+$) 2.2%, 379 ($C_5F_{11}P_2O_3^+$) 10.2%, 311 ($C_4F_8P_2O_3H^+$) 7.0%, 303 ($C_5F_7P_2O_3^+$) 100%, 301 ($C_4F_{10}PO_2^+$) 1.8%, 283 ($C_4F_9PO_2H^+$) 10.8%, 263 ($C_4F_8PO_2^+$) 2.3%, 213 ($C_3F_6PO_2^+$) 1.1%, 183 ($C_2F_5PO_2H^+$) 7.3%, 151 ($C_2F_5PH^+$) 4.2%, 131 ($C_2F_4P^+$) 3.1%, 119 ($C_2F_5^+$) 26.3%, 113 ($CF_2PO_2^+$) 2.4%, 101 ($C_2F_4H^+$) 4.0%, 100 ($C_2F_4^+$) 42.4%, 81 (CF_2P^+) 10.6%, 69 (CF_3^+) 49%, 64 (PO_2H^+) 2.5%, and 51 (CF_2H^+) 8.7%.

Reaction of NO_2 with $C_2F_5PCl_2$ at −48 °C. The procedure is identical with the reaction with $(C_2F_5)_2PCl$. In a trap at −78 °C, $C_2F_5P(O)Cl_2$ (III) was stopped. The ^{19}F NMR spectrum had signals at ϕ −78.6 (CF_3, d or t) ($J_{CF_3-CF_2} = 2.47$ Hz, $J_{CF_3-P} = 0.48$ Hz) and at ϕ −120.2 (CF_2, q of d) ($J_{CF_2-P} = 112.3$ Hz). The ^{31}P NMR spectrum was a triplet at δ 18.4. The infrared spectrum had bands at 1339 s, 1308 s ($\nu_{P=O}$), 1243 s, 1226 s, 1152 vs, 994 s, 758 m, 640 m, 604 s, 578 vs, 529 m, 496 w cm^{-1}. The CI$^+$ mass spectrum had a molecular ion at *m/e* 237 ($M^+ + H$) 87.2%, as well as peaks at *m/e* 217 ($C_2F_4POCl_2^+$) 5.6%, 119 ($C_2F_5^+$) 28.8%, 117 ($POCl_2^+$) 100%, 113 ($CFPOCl^+$) 10.2%, 101 ($C_2F_4H^+$) 27.6%, 100 ($C_2F_4^+$) 87.6%, 97 (CF_2PO^+) 11.8%, 82 ($POCl^+$) 5.2%, 69 (CF_3^+) 59.0%, and 51 (CF_2H^+) 3.4%.

Reaction of NO_2 with $C_2F_5PCl_2$ at 25 °C. This reaction was carried out as with $(C_2F_5)_2PCl$ but at 25 °C for 72 h. The solid that remained in the reaction vessel is *c*-$(C_2F_5PO_2)_3$ (IV) in ~100% yield. The ^{19}F NMR spectrum had a singlet at ϕ −80.79 (CF_3) and a doublet at ϕ −125.8 (CF_2) ($J_{CF_2-P} = 73.24$ Hz). The ^{31}P NMR spectrum had a triplet centered at δ −15.07. The positive CI$^+$ mass spectrum had a molecular ion peak at *m/e* 547 ($M^+ + H$) 5.5%, as well as peaks at *m/e* 527 ($C_6F_{14}P_3O_6^+$) 2.2%, 439 ($C_5F_{10}P_3O_6^+$) 62.1%, 420 ($C_5F_9P_3O_6^+$) 1.6%, 383 ($C_5F_7P_3O_6H^+$) 2.6%, 339 ($C_3F_6P_3O_6^+$) 1.4%, 320 ($C_3F_5P_3O_6^+$) 0.8%, 241 ($C_3F_5P_2O_3^+$) 1.5%, 201 ($C_2F_5PO_3H_3^+$) 100%, 199 ($C_2F_5PO_3H^+$) 2.5%, 191 ($C_2F_3P_2O_3^+$) 4.2%, 189 (P_3O_6) 1.5%, 181 ($C_2F_4PO_3H_2^+$) 16.1%, 163 ($C_2F_4PO_2^+$) 2.5%, 129 ($CF_2PO_3^+$) 1.9%, 119 ($C_2F_5^+$) 20.5%, 100 ($C_2F_4^+$) 3.8%, 81 ($C_2F_3^+$) 91.2%, 79 (PO_3^+) 6.1%, and 69 (CF_3^+) 49%.

Reaction of $C_2F_5PCl_2$ with Cl_2. Into a 50-mL round-bottomed flask at −196 °C that contained $C_2F_5PCl_2$ (1.1 g, 5 mmol) was condensed Cl_2 (0.35 g, 4.9 mmol). The mixture was warmed to −120 °C and warmed slowly to −10 °C over 10 h. After trap-to-trap distillation $C_2F_5PCl_4$ (VI) (95%) and a small amount of III were found in the trap at −55 °C. The ^{19}F NMR spectrum for VI showed peaks at ϕ −72.7 (CF_3, t of d) ($J_{CF_3-P} = 2.07$ Hz, $J_{CF_3-CF_2} = 1.59$ Hz) and at ϕ −107.5 (CF_2, q of t) ($J_{CF_2-P} = 122.1$ Hz). The ^{31}P NMR spectrum contained a triplet centered at δ −48.03. The infrared spectrum had bands at 1322 s, 1236 vs, 1152 s, 992 m, 757 w, 639 s, 602 s, 579 s, and 504 vs (ν_{P-Cl}) cm^{-1}. The CI$^+$ mass spectrum had peaks at *m/e* 255 ($C_2F_5PCl_3^+$) 3.3%, 237 ($C_2F_4PCl_3H^+$) 22.9%, 218 ($C_2F_3PCl_3H^+$) 4.6%, 167 ($CFPCl_3^+$) 2.0%, 153 ($CF_2PCl_2H^+$) 7.7%, 152 ($CF_2PCl_2^+$) 3.7%, 151 ($CF_2PCl_2^+$) 4.2%, 119 ($C_2F_5^+$) 44.8%, 116 (CF_2PCl^+) 59.2%, 102 (PCl_2H^+) 63%, 100 ($C_2F_4^+$) 100%, 69 (CF_3^+) 74.4%, and 67 ($PClH^+$) 5.5%.

Reaction of $(C_2F_5)_2PCl$ with Cl_2. The synthesis of $(C_2F_5)_2PCl_3$ (V) was identical with that of VI, with the temperature being raised slowly from −80 to +25 °C. Trap-to-trap distillation gave V in a trap at −60 °C in ~100% yield. The ^{19}F NMR spectrum had a multiplet centered at ϕ −71.9 (CF_3) and a multiplet centered at ϕ −104.9 (CF_2) ($J_{CF_2-P} = 146.5$ Hz). The ^{31}P NMR spectrum showed a pentet centered at δ −17.45. The infrared spectrum had bands at 1306 s, 1238 vs, 1157 s, 1120 m, 996 m, 950 m, 752 w, 640 w, 601 m, 568 m, 486 m (ν_{P-Cl}) cm^{-1}. The CI$^+$ mass spectrum had peaks at *m/e* 339 ($C_4F_{10}PCl_2^+$) 21.4%, 321 ($C_4F_9PCl_2^+$) 49.2%, 304 ($C_4F_{10}PCl_2H^+$) 2.5%, 255 ($C_2F_5PCl_3^+$) 16.0%, 201 ($C_2F_4PCl_2^+$) 1.6%, 185 ($C_2F_5PCl^+$) 2.6%, 151 ($C_2F_5PH^+$) 6.1%, 131 ($C_2F_4P^+$) 5.8%, 119 ($C_2F_5^+$) 100%, 101 (PCl_2^+) 49.6%, and 85 ($FPCl^+$) 97.1%.

Preparation of $(CF_3)_2P(O)OH$. Tris(trifluoromethyl)phosphine was prepared according to the literature method.[1] $(CF_3)_3P$ was separated by trap-to-trap distillation where it was retained in a trap at −116 °C. The ^{19}F NMR spectrum had a doublet centered at ϕ −49.3, and the ^{31}P NMR spectrum had a dectet centered at δ −2.73 ($J_{P-CF_3} = 83.0$ Hz). Upon oxidation with NO_2,[2] the $(CF_3)_3PO$ that was formed stopped in a trap at −100 °C during trap-to-trap distillation. This compound has a doublet centered at ϕ −64.35 (J_{CF_3-P}) = 117.2 Hz) in the ^{19}F NMR and a dectet centered at δ 4.2 in the ^{31}P NMR. Water (0.09 g, 5 mmol) was weighed into a reaction vessel equipped with a Kontes Teflon stopcock. To this was condensed $(CF_3)_3PO$ (1.23 g, 5 mmol). The mixture was heated at 60 °C with shaking for 3 days. After trap-to-trap distillation, $(CF_3)_2P(O)OH$ (~100%) was found in a trap at −60 °C. The acid was dried further by condensing it onto concentrated H_2SO_4 and vacuum-distilled. The ^1H NMR spectrum had a peak at δ 12.6 (OH) while the ^{19}F NMR had a doublet centered at ϕ −75.5 ($J_{CF_3-P} = 87.9$ Hz). In the ^{31}P NMR spectrum was found a septet at δ −7.4. In the trap at −196 °C ~5 mmol of CF_3H was found [NMR: ^1H, δ 8.03 (CH, q) ($J_{H-F} = 79.34$ Hz); ^{19}F, ϕ −77.3 (CF_3, d)].

Preparation of $CF_3P(O)(OH)_2$. This acid was prepared by literature methods.[2,3] The ^1H NMR spectrum (in $(CD_3)_2SO$) had a peak at δ 13.57 (OH). In the ^{19}F NMR spectrum was found a doublet centered at ϕ −74.2 ($J_{CF_3-P} = 107.4$ Hz), and the ^{31}P NMR spectrum had a quartet centered at δ −6.6. The CI$^+$ mass spectrum had a molecular ion at *m/e* 151 ($M^+ + H$) 100%, as well as peaks at *m/e* 131 ($CF_2PO_3H_2^+$) 17%, 111 ($CFPO_3H^+$) 16%, 82 ($PO_3H_3^+$) 5%, 81 (CF_2P^+, $PO_3H_2^+$) 31%, and 69 (CF_3) 4.1%.

Preparation of $(C_2F_5)_2P(O)OH$ (VII). i. Hydrolysis of I. Water (0.18 g, 10 mmol) and I (3.20 g, 10 mmol) were transferred into a 50-mL round-bottomed flask equipped with a Kontes Teflon stopcock at −196 °C. The mixture was warmed to 25 °C and left for 10 h. The HCl was removed under vacuum, leaving $(C_2F_5)_2P(O)OH$ as a nonvolatile liquid. The ^1H NMR spectrum (in $(CD_3)_2SO$) had a peak at δ 11.5 (OH), and the ^{19}F NMR spectrum had a singlet at ϕ −80.7 (CF_3) and a doublet centered at ϕ −125.6 (CF_2) ($J_{CF_2-P} = 68.32$ Hz). The ^{31}P NMR spectrum had a pentet centered at δ −2.15. The CI$^+$ mass spectrum had a molecular ion at *m/e* ($M^+ + H$), as well as peaks at *m/e* 303 ($C_4F_{10}PO_2H_2^+$) 20.7%, 283 ($C_4F_9PO_2H^+$) 2.4%, 215 ($C_3F_6PO_2H_2^+$) 3.6%, 183 ($C_2F_5PO_2H^+$) 4.4%, 151 ($C_2F_5PH^+$) 1.3%, 150 ($C_2F_5P^+$) 12.6%, 119 ($C_2F_5^+$) 14.0%, 115 ($CF_2PO_2H_2^+$) 2.9%, 100 ($C_2F_4^+$) 29.3%, 79 ($FCPOH^+$) 3.1%, 69 (CF_3^+) 40.4%, 65 ($PO_2H_2^+$) 5.4%, 64 (PO_2H^+) 2%, 51 (CF_2H^+) 8.5%.

Anal. Calcd for $C_4HF_{10}O_2P$: C, 15.89; H, 0.33; P, 10.26. Found: C, 15.12; H, 0.57; P, 9.97.

ii. Hydrolysis of V. When one part V and 2 parts H_2O were reacted at 25 °C, $(C_2F_5)_2P(O)OH$ was formed essentially quantitatively.

iii. Hydrolysis of II. Two millimoles of H_2O was reacted with 1 mmol of II to give $(C_2F_5)_2P(O)OH$ (~100%).

Preparation of $C_2F_5P(O)(OH)_2$ (VIII). i. This acid was prepared via the method of Emeléus and Haszeldine.[1] The pure acid that was obtained in 90% yield after sublimation at 70 °C (0.1 torr) had a melting point of 55 °C. The ^1H NMR spectrum ($(CD_3)_2SO$) showed a peak at δ 13.75 (OH) while in the ^{19}F NMR there was a triplet centered at ϕ −79.98 (CF_3) ($J_{CF_3-CF_2} = 1.83$ Hz) and a resonance centered at ϕ −125.6 (CF_2, q of d) ($J_{CF_2-P} = 78.13$ Hz). The ^{31}P NMR spectrum had a pentet centered at δ −12.3. The CI$^+$ mass spectrum had peaks at *m/e* ($M^+ + H$), 201 ($C_2F_5PO_3H_3^+$) 53.9%, 181 ($C_2F_4PO_3H_2^+$) 7.3%, 131 ($CF_2PO_3H_2^+$) 1.9%, 119 ($C_2F_5^+$) 3.6%, 100 ($C_2F_4^+$) 39.69%, 82 ($C_2F_3H^+$, $PO_3H_3^+$) 43.9%, 81 ($C_2F_3^+$, $PO_3H_2^+$) 100%, and 69 (CF_3^+) 17.1%.

Anal. Calcd for $C_2H_2F_5O_3P$: C, 12.0; H, 1.0; P, 15.5. Found: C, 12.32; H, 1.23; P, 14.32.

ii. Hydrolysis of III. Distilled water (10 mmol, 0.18 g) was transferred into a round-bottomed flask equipped with a Kontes Teflon stopcock. To this was transferred 10 mmol (2.32 g) of III at −196 °C, and the reaction proceeded at 25 °C for 10 h. Hydrogen chloride was removed under vacuum, leaving behind a sublimable (75 °C, 0.1 torr) white solid, $C_2F_5P(O)(OH)_2$, in 90% yield.

iii. Hydrolysis of VI. VI was hydrolyzed in the same manner as III by using a stoichiometry of 1VI:3H_2O to give VIII in 85% yield.

Preparation of $(n\text{-}C_4F_9)_2P(O)OH$ (IX). Approximately 20 mmol (15 g) of a mixture of $(n\text{-}C_4F_9)_3PO$ (95%) and $(n\text{-}C_4F_9)_3PF_2$ were transferred into a flask, and 27 mmol (0.49 g) of water was added. After 48 h at

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44 °C, any volatile material was removed under dynamic vacuum to leave the nonvolatile liquid IX. The ^1H NMR spectrum in $(CD_3)_2SO$ showed a peak at δ 10.8 (OH). The ^{19}F NMR spectrum (n-$C^1F_3C^2F_2C^3F_2C^4F_2)_2P(O)OH$) had a triplet at ϕ −80.38 (C^1F_3) ($J_{C^1F_3-C^2F_2}$ = 9.33 Hz), a broad peak at ϕ −120.4 (C^2F_2), a doublet of multiplets centered at ϕ −121.4 (C^4F_2) ($J_{C^4F_2-P}$ = 68.35 Hz), and a triplet at ϕ −125.4 (C^3F_2) ($J_{C^3F-C^4F_2}$ = 11.5 Hz). The ^{31}P NMR spectrum gave a pentet centered at δ −2.4. The positive CI mass spectrum has a molecular ion at *m/e* 503 ($M^+ + H$) 2.4%, as well as peaks at *m/e* 466 ($C_8F_{17}PO^+$) 0.7%, 447 ($C_8F_{16}PO^+$) 32.2%, 283 ($C_4F_9O_2PH^+$) 0.7%, 219 ($C_4F_9^+$) 0.9%, 215 ($C_3F_6O_2PH_2^+$) 1.6%, 169 ($C_3F_7^+$) 5.6%, 119 ($C_2F_5^+$) 9.9%, 100 ($C_2F_4^+$) 13.8%, 81 (CF_2P^+) 100%, 69 (CF_3^+) 69%, 65 ($PO_2H_2^+$) 2.1%, and 51 (CF_2H^+) 5.6%.

Anal. Calcd for $C_4F_{19}PO_2H$: C, 19.12; H, 0.2; P, 6.17. Found: C, 19.38; H, 0.25; P, 5.99.

Preparation of (n-$C_4F_9)_2P(O)OH\cdot H_2O$ (XI). A 30:70 mixture of (n-$C_4F_9)_3PO$ and (n-$C_4F_9)_3PF_2$ (15 g) and 100 mmol of water were transferred into a flask. After the flask had warmed to 25 °C, an exothermic reaction occurred. The mixture was allowed to remain at 25 °C for 10 h. After removal of the volatile materials, HF, C_4F_9H, and H_2O, a sublimable (70 °C, 0.1 torr) white solid, XI, remained in 90% yield. In $(CD_3)_2SO$ the proton NMR spectrum had a resonance peak at δ 10.1 (OH). The ^{19}F NMR spectrum (n-$C^1F_3C^2F_2C^3F_2C^4F_2)_2P(O)OH\cdot H_2O$ showed a triplet of triplets at ϕ −81.78 (C^1F_3) with $J_{C^1F_3-C^2F_2}$ = 9.4 Hz and $J_{C^1F_3-C^3F_2}$ = 2.57 Hz, a broad peak at ϕ −121.45 (C^2F_2), a doublet of multiplets at ϕ −122.4 (C^4F_2), and a multiplet of triplets at ϕ −126.5 (C^3F_2) ($J_{C^3F_2-C^4F_2}$ = 12.5 Hz). The ^{31}P NMR spectrum showed a pentet centered at δ −0.9 with J_{P-CF_2} = 66.41 Hz.

Anal. Calcd for $C_8F_{18}PO_3H_3$: C, 18.46; H, 0.57; P, 5.76. Found: C, 18.89; H, 0.51; P, 6.46.

Preparation of n-$C_4F_9P(O)(OH)_2\cdot H_2O$ (XII). XI (5 mmol, 2.65 g) was transferred into a thick-walled Pyrex tube. To this was added distilled water (15 mmol, 0.27 g). The tube was evacuated at −196 °C and sealed off. It was heated at 150 °C for 36 h. Left behind after evacuation of the volatile materials was a sublimable (110 °C, 0.1 torr) white solid, XII. The ^1H NMR spectrum in $(CD_3)_2SO$ gave δ 12.5 (OH). The ^{19}F NMR spectrum ((n-$C^1F_3C^2F_2C^3F_2C^4F_2)P(O)(OH)_2\cdot H_2O$ had a triplet of triplets at ϕ −80.25 (CF_3) ($J_{C^1F_3-C^2F_2}$ = 9.62 Hz, $J_{C^1F_3-C^3F_2}$ = 3.18 Hz), a quartet centered at ϕ −121.9 (C^2F_2), a triplet of triplets of doublets centered at ϕ −123.7 (C^4F_2) ($J_{C^4F_2-P}$ = 78.12 Hz, $J_{C^4F_2-C^3F_2}$ = 13.04 Hz, $J_{C^4F_2-C^2F_2}$ = 2.63 Hz), and a triplet at ϕ −126.26 (C^3F_2). The ^{31}P NMR had a triplet centered at δ −3.98. The CI^+ mass spectrum has a molecular ion peak at *m/e* ($M^+ + H$) 32.6%, as well as peaks at *m/e* 281 ($C_4F_8PO_3H_2^+$) 2.6%, 231 ($C_3F_6PO_3H_2^+$) 0.9%, 181 ($C_2F_4PO_3H_2^+$) 6.4%, 131 ($CF_2PO_3H_2^+$) 56.1%, 100 ($C_2F_4^+$) 32.8%, 82 ($PO_3H_3^+$) 48.2%, 81 ($PO_3H_2^+$) 100%, 69 (CF_3^+) 69.3%, and 51 (CF_2H^+) 17.5%.

Anal. Calcd for $C_4F_9PO_4H_4$: C, 15.09; H, 1.25; P, 9.74. Found: C, 13.90; H, 1.27; P, 9.18.

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Contribution from the Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

Kinetics of the Reaction of Nitric Oxide with Sulfite and Bisulfite Ions in Aqueous Solution

David Littlejohn, K. Y. Hu, and S. G. Chang*

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The kinetics of the reaction of dissolved nitric oxide with sulfite and bisulfite ions was studied over a pH range of 4–10 by monitoring the reaction product, *N*-nitrosohydroxylamine-*N*-sulfonate (NHAS), with rapid-mixing, continuous-flow and stopped-flow systems. The kinetics of the reaction can be described as $d[NHAS]/dt = k_a[NO][HSO_3^-] + k_a[NO][SO_3^{2-}]$ where $k_a = 32 \pm 10\ M^{-1}\ s^{-1}$ and $k_b = 620 \pm 100\ M^{-1}\ s^{-1}$ at $T = 298$ K. The reaction was also studied at 284 and 323 K. The hydrolysis rate of NHAS was determined over a pH range of 4–6.

There have been several studies[1–4] of the reaction of nitric oxide with forms of dissolved sulfur dioxide. Most of the studies were done under dissimilar conditions, and are not directly comparable. An early study was done by Terres and Lichti,[1] who observed the decrease in pressure of nitric oxide in the presence of K_2SO_3, $KHSO_3$, and $SO_2\cdot H_2O$. They were unable to obtain rate constants, but decided that a $(ONSO_3)^{2-}$ intermediate was involved and that the reaction between nitric oxide and bisulfite ion was first order in both species. Nunes and Powell[2] investigated the reaction of NO with SO_3^{2-} at pH 13–14 by observing the decrease in pressure of NO over the sulfite solution in a well-stirred reactor. The rate expression they obtained consisted of a sulfite-dependent term and a sulfite-independent term. They found that the dissolution process that NO undergoes influenced the kinetics. Takeuchi et al.[3] observed the loss of nitric oxide diluted with nitrogen after it either flowed over a sulfite solution surface or was bubbled through a sulfite solution. They found the reaction had second-order dependence on nitric oxide and zero-order dependence on sulfite concentration. Their results, although not quantitative, indicated that the reaction was very fast. Martin et al.[4] used a stopped-flow system to observe the reaction between dissolved nitric oxide and dissolved sulfur dioxide at pH ≤3 by monitoring $SO_2\cdot H_2O$ at 280 mm. They found that the reaction was very slow and could only obtain an upper limit for the rate. Since none of these studies measured the rates of the reactions of predissolved NO with SO_3^{2-} and with HSO_3^-, we decided to investigate the kinetics of these systems.

Experimental Section

For the experiments, a continuous-flow rapid-mixing system was assembled. The system could also be used for stopped-flow experiments. The system was constructed entirely of glass and plastic to minimize contamination by metal ions. House-deionized water was run through two nonmetallic deionizing columns and stored in a plastic container prior to use in the experiments. Both tanks for the reactant solutions were filled with the processed water and degassed by passing argon through them for 2 h. Nitric oxide (Matheson, CP) was purified by passing it through a concentrated sodium hydroxide solution and then through a cold trap at dry ice temperature. The treated nitric oxide was then passed through one of the tanks for at least 1 h. Checks done on the dissolved NO concentration indicated this was sufficient to saturate the solution. A lower flow of nitric oxide was passed through the solution during the

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