

Synthesis and Properties of Difluorodithiophosphoric Acids, HPS_2F_2 and DPS_2F_2

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Abstract: The difluorodithiophosphoric acids HPS_2F_2 and DPS_2F_2 have been prepared. Their physical properties, including a vibrational analysis, are reported. Evidence suggests that these new acids exist as hydrogen-bonded species.

The difluorodithiophosphate anion, PS_2F_2^- , has recently been reported.^{1,2} The hydronium salt of the PS_2F_2^- ion has been mentioned as a product that distilled with some decomposition;¹ however, no details were reported regarding its synthesis or properties. It was, therefore, of interest to investigate the chemistry of this anion further and find whether the acid could be prepared. The reaction between concentrated sulfuric acid (H_2SO_4 or D_2SO_4) or phosphoric acid and a difluorodithiophosphate salt does yield the desired acids in high yield.

Because of the considerable recent interest in the spectra of the thiophosphoryl halides³ and dihalothio-phosphate salts,^{4,5} the infrared and Raman spectra of the difluorodithiophosphate anion and the corresponding acid have been measured. Vibrational assignments for many of the fundamentals have been made.

Experimental Section

Reagents. Difluorodithiophosphate salts were synthesized by the literature method.² Deuteriosulfuric acid was prepared by the equimolar combination of D_2O (Bio-Rad Laboratories) and "Sulfan B," stabilized SO_3 (General Chemical Division, Allied Chemical Corp.).

Spectral Instrumentation. The infrared spectra were obtained with a Beckman IR7 spectrophotometer. Measured gas-phase spectra were obtained with a 10-cm path length cell using polyethylene windows ($250\text{--}500\text{ cm}^{-1}$), CsBr windows ($500\text{--}650\text{ cm}^{-1}$), and NaCl windows ($650\text{--}4000\text{ cm}^{-1}$). Both the NaCl and CsBr windows showed attack as evidence by some absorptions remaining after evacuation of the cell. These absorptions were due to the formation of the PS_2F_2^- anion which could not be removed. Liquid-phase bands were measured in the $600\text{--}4000\text{ cm}^{-1}$ region. Infrared spectra were obtained for CsPS_2F_2 in a Nujol mull and in solution: acetonitrile ($200\text{--}600\text{ cm}^{-1}$) and acetone ($600\text{--}900\text{ cm}^{-1}$). Raman spectra were obtained employing a Cary Model 81 spectrometer. The Raman spectrum of HPS_2F_2 was obtained as a liquid sample in a 2-mm cell. The bands from CsPS_2F_2 were observed using a saturated aqueous solution in a 7-mm cell.

Mass spectra were obtained with a Consolidated Engineering Corp. Model 61-620 mass spectrometer at an ionization potential of 100 eV. The ^{19}F and ^1H nmr spectra were taken with a Varian Model V4310 spectrometer operating at 40 Mc, and the ^{31}P spectra were obtained at 12.8 Mc. Samples were measured at ambient temperature in 5-mm o.d. Pyrex tubes using CCl_3F and TMS as internal standards for ^{19}F and ^1H spectra, respectively, and H_3PO_4 as an external standard for the phosphorus spectra.

General Procedure. Transfer and purification of volatile compounds were accomplished by the use of a standard Pyrex vacuum apparatus. The reactor used for the synthesis of HPS_2F_2 and DPS_2F_2 was a 100-ml Pyrex bulb with a Fischer-Porter Teflon valve used as an inlet. A trap was attached to the reactor *via* a stopcock so that gaseous materials could be removed immediately after their formation.

Synthesis of HPS_2F_2 . A large excess of 95–98% H_2SO_4 (50 ml) was placed into a 100-ml Pyrex vessel containing 12.87 mmoles of CsPS_2F_2 at -80° under a nitrogen atmosphere. The reactor was allowed to warm to room temperature slowly while pumping through the attached trap held at -196° . When the reaction mixture melted, it was stirred. The mixture was then allowed to stand for 2 hr. The products were then passed through traps set at -80 and -196° . The -80° trap contained 10.17 mmoles of HPS_2F_2 (79.0% yield) while the -196° held 1.2 mmoles of SO_2 and 0.15 mmole of SiF_4 .

In a similar reaction, 13.54 mmoles of CsPS_2F_2 and 25 ml of orthophosphoric acid were combined and allowed to react in the manner detailed above. After rectification 7.49 mmoles of HPS_2F_2 (55.3% yield), 0.66 mmole of H_2S , 0.01 mmole of SO_2 , and 0.23 mmole of SiF_4 were recovered.

Synthesis of DPS_2F_2 . Likewise, 16.7 mmoles of CsPS_2F_2 and 50 ml of 100% D_2SO_4 were combined. The products were fractionated as described previously and 6.1 mmoles of DPS_2F_2 was formed (36.5% yield) as well as 5.5 mmoles of SO_2 . The difference between the yields of DPS_2F_2 and HPS_2F_2 may be explained by the fact that the former was prepared in a stronger oxidizing medium. Consequently, more SO_2 and less DPS_2F_2 are formed.

Chemical Analysis. The total fluorine was determined by reduction of weighed samples with lithium in *n*-propylamine followed by distillation of the fluoride as H_2SiF_6 and titration with thorium nitrate. For phosphorus analyses, samples were introduced into 1 *N* NaOH solutions and heated 48 hr at 65° , and then the phosphate content was measured. Hydrogen was determined by conventional combustion. *Anal.* Calcd for F_2HPS_2 : F, 28.33; H, 0.75; P, 23.12. Found: F, 28.4; H, 1.0; P, 22.6. Calcd for DF_2PS_2 : F, 28.13, D, 1.48. Found: F, 29.1; D, 1.47.

Molecular Weights. The molecular weights were determined by vapor density measurements assuming perfect gas behavior. A 208.2-ml Pyrex bulb was used for weighing gaseous samples at measured pressures. The molecular weight found for HPS_2F_2 was 134.4/g molecular volume (calcd 134.1) and that for DPS_2F_2 was 135.6 (calcd 135.1).

Melting Points. Samples of HPS_2F_2 and DPS_2F_2 were placed in 5-mm o.d. Pyrex tubes and cooled. In both cases, only glasses were formed.

Vapor Pressures. These were measured at various temperatures and at constant volume by a diaphragm pointer gauge similar to that reported by Foord.⁶ The following are some of the data for HPS_2F_2 given as [T ($^\circ\text{C}$), P (mm)]: 1.2, 40.4; 6.6, 52.9; 15.0, 79.8; 29.2, 148.7; 47.7, 309.4; 58.1, 452.7. The values for DPS_2F_2 are 0.3, 38.4; 16.3, 86.4; 22.3, 111.2; 30.5, 162.0; 35.7, 200.2; 41.8, 256.4; 50.5, 368.7; 55.4, 433.9. The extrapolated boiling point for HPS_2F_2 was found to be $74.0 \pm 1.1^\circ$, and that for DPS_2F_2 was $72.3 \pm 0.4^\circ$. The temperature–pressure relationship follows the equation, $\log P$ (mm) = $7.501 - (1604/T)$ for HPS_2F_2 and $\log P$ (mm) = $7.671 - (1655/T)$ for DPS_2F_2 . The heat of vaporization

(1) H. W. Roesky, F. N. Tebbe, and E. L. Muettterties, *J. Am. Chem. Soc.*, **89**, 1271 (1967).

(2) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **6**, 2115 (1967).

(3) A. Müller, H. G. Horn, and O. Glemser, *Z. Naturforsch.*, **20b**, 1150 (1965).

(4) H. W. Roesky, *Chem. Ber.*, **100**, 950 (1967).

(5) H. W. Roesky, *ibid.*, **100**, 1447 (1967).

(6) S. G. Foord, *J. Sci. Instr.*, **11**, 126 (1934).

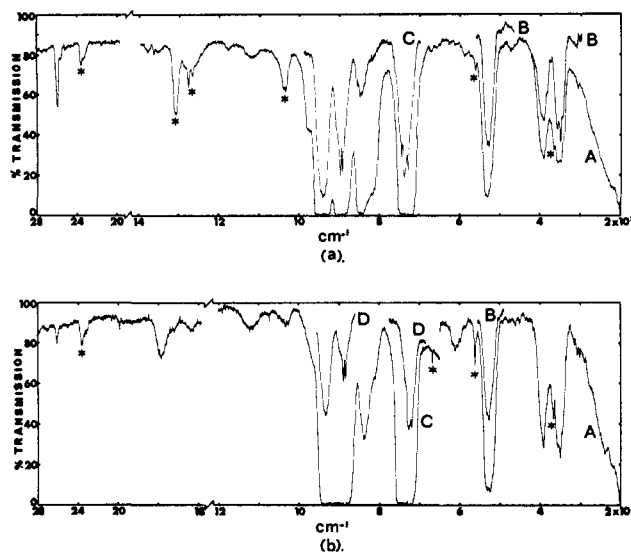


Figure 1. Vapor-phase infrared spectra of (a) HPS_2F_2 and (b) DPS_2F_2 . In (a) spectrum A was taken with 85 mm pressure in a 7.5-cm cell with CsBr windows, B with 50 mm pressure, and C with 5 mm pressure. In (b) spectrum A was taken with 60 mm pressure in the 7.5-cm cell, B with 15 mm pressure, C with 95 mm pressure in a 10-cm NaCl cell, and D with 4 mm pressure in this cell. Impurity bands are marked with an asterisk (see footnote 8).

and Trouton constant are 7.340 kcal and 21.40 eu, respectively, for HPS_2F_2 , while those for DPS_2F_2 are 7.573 kcal and 21.91 eu.

Results and Discussion

Diffluorodithiophosphoric acid is formed in good yield by the reaction of sulfuric or phosphoric acid with CsPS_2F_2 . The corresponding deuterium-substituted acid is prepared in a similar manner by treating the cesium salt with D_2SO_4 . The new acid, HPS_2F_2 , represents the last member of the series of which difluorodioxophosphoric acid, HPO_2F_2 , and difluorooxothio-phosphoric acid, HPOSF_2 , are the other constituents.

The ^{19}F nmr spectrum of HPS_2F_2 shows a doublet of resonances consistent at ϕ 15.8 ($J_{\text{P-F}} = 1212$ cps), which is consistent with a structure in which two equivalent fluorine nuclei interact with a single phosphorus nucleus. The ^1H spectrum consists of a sharp singlet at -3.80 ppm, while the ^{31}P spectrum reveals a triplet centered at -79.8 ppm ($J_{\text{P-F}} = 1210$ cps). The absence of coupling between hydrogen and either the phosphorus or fluorine nuclei through sulfur in the HPS_2F_2 spectrum suggests rapid exchange of the proton between two sulfur atoms. A similar exchange has also been postulated in the recently prepared perfluoromethyl derivative, $\text{HPS}_2(\text{CF}_3)_2$.⁷ The spectrum of DPS_2F_2 exhibits ^{19}F and ^{31}P resonances at ϕ 15.9 and -79.8 ppm, respectively, which are close to the positions given above for the protonated molecule.

Reproducible molecular weight determinations of HPS_2F_2 and DPS_2F_2 indicate that both compounds are monomeric in the vapor phase. Moreover, the mass spectra of the acid are similar and confirm the assigned molecular formulas. For example, in the mass spectrum of HPS_2F_2 , peaks are recorded in the region, $m/e > 31$, as mass number (species) and relative abundance: 31 (P^+) 6.1; 32 (S^+) 23.8; 34 ($^{34}\text{S}^+$) 1.2; 33 (SH^+) 16.8; 35 ($^{34}\text{SH}^+$) 0.8; 50 (PF^+) 9.2; 63 (PS^+)

(7) K. Gosling and A. Burg, *J. Am. Chem. Soc.*, **90**, 2011 (1968).

9.6; 64 (S_2^+) 57.1; 65 (S_2H^+ , P^{34}S^+) 7.0; 66 ($^{34}\text{S}_2^+$) 5.0; 69 (PF_2^+) 92.0; 82 (FPS^+) 6.3; 101 (F_2PS^+) 41.5; 103 ($\text{F}_2\text{P}^{34}\text{S}^+$) 1.8; 115 (FPS_2H^+) 3.2; 134 (HPS_2F_2^+) 100.0; 136 ($\text{HP}^{32}\text{S}^{34}\text{SF}_2^+$) 9.1.

A vibrational study of the difluorodithiophosphoric acids was undertaken in order to investigate the behavior of the acids in the vapor and liquid phases and also to assign the 12 fundamental frequencies. Two fundamentals which were not observed were either too weak to be measured, overlapped by the stronger bands between 300 and 400 cm^{-1} , or occurred below the spectral region under consideration. The data obtained from infrared and Raman measurements on the acids and on the cesium salt of the PS_2F_2^- anion are listed in Table I. The assignments listed in the table are based on the vapor-phase infrared spectrum of HPS_2F_2 , and the point group is arbitrarily assumed to be C_1 , since there is no evidence from the spectral data to support higher symmetry. Vapor-phase infrared spectra⁸ of the acids are shown in Figure 1. No bands were observed between 1400 and 2400 cm^{-1} in the spectrum of HPS_2F_2 or between 1200 and 2300 cm^{-1} in the spectrum of DPS_2F_2 . Likewise, no bands were present at frequencies higher than the S-H and S-D stretching frequencies. Consequently, these regions have been omitted in Figure 1.

An examination of the spectra in Figure 1a reveals that some of the absorption bands appear to be split into doublets. This is particularly noticeable at (725, 742), (813, 840), and (2570, 2606) cm^{-1} . The possibility of P-Q-R structure as an explanation of the additional bands has been eliminated by a detailed examination of the band contours. A possible cause of this splitting is the coexistence of hydrogen- and nonhydrogen-bonded entities in the vapor phase. The presence of the S_2H^+ and S_2^+ fragment ions in the mass spectrum of HPS_2F_2 provides supporting evidence for hydrogen-sulfur association (*vide supra*). It is also expected that hydrogen bonding would be maximized in the liquid phase and therefore cause the S-H stretch to shift to a lower frequency. Accordingly, the S-H stretch located at 2606 cm^{-1} in the vapor phase occurs as a broad band at 2506 cm^{-1} when recorded in the liquid phase. Moreover, nmr data are consistent with rapid proton exchange between two sulfur atoms.

The Raman spectrum of HPS_2F_2 is reproduced in Figure 2. Eight bands were observed, and of these reliable polarization measurements were obtained for only four bands, at 348, 389, 527, and 714 cm^{-1} , and all appeared to be polarized. An attempt was made to measure the Raman spectrum of CsPS_2F_2 in solution in order to corroborate some of the assignments for the acid. Unfortunately, the spectrum was too weak to be of assistance.

The vibrational assignments for HPS_2F_2 and DPS_2F_2 are contained in Table II. Also, included for comparison are the literature assignments for PSF_2Cl ,⁹ $\text{CH}_3\text{P}(\text{O})\text{F}_2$,¹⁰ and $\text{HPS}_2(\text{CF}_3)_2$.⁷ Generally, the assign-

(8) The bands observed in both spectra at 1033 cm^{-1} are due to SiF_4 , and the two bands at 368 and 561 cm^{-1} are due to CsPS_2F_2 . Bands at 667 and 2350 cm^{-1} are due to atmospheric CO_2 . Two bands near 1300 cm^{-1} in Figure 1a are due to an impurity. Due to rapid hydrogen-for-deuterium exchange in Pyrex, the spectrum in Figure 1b exhibits bands ascribed to HPS_2F_2 .

(9) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **46**, 3057 (1967).

(10) J. R. Durig, B. R. Mitchell, J. S. DiYoris, and F. Black, *J. Phys. Chem.*, **70**, 3190 (1966).

Table I. Infrared and Raman Data for HPS₂F₂, DPS₂F₂, and CsPS₂F₂

HPS ₂ F ₂		DPS ₂ F ₂		CsPS ₂ F ₂				Assignments ^a						
Ir (vapor) ν , cm ⁻¹	Rel int	Ir (liquid) ν , cm ⁻¹	Rel int	Ir (vapor) ν , cm ⁻¹	Rel int	Ir (liquid) ν , cm ⁻¹	Rel int		Ir (soln) ν , cm ⁻¹	Ir (mull) ν , cm ⁻¹	Raman (soln) ν , cm ⁻¹	Rel int	Pol	
307	w	197	m ?	300, 307	w			322	m	328	m		ν_{10}	
349	m	~310	w	349	s			368	s	368	s	365	w	ν_9
392	m	348	m P	389	s			391	s	392	m	392	m	ν_7
531	s	389	m P	527	vs	607	w	561	m	561	s	560	s	ν_6
		527	s P											ν_4 (D)
								655	m	655	s			$2 \times 328 = 656$ (Cs)
725	vs	714	vs	714	m P	722	vs	694	s	732	vs	722	vs	ν_5
742	s					739	s	721	vs	761	m-s			ν_5 (?) ^b
813	s	815	vs	815	w	813	w	818	s					ν_4 (?)
840	s-vs	~845				838 ^c	w-m	~845	Overlapped					ν_4 (?)
889	s	875	vs			887, 892	s	~880	Overlapped	786	s			ν_3
937	vs	928	vs			936	vs	917	Overlapped	813	s	812	vs	ν_2
1115	w	1114	m			1124	w	1127	m					$\nu_5 + \nu_7 = 1117$
1174	w													$\nu_4 + \nu_8 = 1189$
		1204	m					1203	m					$\nu_4 + \nu_7 = 1238$
		1236	m					1241	m					(gas)
														$\nu_3 + \nu_8 = 1238$
														(gas)
1274	w (broad)	1270	m			1262 ?	w							$\nu_3 + \nu_7 = 1281$
		1433	w											$2\nu_5 + 1450$
		1637	w											(gas)
		1745	w											$\nu_2 + \nu_5 = 1662$
														(gas)
						1889	w	1821	s					$2\nu_5 + \nu_9 = 1757$
2570	w													ν_1 (D)
2606	w-m	2506	s	~2530	s			2506 ^c	w					ν_1 (?)
		2720	w											ν_1
														$2\nu_2 + \nu_3 = 2731$
														(liquid)
		3352	w											?

^a Assignments for HPS₂F₂ except those marked with a D or Cs in parentheses for DPS₂F₂ and CsPS₂F₂, respectively. ^b This band could also be due to $\nu_7 + \nu_8 = 741$. ^c Band due to protonated molecule.

Table II. Vibrational Assignments for HPS₂F₂, DPS₂F₂, P(S)F₂Cl, CH₃P(O)F₂, and HPS₂(CF₃)₂

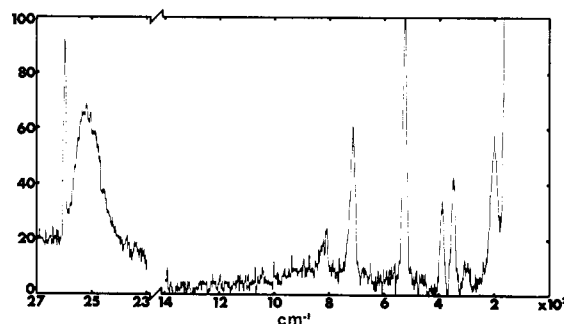
Approx description	HPS ₂ F ₂	DPS ₂ F ₂	P(S)-F ₂ Cl	CH ₃ P(O)F ₂	HPS ₂ (CF ₃) ₂
S-H stretch ν_1	{2606 2570}	1889			{2581 2566}
sPF ₂ stretch ν_2	937	946	936	878	
aPF ₂ stretch ν_3	889	887	914	858	
S-H bend ν_4	{840 813}	607			{849 845}
P=S stretch ν_5	{725 742}	722	738		731
P-S stretch ν_6	531	527			
P-F wag. ν_7	392	389	395	469	
PF ₂ scissor ν	349	349	361	291	
PF ₂ twist ν_9	307	300	317	408	
PF ₂ rock			
P=S bend	197	...	198 ^a		362
P-S bend	251 ^b		

^a SPCl out-of-plane bend. ^b SPCl in-plane bend.

ments are in accord with the ranges found in the literature for P-F¹⁰⁻¹² and P-S vibrations.^{13,14} How-

(11) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

ever, several comments seem appropriate concerning some of the assignments for HPS₂F₂.

Figure 2. Raman spectrum of liquid HPS₂F₂.

The assignment of the S-H stretching vibration to the band at 2606 cm⁻¹ is supported by Bellamy¹⁵ and con-

- (12) I. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).
 (13) R. A. Nyquist and W. W. Muellder, *Spectrochim. Acta*, **22**, 1563 (1966).
 (14) R. A. Chittenden and L. C. Thomas, *ibid.*, **20**, 1679 (1964).

firmed by the observed shift to 1889 cm^{-1} upon deuteration.⁸ Colthup, *et al.*,¹⁶ have reported a frequency range of $835\text{--}865\text{ cm}^{-1}$ for S–H bending vibrations in dithiophosphoric acid. The strong band observed in the HPS_2F_2 spectrum at 840 cm^{-1} is present as a low intensity absorption in the spectrum of DPS_2F_2 . A new band is observed in the DPS_2F_2 spectrum at 607 cm^{-1} . The intensity of this band does not compare with that of the 840-cm^{-1} band, but decreased intensity is often encountered in the same bands of an isotopic derivative. The frequency shift is approximately that which is expected, and therefore the 840-cm^{-1} band is assigned to the S–H bending vibration of the hydrogen-bonded molecule.¹⁷ A second band in this region at 813 cm^{-1} also decreases in intensity in the DPS_2F_2

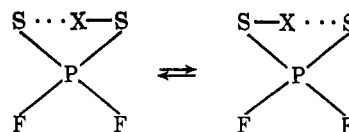
(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 350–352.

(16) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 304.

(17) See ref 16, p 189.

spectrum. The band cannot be assigned as an overtone or combination of any observed fundamental and therefore may be associated with the S–H bending mode of a nonhydrogen-bonded species.

In conclusion, the physical data support the structure where $X = \text{H}$ or D for the difluorodithiophosphoric acid gaseous molecule. In the liquid state, the acid



is also highly associated; however, the present data do not distinguish between intra- and intermolecular hydrogen bonding.

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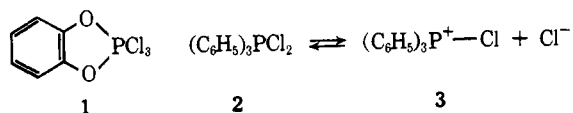
Structures of Several Phenylchlorophosphoranes in Solution¹

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Contribution from the School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. Received January 27, 1968

Abstract: The ^{31}P nmr spectra of the reaction products of chlorine with triphenylphosphine, diphenylchlorophosphine, and phenyldichlorophosphine have been determined in nitrobenzene. The results indicate these products exist in this solvent as the pentacoordinated materials. Addition of excess chlorine promotes dissociation to a phosphonium cation trichloride anion ion pair. Hydrogen chloride also promotes dissociation of triphenyldichlorophosphorane to triphenylchlorophosphonium bichloride. Ionization by chlorine becomes less facile as the number of chlorines bonded to phosphorus is increased.

It has long been recognized that phosphorus pentachloride can exist as pentachlorophosphorane or as tetrachlorophosphonium hexachlorophosphate.² The structures of pentacoordinate chloroalkyl, chloroaryl, and chloroaryloxy phosphorus compounds have received some study.³ Compound **1** has been studied by Jones and Katritzky^{3a} who have reported that it has a ^{31}P nmr chemical shift of $+26\text{ ppm}$ relative to 85% phosphoric acid. The relatively large positive chem-



ical shift suggests that the material exists as the phosphorane rather than as the phosphonium chloride.

(1) This research has been supported by the National Science Foundation under NSF GP 4997X and by the National Institutes of Health under GM 12625.

(2) For an excellent review see D. S. Payne in "Topics in Phosphorus Chemistry," Vol. 4, Interscience Publishers, New York, N. Y., 1967, p 85.

(3) (a) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, **74**, 60 (1962); (b) J. E. Griffiths, *J. Chem. Phys.*, **41**, 3510 (1964); (c) H. J. Emeleus and G. S. Harris, *J. Chem. Soc.*, 1494 (1959); (d) H. J. Emeleus and J. M. Miller, *J. Inorg. Nucl. Chem.*, **28**, 662 (1966); (e) J. F. Nixon, *ibid.*, **27**, 1281 (1965); (f) G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 4617 (1956).

It is not possible, however, to rule out a rapidly equilibrating mixture of these two substances with an equilibrium constant which highly favors **1**.

Recently, Wiley and Stine⁴ have investigated the structures of the products obtained by adding chlorine to triphenylphosphine and tributylphosphine. The tributylphosphine–chlorine adduct exhibited large negative, *ca.* -105 ppm , chemical shifts in the ^{31}P nmr spectra in either acetonitrile or nitrobenzene. These shifts were not changed when antimony pentachloride was added. The authors concluded that the tributylphosphine–chlorine reaction product exists as tributylchlorophosphonium chloride in these solvents.

The triphenylphosphine–chlorine adduct in acetonitrile in the presence of 1 equiv of antimony pentachloride or in its absence had ^{31}P nmr spectra with one absorption at -66 and -62 ppm , respectively. It was suggested therefore that the material is best represented as triphenylchlorophosphonium chloride (**3**) in acetonitrile. In nitrobenzene one absorption was found at -8 ppm . Addition of 1 equiv of aluminum chloride shifted the absorption to -65 ppm . It was suggested therefore that the phosphorane **2** prevails in nitro-

(4) G. A. Wiley and W. R. Stine, *Tetrahedron Letters*, 2321 (1967).