

The Thermal Rearrangement of Phosphorus Pentafluoride Adducts of Dimethyl Ether and Dimethyl Sulfide

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Abstract: The molecular adduct $(\text{CH}_3)_2\text{OPF}_5$ is shown to rearrange slowly at room temperature according to the equation $3(\text{CH}_3)_2\text{OPF}_5 \rightarrow 2(\text{CH}_3)_3\text{O}^+\text{PF}_6^- + \text{POF}_3$. The reaction of $(\text{CH}_3)_2\text{SPF}_5$ was also studied and found to be dissimilar to the ether system in that two solid salts were formed along with gaseous PF_3 ; viz., $3(\text{CH}_3)_2\text{SPF}_5 \rightarrow (\text{CH}_3)_3\text{S}^+\text{PF}_6^- + (\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^- + \text{PF}_3$. These reactions are surprising in that they have no analogy in any previously studied systems of boron or fluorophosphorane adducts with Lewis bases. Characterization of the stable solid salts by infrared and proton nmr is reported.

In conjunction with previous work on fluorophosphoranes,¹ we chose to examine several adducts of PF_5 with various Lewis bases. From this work we wish to report the unusual decomposition reactions of the dimethyl ether and dimethyl sulfide adducts of this Lewis acid.

Experimental Section

This work was carried out using standard vacuum techniques. Gaseous reactants and products were measured by means of a calibrated volume and are reported here in millimoles. Infrared spectra were run on a Beckman IR-10 spectrometer, using 10-cm gas cells fitted with KBr windows. Proton nmr spectra were obtained on a Varian A-60 spectrometer.

Phosphorus pentafluoride from the Matheson Co. was fractionated in the vacuum system from a trap held at -112° through traps at -126 , -145 , and -196° . After several similar refractionations, the -145° fraction was used for all reactions, it being tensimetrically pure with a vapor pressure of 363 mm at -95.6° (calculated² 362 mm). Dimethyl ether from the Matheson Co. was condensed onto LiAlH_4 and left for 2 hr at -64° . The ether was then introduced into the vacuum line and fractionated several times through traps held at -78 , -96 , and -112° . A center cut of the -112° fraction was used, having a vapor pressure of 87.1 mm at -64° (calculated³ 87.3 mm). Dimethyl sulfide from Aldrich Chemical Co. was dried for 24 hr over LiAlH_4 and transferred to the vacuum line; a center cut was used without further treatment. The vapor pressure at 0° was 168 mm (lit.⁴ 167 mm at 0°).

Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of Dimethyl Ether and Phosphorus Pentafluoride. A 500-ml reaction bulb was prepared and 34.6 mmoles each of $(\text{CH}_3)_2\text{O}$ and PF_5 were condensed into the bulb at -196° . The bulb was sealed from the line. The white solid adduct $(\text{CH}_3)_2\text{OPF}_5$,^{5,6} formed on warming the bulb to room temperature. This adduct, when pure, is a solid at room temperature; it melts at 29° . The reaction bulb was placed in a 34° oven in order to maintain the adduct as a liquid since this served to facilitate the reaction. During a 5-day period white crystals formed in the liquid. The bulb was then cooled to -196° and attached to the vacuum line *via* a tube-opening device and opened. Gradual warming transferred the volatile products into a -196° trap, after which the bulb was warmed to 50° and pumped on for 1 hr through this trap. The total volatile components collected were fractionated through traps maintained at -96 , -126 , and -196° . The -96° trap contained a solid which registered a saturation pressure of 25 mm at 0° (reported for $(\text{CH}_3)_2\text{OPF}_5$,^{5,6} 24.9 mm). By transferring this fraction to a preweighed ampoule fitted with a stopcock, a rela-

tively accurate weight of 3.51 ± 0.01 g (20.4 mmoles) was obtained, although some difficulty was encountered in obtaining complete transfer without decomposition within the vacuum system. The -126° trap contained 4.74 mmoles of POF_3 , identified by its infrared spectrum.⁷ The -196° trap contained less than 0.5 mmole of gas. The gas phase infrared spectrum of this fraction, run at 80 mm, showed that this was a mixture of POF_3 and a trace amount of dimethyl ether. The white crystals remaining in the reaction bulb weighed 1.87 g. (9.1 mmoles of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$). It needed no further purification.

Anal. Calcd for $\text{C}_3\text{H}_9\text{OPF}_6$: C, 17.47; H, 4.37; P, 14.63; F, 55.34. Found: C, 17.64; H, 4.03; P, 14.90; F, 55.37.

The above run gave an over-all conversion of the dimethyl ether-phosphorus pentafluoride molecular adduct to the ionic trimethyl-oxonium hexafluorophosphate of 26.3%. Higher conversions were observed for longer reaction times.

When stored *in vacuo*, in a glass ampoule, samples of trimethyl-oxonium hexafluorophosphate showed no decomposition over a period of several months. In stoppered vials slow hydrolysis occurred and HF was evolved; however, the extent of hydrolysis after several months was still very small.

The oxonium salt reacted rapidly with acetone and dimethylformamide, as evidenced by evolution of gaseous dimethyl ether. It was slightly soluble in dry nitromethane with no apparent decomposition occurring in several hours. It was more soluble in acetonitrile but also slowly reacted with this solvent; nevertheless, by working quickly we could obtain infrared or nmr spectra of these solutions.

A freshly prepared solution of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ in acetonitrile showed a single sharp proton nmr resonance at τ 5.58. During a 15-min period this peak diminished to about 10% of its original intensity; at the same time a singlet at τ 6.75 and multiplets at τ 6.28 and 7.23 appeared and grew in intensity. The singlet was due to dimethyl ether.⁸ The two multiplets were due to the methylnitrilium salt $\text{CH}_3\text{C}\equiv\text{NCH}_2^+\text{PF}_6^-$ which was formed in addition to dimethyl ether when the trialkyloxonium salt reacted with acetonitrile.

The nitrilium salt $\text{CH}_3\text{C}\equiv\text{NCH}_2^+\text{PF}_6^-$, mp 38° , could be isolated by dissolving $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ in acetonitrile and allowing the mixture to stand for 20 min, then pumping off the solvent until the solid crystallized out, filtering, and drying under high vacuum or several hours.

Anal. Calcd for $\text{C}_3\text{H}_8\text{F}_6\text{NP}$: C, 17.91; H, 2.99; F, 56.72; N, 6.97. Found: C, 17.79; H, 3.69; F, 56.45; N, 7.18.

Similar reactions to prepare other nitrilium salts have been reported.^{9,10} A Nujol mull spectrum of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ showed the

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(2) I. G. Rys, Ed., "Chemistry of Fluorine and Its Inorganic Compounds," State Publishing House for Scientific, Technical and Chemical Literature, Moscow, 1956, p 266.

(3) "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p D-126.

(4) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(5) I. K. Gregor, *Chem. Ind. (London)*, 385 (1965).

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(8) G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance (NMR) Shielding Values (Spectral Positions) for Hydrogen in Organic Structures," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958, part I, p 15.

(9) H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).

(10) It has been suggested that nitrilium salts react further with nitriles to give polymeric species; e.g., $\text{CH}_3\text{C}\equiv\text{NCH}_2^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_2-\text{[N}=\text{C}(\text{CH}_3)\text{]}_x^+$; J. E. Gordon and C. G. Turrell, *J. Org. Chem.*, **24**, 268 (1959). Indeed in all acetonitrile solution infrared spectra of nitrilium salts we see several strong $\text{C}=\text{N}$ stretching frequencies around 1650 cm^{-1} in addition to the $\text{C}\equiv\text{N}$ stretch at 2416 cm^{-1} .

principal oxonium band at 920 cm^{-1} (m), and PF_6^- absorptions at 845 (s) and 559 (m) cm^{-1} .¹¹ In acetonitrile the intensity of the 920- cm^{-1} band rapidly diminished. Peaks appeared corresponding to dimethyl ether (2915 (sh), 2890 (s), 2818 (s), 1162 (s), 1089 (s), 920 (sh), and 908 (m) cm^{-1}) and to the nitrilium ion-acetonitrile polymer (1720 (w), 1681 (w), 1647 (w) cm^{-1}).

Reaction of Dimethyl Sulfide with Phosphorus Pentafluoride. The $(\text{CH}_3)_2\text{SPF}_5$ system was examined in a similar fashion. This adduct was prepared in a 500-ml reaction bulb from 25.7 mmoles of PF_5 and 26.2 mmoles of $(\text{CH}_3)_2\text{S}$; it was a liquid at room temperature.⁶ Within 2 days colorless crystals appeared. After 5 days the bulb was opened on the vacuum line and warmed to 50° to effect complete removal of the volatile products; these products were then fractionated several times through -112, -145, and -196° traps. The contents of the -112° trap were refractionated by expansion from a trap maintained at -64° into a trap at -196°. The latter -196° trap condensed 0.4 mmole of $(\text{CH}_3)_2\text{S}$ while the -64° trap contained 2.97 g (15.9 mmoles) of the molecular adduct $(\text{CH}_3)_2\text{SPF}_5$ which had a vapor pressure of 40 mm at 0° (reported for $(\text{CH}_3)_2\text{SPF}_5$,⁸ 39 mm at 0°). The original -145° trap contained approximately 0.1 mmole of PF_5 and POF_3 as shown by a gas infrared spectrum run at 12 mm.^{7,12} The original -196° trap held 2.88 mmoles of PF_5 as shown by the gas infrared spectrum^{7,13} and by gas density measurements. The average molecular weight of two determinations in a calibrated bulb with pressures of 67 and 77 mm was 89 (calculated for PF_5 , 88).

The white solid which remained in the reaction bulb was transferred in a nitrogen flushed drybag into a sample vial and weighed, giving 1.46 g. When exposed to air the solid remained unchanged. However, samples which had not been warmed while removing the last traces of the volatile products tended to decompose.

Infrared spectra were run on the solid reaction product in Nujol and in acetonitrile. Spectra of the known compounds $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ and $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$ ^{14,15} were also run. These spectra clearly indicate that the reaction product was a mixture of $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ and $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$.

Reaction product (Nujol mull, NaCl plates): 3100 (m), 1040 (m), 990 (m), 968 (m), 845 (vs, broad) cm^{-1} ; $(\text{CH}_3)_2\text{CN}$ solution, NaCl cells) 3030 (m), 2940 (w), 1040 (m), 990 (m), 968 (m), 943 (m), 845 (vs, broad), 775 (w, sh), 755 (w, sh), 740 (w, sh) cm^{-1} . Within 20 min the 990- and 968- cm^{-1} bands decreased in intensity, and peaks at 2300, 2260, and 920 cm^{-1} appeared.

$(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ (prepared by a metathetical reaction of $(\text{CH}_3)_3\text{S}^+\text{I}^-$ and $\text{NH}_4^+\text{PF}_6^-$; CH_3CN solution, NaCl cells): 3030 (m), 2940 (w), 1040 (m), 940 (m), 845 (vs, broad) cm^{-1} .

$(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$ (prepared by the literature method,^{14,15} CH_3CN solution, NaCl cells): 990 (m), 968 (m), 845 (vs, broad), 775 (w, sh), 755 (w, sh) cm^{-1} . After several minutes all bands except the PF_6^- band at 845 cm^{-1} had visibly decreased in intensity and after 1.5 hr had completely disappeared, and new bands had appeared at 2300 (m), 2260 (m), and 920 (m) cm^{-1} .

The proton nmr spectrum of a freshly prepared solution of the original solid in acetonitrile showed two singlets with an intensity ratio of 1:2 at τ 6.90 and 7.20, respectively. The $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ singlet appeared at τ 7.20, and $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$ gave two singlets in the ratio of 2:1 at τ 6.90 and 7.20.

Iodine was produced when the solid product dissolved in acetonitrile was treated with sodium iodide. The known sample of $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$ behaved in a similar way. Pettit and Helmkamp¹⁴ report that the reaction $2(\text{CH}_3)_2\text{SSCH}_3^+ + 2\text{I}^- \rightarrow 2(\text{CH}_3)_2\text{S} + \text{CH}_3\text{SSCH}_3$ proceeds rapidly and quantitatively. From the reaction of the solid product and iodide ion, the salt $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ was recovered in pure form.

Discussion

On standing the Lewis acid-base adduct $(\text{CH}_3)_2\text{OPF}_5$ slowly deposited white involatile crystals. Isolation and examination of this solid showed that it was the ionic compound $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$. A careful study of the stoichiometry of the reaction (Table I) showed the following relationship.



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(12) J. P. Pemsler and W. G. Planet, *J. Chem. Phys.*, **24**, 920 (1956).

(13) M. K. Wilson and S. R. Polo, *ibid.*, **20**, 1716 (1952).

(14) D. J. Pettit and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963).

(15) H. Meerwein, K. F. Zenner, and R. Gipp, *Ann. Chem.*, **688**, 67 (1965).

This reaction proceeded very slowly if the pure adduct was a solid (<29°), and rapidly if the adduct was maintained in the liquid state. Approximately 26% of the initial adduct was converted to the oxonium compound in 5 days at 34°. The oxonium salt was separated as analytically pure material without further treatment simply by pumping off the volatile products (including unreacted adduct) *in vacuo* while mildly warming the reaction bulb to effect complete transfer. The oxonium compound is thermally stable; it could be stored in stoppered vials with only slight hydrolysis occurring in a several month period. To rigorously protect samples of the oxonium compound from hydrolysis, it is necessary to seal them in glass ampoules.

In a similar reaction of the adduct $(\text{CH}_3)_2\text{SPF}_5$, gaseous PF_3 rather than PSF_3 was formed. The solid product of the reaction contained two compounds, $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ and $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$, in equal quantities. The stoichiometry of the reaction (Table I) is defined by the equation

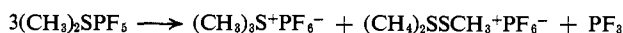


Table I. Material Balance for Rearrangement Reactions of $(\text{CH}_3)_2\text{OPF}_5$ and $(\text{CH}_3)_2\text{SPF}_5$ ^a

PF ₅ as P	(CH ₃) ₂ O as O	
	9.1	9.1
20.4	20.4	Adduct: (CH ₃) ₂ OPF ₅
4.7	4.7	Gas: POF ₃
34.2	34.2	Total recovered ^b
34.6	34.6	Initial reactants
PF ₅ as P	(CH ₃) ₂ S as S	
	6.1	9.2
15.9	15.9	Adduct: (CH ₃) ₂ SPF ₅
3.0	0.4	Gases: PF ₃ , POF ₃ , POF ₃ , (CH ₃) ₂ S
25.0	25.5	Total recovered ^b
25.7	26.2	Initial reactants

^a Quantities reported in mmoles. ^b The insignificant loss of reactants in 1:1 ratio can be accounted for in the error involved in transferring and weighing the molecular adducts remaining, since some decomposition was usually observed.

Both ionic materials from this reaction, $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ and $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$,¹⁴ were prepared independently. By comparisons of these materials with the reaction product positive identification of each in the latter mixture was obtained. This infrared and proton nmr spectra of the reaction product were identical with that expected for a mixture of the two pure components. Moreover, the compound $(\text{CH}_3)_2\text{SSCH}_3^+\text{PF}_6^-$ from this mixture reacts selectively with iodide ion to give elemental iodine (as does the pure sample of this material¹⁴); $(\text{CH}_3)_3\text{S}^+\text{PF}_6^-$ which does not react with iodide ion can then be obtained in pure form.

No similar rearrangement reactions have been reported to occur with other molecular adducts of boron or phosphorus Lewis acids. The difference between ether and sulfide adduct reactions was not expected. The gaseous substance PSF_3 , while less thermally stable than POF_3 , is a well-characterized substance.¹⁶

(16) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

Trialkyloxonium salts are known to be strong alkylating agents toward substances possessing a lone pair of electrons.^{9,17} Thus the reaction of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ with polar solvents used here was not unexpected. The alkylation reaction which occurs with acetonitrile was slow, however, so that useful spectral data using this solvent could be obtained. Our nmr data on approximately 40% solutions of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ in acetonitrile suggest that over a 15-min period reac-

(17) H. Meerwein, G. Hinz, P. Hoffmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937); H. Meerwein, H. Gold, E. Pfeil, and G. Willfang, *ibid.*, **154**, 83 (1939) (these are the two basic papers in this field; other isolated references have appeared since).

tion to give the methylnitrilium ion $\text{CH}_3\text{C}\equiv\text{NCH}_3^+$ occurs to the extent of about 90%. Similar results were obtained from the infrared spectra taken in this solvents.

Trimethylsulfonium hexafluorophosphate did not react with acetonitrile. However, a slow reaction of $(\text{CH}_3)_3\text{SSCH}_3^+\text{PF}_6^-$ was observed in this solvent. No product was characterized from this reaction.

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Kinetics of the Addition of Hydrogen, Oxygen, and Methyl Iodide to Some Square-Planar Iridium(I) Complexes¹

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Abstract: A study is described of the kinetics of the following series of reactions in benzene and dimethylformamide, $\text{trans-IrX}(\text{CO})(\text{PPh}_3)_2 + \text{YZ} \rightarrow \text{IrXYZ}(\text{CO})(\text{PPh}_3)_2$, where X = Cl, Br, and I and YZ = H₂, O₂, and CH₃I. The kinetics, in each case, were found to obey the second-order rate law, $\text{rate} = k_2[\text{IrX}(\text{CO})(\text{PPh}_3)_2][\text{YZ}]$. The kinetic patterns of the reactions with H₂ and O₂ were very similar. The activation parameters for these reactions, in benzene, were all in the range $\Delta H^* = 10.8$ to 13.1 kcal/mole and $\Delta S^* = -14$ to -24 eu. In each case the dependence of rate on the halogen followed the order I > Br > Cl. The reactions with CH₃I exhibited a somewhat different reactivity pattern, the dependence of the rate on the halogen following the reverse order, Cl > Br > I. The activation parameters for these reactions (in benzene) were in the range $\Delta H^* = 5.6$ to 8.8 kcal/mole and $\Delta S^* = -43$ to -51 eu and exhibited a marked solvent dependence. The mechanistic implications of these results are discussed.

Complexes of group VIII metals of d⁸ configuration, notably square-planar complexes of platinum(II),²⁻⁴ iridium(I),⁵⁻⁷ and rhodium(I)^{7,8} (as well as certain pentacoordinated ruthenium(0) complexes^{9,10}) are well known to add a variety of covalent molecules such as hydrogen,⁵ halogens,^{5,9} hydrogen halides,³⁻⁹ methyl iodide,^{2,7} and oxygen⁶ to form (generally hexacoordinated) complexes of d⁶ configuration. In recent years such oxidative addition reactions have attracted widespread interest and have been studied extensively from the standpoint of their novel stoichiometry and products and also of their significance in homogeneous catalytic reactions such as hydrogenation and hydro-

formylation.¹¹⁻¹³ However, the study of the kinetics and mechanisms of these reactions has hitherto received virtually no attention. We report here the results of the first such systematic investigation of the kinetics of the series of reactions



where Ph = C₆H₅, X = Cl, Br, and I and YZ = H₂, O₂, and CH₃I.

Experimental Section

Materials. *trans-IrCl(CO)(PPh₃)₂* was prepared by the method described by Johnson.¹⁴ H₂IrCl₆·6H₂O was dissolved in 2-methoxyethanol and neutralized with sodium carbonate. The solution was refluxed for about 5 hr, while CO was continuously bubbled through, until reduction to iridium(I) (presumably IrCl(CO)₂) was achieved, the solution at this stage being light yellowish brown in color. The mixture was then cooled and the stoichiometric equivalent of triphenylphosphine added. The yellow product which separated out was recrystallized from toluene. *Anal.* Calcd for IrCl(CO)[P(C₆H₅)₃]₂: C, 56.96; H, 3.88; P, 7.94. Found: C, 56.7; H, 4.1; P, 7.64.

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(13) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

(14) N. P. Johnson, Ph.D. Thesis, University of London, 1964. The preparation of *trans-IrBr(CO)(PPh₃)₂* from Ir(CO)₂Br was first reported by M. Angoletta, *Gazz. Chim. Ital.*, **89**, 2359 (1959).

(1) Support of this work by grants from the National Institutes of Health and the National Science Foundation and by a grant to the University of Chicago from the Advanced Research Projects Agency is gratefully acknowledged.

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