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Oxygen Chemistry of the $(CF_3)_2P$ Group: the Diphosphoxane; the Phosphinous Acid, Esters and Related Phosphine Oxides; Phosphinyl Halides and Infrared Spectra[1]

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The diphosphoxane $(CF_3)_2POP(CF_3)_2$ (m.p. −53°; b.p. est. 78°), made from $(CF_3)_2PI$ with Ag_2CO_3 and stable up to 250°, behaves as a weak Lewis acid rather than a base; yet HCl easily converts it to $(CF_3)_2PCl$ and the H-bond associated protic acid $(CF_3)_2POH$ (m.p. −21°; b.p. est. 61°). This does not rearrange to $(CF_3)_2HPO$; indeed this phosphine oxide, made from $(CF_3)_2PH$ and HgO, changes to $(CF_3)_2POH$, $(CF_3)_2PH$ and $(CF_3)_2POOH$. However, the phosphinous esters $(CF_3)_2POR$, made by ROH-cleavage of $P_2(CF_3)_4$, can be rearranged to $R(CF_3)_2PO$ by CH_3I catalysis—very easily when R is *t*-butyl but with difficulty when R is methyl. A similar Arbuzov-type rearrangement would explain why $(CH_3)_2POP(CF_3)_2$ could not be made from $(CH_3)_2PH$ and $(CF_3)_2POP(CF_3)_2$, which gave instead $(CF_3)_2PH$, $P_2(CF_3)_4$, $(CH_3)_2PP(CF_3)_2$ and what seemed to be $(CH_3)_4P_2O_2$ (m.p. 132°; vacuum-sublimable); some stages of this reaction were demonstrated. The infrared spectra of all of these $(CF_3)_2PO$ compounds were compared for confirmation of assignments. In this relation $(CF_3)_2POCl$ (b.p. est. 52°) and $(CF_3)_2POBr$ (m.p. −35°; b.p. est. 78°) were made by different methods and used for a spectroscopic recheck of the electronegativity of the CF_3 group.

Compounds of the hydrocarbon–phosphorus–oxygen types R_2POH and R_2POPR_2 have been lacking, evidently because they would rearrange in the Arbuzov manner to $R_2P^{O}_{H}$ and $R_2P^{O}_{PR_2}$, either of which would disproportionate very soon. But when R is a fluorocarbon group, R_2POH and R_2POPR_2 are permanently stable[2]; indeed, $(CF_3)_2HPO$ actually converts to $(CF_3)_2POH$.[3] Here it seems that the $(CF_3)_2P$ group is so weakly basic that oxygen holds the proton more firmly. Similarly, one reason that $(CF_3)_2POP(CF_3)_2$ does not change to the $R_2P\text{–}P^{O}_{R_2}$ form is that the virtually non-basic P atom in a $(CF_3)_2\ddot{P}\text{–}X$ type molecule cannot bond a $^{+}\ddot{P}(CF_3)_2$ group so strongly as oxygen does. A secondary reason is the electron-acceptor character of the $(CF_3)_2P$ group, such as to support a fairly strong two-way dative π bonding by the oxygen lone-pair electrons to two pairs of P_{3d} orbitals; whereas in the $R_2P\text{–}P^{O}_{R_2}$ form such π bonding would involve only one P atom instead of two. Neither of these stabilizing effects would apply well to $(CH_3)_2POP(CH_3)_2$, wherein P would be far more basic and less receptive to a dative π bond.

A phosphinous ester such as $(CF_3)_2POCH_3$ should be less stable than the corresponding phosphine oxide for two reasons: an alkyl group tends to attach permanently to phosphorus; and the O–P π-dative bonding should be stronger in $(CF_3)_2RPO$ than in the ester. Thus it is not surprising that such esters can rearrange to phosphine oxides, when aided by heat and catalysts.

Attempts to make $(CH_3)_2POP(CF_3)_2$ from $(CF_3)_2POP(CF_3)_2$ and $(CH_3)_2PH$ led to an interesting series of reactions. The desired diphosphoxane may well have been formed, but since the $(CH_3)_2P$ group is strongly basic, the $^{+}P(CF_3)_2$ group soon would move from O to the basic phosphorus atom, forming $(CH_3)_2\overset{O}{P}\text{–}P(CF_3)_2$. This could be expected to disproportionate by P–P bond exchange to form the new $(CH_3)_2\overset{O}{P}\text{–}\overset{O}{P}(CH_3)_2$ and the known $(CF_3)_2P\text{–}P(CF_3)_2$; however, the latter has been found to react rapidly with $(CH_3)_2PH$ to make $(CF_3)_2PH$ and $(CH_3)_2P\text{–}P(CF_3)_2$. Our quantitative experiments agreed (within 7% at most) with this pattern of events, summarized by the equation $3(CH_3)_2PH + 2(CF_3)_2POP(CF_3)_2 \rightarrow 3(CF_3)_2PH + (CH_3)_2P\text{–}P(CF_3)_2 + [(CH_3)_2PO]_2$. Certain steps of this over-all process were individually demonstrated.

There remains the interesting question of what permanently stable diphosphoxanes, phosphinous acids and esters could exist with substituent groups making phosphorus somewhat more basic and less electronegative. Our recent colleague Dr. K. K. Joshi made a series of phosphines based upon the CH_3CF_3P group, but their conversion to oxyphosphines has not been attempted.

The experimental work here described was done by means of high-vacuum manifolds with U-traps interconnected by Stock-type mercury float-valves or chlorofluorocarbon-greased stopcocks (for oxidizing materials)—permitting quantitative account of all volatile substances. For accurate pressure measurements, wide-arm mercury manometers were silhouetted by horizontal-beam light and sighted by cathetometers with 0.01 mm. reproducibility. Mercury-reactive vapors were measured by means of a null-indicating spoon-gauge. Temperatures above −30° were measured by mercury-in-glass thermometers calibrated to 0.05° or better; and for lower temperatures the appropriate Stock-vapor-tension thermometers were employed.

The Diphosphoxane $(CF_3)_2POP(CF_3)_2$

Synthesis and Characterization.—The reaction $2(CF_3)_2PI + Ag_2CO_3 \rightarrow 2AgI + CO_2 + (CF_3)_2POP(CF_3)_2$ occurred easily at room temperature, giving a high yield of the diphosphoxane.

A 15.9 mmole sample of $(CF_3)_2PI$ (44.0 mm. at 0°, in accord with the known vapor tension)[4] was shaken with dry silver carbonate in a tube closed by a stop-cock, until the evolution of carbon dioxide had virtually ceased. The volatile mixture was similarly exposed to three fresh samples of silver carbonate to minimize the residual $(CF_3)_2PI$. The last of this finally was converted (by reaction with AgCl)[5] to

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(1) This research was supported by the United States Air Force under a subcontract of Prime Contract AF 33(616)-6913, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).

(3) J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc.*, 12 (1961).

(4) A. B. Burg, Walter Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, *J. Am. Chem. Soc.*, **79**, 247 (1957).

(5) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

$(CF_3)_2PCl$ (0.14 mmole), the relatively high volatility of which permitted its easy removal from the diphosphoxane by high-vacuum fractional condensation. The diphosphoxane passed a trap at −45° and condensed completely at −78°. The yield was 6.27 mmoles, representing 79% of the initial $(CF_3)_2PI$.

The pure diphosphoxane melted in the range −53.1 to −52.6°. Its vapor tensions are shown in Table I. The equation (more accurate than the earlier one)[2] gives the normal b.p. as 78.4° and the Trouton constant as 22.3 cal./deg. mole.

TABLE I

VAPOR TENSIONS OF $(CF_3)_2POP(CF_3)_2$

$(\log P_{mm.} = 6.2498 + 1.75 \log T - 0.00529\ T - 2097/T)$

t (°C.)	−10.6	0.00	10.8	24.2	37.7	47.7	61.1
$P_{mm.}$ (obsd.)	12.78	24.4	45.4	89.5	166.7	252.8	421.8
$P_{mm.}$ (calcd.)	12.82	24.6	45.3	89.7	166.6	252.9	421.9

Proof of Formula.—The formula $(CF_3)_2POP(CF_3)_2$ was confirmed by the vapor-phase (mol. wt. 354.2 *vs.* calcd. 354.0) and the hydrolysis of a 42.0 mg. sample with 10% sodium hydroxide (1.7 ml., 100°, 14 hr.) to give 32.7 mg. of HCF_3 (calcd. 33.2 mg. for $4CF_3$). The presence of $(CF_3)_2P$ groups was confirmed by three strong infrared bands for C–F stretching (Table XII); also the expected two modes of P–O–P stretching were found, and there was no band assignable to P=O stretching.

Decomposition.—The thermal decomposition of the diphosphoxane $(CF_3)_2POP(CF_3)_2$ was as previously described,[2] giving major proportions of CO, PF_3, $(CF_3)_2PF$ and $(CF_3)_3P$. A less volatile mixture (12% of the initial sample-weight) showed infrared bands corresponding to C–F, P–F and P–O–P stretching. The non-volatile black solid residue (7%) apparently included white phosphorus or polyphosphines (or both), for it was noticeably reactive toward air.

Acid-Base Behavior.—The previously mentioned adduct $(CF_3)_2POP(CF_3)_2 \cdot (CH_3)_3N$[2] was demonstrated by a pressure-composition isotherm at −78.5°, after relatively rapid formation at −50°. Beyond the 1:1 ratio the amine was only slightly absorbed.

The equation for the solid–vapor equilibrium pressures (Table II) does not perfectly describe the dissociation of the solid into free amine and diphosphoxane vapors, for the average mol. wt. of a vaporized sample at 24° was 229.6, corresponding to 19% formation of the adduct. The solid-vapor equilibrium measurements could not usefully be extended above −23° because this was close to the point at which the diphosphoxane would begin to form a liquid.

TABLE II

SOLID–VAPOR EQUILIBRIA OF $(CF_3)_2POP(CF_3)_2 \cdot (CH_3)_3N$

$(\log P_{mm.} = 8.777 - 1985/T)$

t (°C.)	−78.5	−63.5	−45.3	−30.6	−23.2
$P_{mm.}$ (obsd.)	0.04	0.22	1.13	3.92	6.85
$P_{mm.}$ (calcd.)	0.04	0.20	1.16	3.92	6.85

As indicated before,[2] these dissociation data show that the phosphorus atom here actually has stronger Lewis-acid character than in PF_3; for the solid-vapor equilibrium pressures of $PF_3 \cdot (CH_3)_3N$ were measured as 1.9 mm. at −95.8°, 8.3 mm. at −80.3° and 9.1 mm. at −78.5 ($\log P_{mm.} = 8.08 - 1384/T$; point of appearance of liquid, near −76°). The difference may be due at least partly to F_{2p}–P_{3d} π-bonding by three fluorine atoms (whereby the 3d orbitals of P in PF_3 are mostly filled), in contrast to π-bonding only by one oxygen (toward both P atoms) in the diphosphoxane.

The reactions of the diphosphoxane with hydrogen chloride and with dimethylphosphine are described in the following main sections. Its failure to react with such Lewis acids as boron trifluoride and sulfur dioxide was mentioned before.[2]

The Phosphinous Acid $(CF_3)_2POH$

Synthesis and Characterization.—The compound $(CF_3)_2POH$ was made first by heating 1.562 mmoles of $(CF_3)_2POP(CF_3)_2$ with 1.722 mmoles of dry HCl in a sealed glass tube for 8 days at 80°. The tube was fitted with a thin glass magnetic break-off tip to permit all-glass connection to the high-vacuum system. This was necessary because the stop-cock grease in the more usual tube-opener would have seriously absorbed the product. However, this absorption was not too serious when the material was passed at a very low pressure through a ground joint which was made tight by a shellac-base vacuum cement.

The reaction products were separated by high-vacuum fractional condensation, with isolation of 0.137 mmole of HCl and measurement of the products. The empirical equation was $1.562(CF_3)_2POP(CF_3)_2 + 1.584\ HCl \rightarrow 1.568(CF_3)_2PCl + 1.337\ (CF_3)_2POH$. The 86% yield of $(CF_3)_2POH$ represents a lower limit, for the determination was by vapor volume, which is affected by a contraction effect possibly due to hydrogen bonding. For example, a sample which seemed to represent 0.166 mmole of $(CF_3)_2POH$ vapor was analyzed by basic hydrolysis to give 0.391 mmole of HCF_3, corresponding to 0.195 mmole of actual $(CF_3)_2POH$. By reference to this result, the true yield of $(CF_3)_2POH$ would be estimated as 1.57 mmole, or essentially quantitative.

The vapor-phase mol. wt. of $(CF_3)_2POH$ was determined at a relatively high temperature and low pressure (with all possible avoidance of the effects of greases and waxes), so that the result (184.8 *vs.* calcd. 186.0) probably is dependable. The infrared spectrum included bands corresponding to O–H bending and stretching, and for P–OH stretching (but none attributable to P–H or terminal P=O), confirming the structural pattern indicated by the formula as written.

The vapor tensions of liquid $(CF_3)_2POH$ are given in Table III, with an equation giving the normal b.p. as 61.4° and the Trouton constant as 21.2 cal./deg. mole. Taking this equation with that for the solid (Table IV), we compute the m.p. as −20.8° (obsd., −21.3 to −21.1°) and the enthalpy of fusion as 1913 cal./mole. The high value of the term $0.01090T$ in the equation for the liquid (normal average value near $0.005\ T$) describes a strong downward concavity in the log P *vs.* $1/T$ curve. This effect is not unusual for strongly hydrogen-bonded substances.

TABLE III

VAPOR TENSIONS OF LIQUID $(CF_3)_2POH$

$(\log P_{mm.} = 9.6392 + 1.75 \log T - 0.01090\ T - 2519/T)$

t (°C.)	−16.3	−12.3	−4.5	0.0	10.6	14.7
$P_{mm.}$ (obsd.)	17.75	23.34	38.5	50.6	91.6	113.4
$P_{mm.}$ (calcd.)	17.76	23.34	38.5	50.6	91.6	113.3

TABLE IV

VAPOR TENSIONS OF SOLID $(CF_3)_2POH$

$(\log P_{mm.} = 10.7590 - 2435/T)$

t (°C.)	−39.4	−34.8	−28.1	−27.0	−23.4	−21.3
$P_{mm.}$ (obsd.)	2.19	3.55	6.63	7.34	10.30	12.33
$P_{mm.}$ (calcd.)	2.20	3.50	6.65	7.36	10.22	12.33

The Deuterio-phosphinous Acid.—The deuterio-acid $(CF_3)_2POD$ was made as an aid in the interpretation of the infrared spectrum of $(CF_3)_2POH$. The diphosphoxane was cleaved by DCl containing about 10% HCl, during 72 hr. in a sealed tube at

100°. The resulting mixture was brought into the vacuum system through a magnetic breaker and resolved by fractional condensation as before, leading to the empirical equation (quantities in mmoles): $0.552(CF_3)_2POP(CF_3)_2 + 0.558DCl \rightarrow 0.468(CF_3)_2POD + 0.562(CF_3)_2PCl$. Since the resulting phosphinous acid again was measured as a gas, the 17.5% correction may be applied to estimate the actual yield as 0.55 mmole, or essentially quantitative.

The 90%-deuterated phosphinous acid melted in the range −19.3 to −19.2°, *vs.* −21.3 to −21.1° for pure $(CF_3)_2POH$. Thus the m.p. of pure $(CF_3)_2POD$ is extrapolated as −19.0°. Similarly, the 0° vapor tensions 50.58 mm. for $(CF_3)_2POH$ and 52.96 mm. for 90% $(CF_3)_2POD$ indicate 53.2_2 mm. at 0° for pure $(CF_3)_2POD$.

The Trimethylammonium Salt.—A white solid was formed when 0.635 mmole of $(CH_3)_3N$ and a gas-volume-measured 0.199 mmole (0.231 mmole as corrected) sample of $(CF_3)_2POH$ were warmed together from −78° to 0° during 3 hr. The excess amine was distilled off and measured as 0.403 mmole; consumed, 0.232 mmole, representing quantitative formation of the salt $(CH_3)_3NH^+(CF_3)_2PO^-$. This product absorbed 0.232 mmole of HCl, rapidly forming a viscous liquid from which 0.161 mmole (by an uncorrected gas-volume measurement) of $(CF_3)_2POH$ could be distilled off under high vacuum with great difficulty during four days, leaving a solid residue of trimethylammonium chloride. Also formed were 0.019 mmole of $(CF_3)_2PCl$ and 0.005 mmole of HCF_3.

The adduct $(CH_3)_3N{\cdot}(CF_3)_2POH$ was too hygroscopic for any very thorough study of its infrared spectrum by the KBr-pellet method, but its phosphinite-salt character was quite clearly indicated by the disappearance of the P–OH stretching band at 854 cm.$^{-1}$ and the appearance of a strong band at 1305 cm.$^{-1}$, assigned to terminal P=O stretching. Thus the product could not be regarded as an N–P dative-bonded complex like the far less stable $(CF_3)_2POP(CF_3)_2{\cdot}(CH_3)_3N$.

Rearrangement of the Phosphine Oxide.—The phosphinous acid appeared also as a product of the HgO-oxidation of $(CF_3)_2PH$. The results suggest that the initial product was the phosphine oxide $(CF_3)_2HPO$, part of which disproportionated to $(CF_3)_2PH$ and $(CF_3)_2POOH$ while the rest rearranged to $(CF_3)_2POH$. The latter process has been called an anti-Arbuzov rearrangement[3] because it suggests a reversal of the Arbuzov-type reaction $R_2POR' \rightarrow R_2R'PO$.

The HgO-oxidation was done in an all glass mercury high-vacuum system, first by a static method and later by a flow process which permitted a more detailed study of the immediate volatile product. In the first experiment 0.969 mmole of $(CF_3)_2PH$ was allowed to expand into a tube containing 0.89 mmole of mercuric oxide—purposely deficient in order to minimize oxidation to $(CF_3)_2POOH$. The reaction was immediate and exothermic, giving white fumes and metallic mercury. After 4 min. the volatile components were fractionally condensed under high vacuum at −78°, with only the $(CF_3)_2PH$ passing through to the final trap at −196°. When the −78° condensate was warmed briefly, it produced more $(CF_3)_2PH$ than could be ascribed to solubility effects, suggesting the disproportionation $2(CF_3)_2HPO \rightarrow (CF_3)_2POOH + (CF_3)_2PH$. Now all volatile components were returned to the reaction tube for further oxidation during 10 min. at room temperature. The final mixture included 0.421 mmole of $(CF_3)_2PH$, 0.196 mmole of $(CF_3)_2POH$, 0.276 mmole of the slightly volatile $(CF_3)_2POOH$ and 0.825 mmole of metallic mercury. These results can be interpreted as follows, with the hypothetical aspect enclosed in brackets.

$$0.825(CF_3)_2PH + 0.825HgO \longrightarrow 0.825Hg + [0.825(CF_3)_2HPO]$$

$$[0.552(CF_3)_2HPO] \longrightarrow 0.276(CF_3)_2PH + 0.276(CF_3)_2POOH$$

$$[0.196(CF_3)_2HPO] \longrightarrow 0.196(CF_3)_2POH$$

0.077 mmole $(CF_3)_2POH$ deficiency ascribed to the volume-contraction effect and to adsorption.

The direct formation of $(CF_3)_2HPO$, followed by its two-way alteration (without catalytic effect by the HgO) was indicated again by an experiment in which 0.702 mmole of $(CF_3)_2PH$ vapor at 6 mm. pressure was allowed to pass over a bed of mercuric oxide, kept at 60–65° to minimize adsorption. The effluent vapors were fractionally condensed at −45, −96 and −196° and the HgO-tube was sealed off to prevent further contact with the condensates. All of the effluent $(CF_3)_2PH$ (0.128 mmole) was found in the −196° trap, while the trap at −96° held only 0.03 mmole of $(CF_3)_2POH$. The initial main product, found in the −45° trap, would not have contained appreciable amounts of $(CF_3)_2PH$, but after 14 hr. at room temperature it had generated 0.129 mmole of $(CF_3)_2PH$ and 0.128 mmole of $(CF_3)_2POH$. The less volatile product was analyzed by alkaline hydrolysis, forming an amount of HCF_3 corresponding to 0.088 mmole of $(CF_3)_2POOH$. Since $(CF_3)_2POH$ could not have been present in the −45° trap, and in any case would not have disproportionated to give $(CF_3)_2PH$ and $(CF_3)_2POOH$, it is apparent that the formation of all three products must have been due to $(CF_3)_2HPO$, as the main component of the −45° condensate.

The $(CF_3)_2POH$ could not have been formed by the reversed disproportionation $(CF_3)_2PH + (CF_3)_2POOH \rightarrow 2(CF_3)_2POH$, for known samples of the phosphinic acid (made as next described) and the phosphine were mixed and held at 60° for 16 hr. without reaction. Thus it appears that the rearrangement $(CF_3)_2HPO \rightarrow (CF_3)_2POH$ occurred simultaneously with the disproportionation, which was not part of the path to $(CF_3)_2POH$.

Direct Synthesis of the Phosphinic Acid.—For a higher yield of the phosphinic acid $(CF_3)_2POOH$, a 1.593 mmole sample of $(CF_3)_2PH$ was condensed in a glass tube containing mercuric oxide in great excess. The tube was alternately warmed to room temperature and cooled to −78° in order to ensure adequate contact of the phosphine with the oxide. A clear but viscous liquid was observed to form, and the mercuric oxide became consolidated into a cake. Traces of oxygen and fluoroform were removed, and the other volatile components were condensed into a trap, which was allowed to stand at room temperature for 10 min. Now a small amount of $(CF_3)_2PH$ (0.01 mmole) was removed by distillation, leaving 122.4 mg. (0.606 mmole) of virtually pure $(CF_3)_2POOH$. This product was subjected to alkaline hydrolysis at room temperature, yielding 0.597 mmole of well identified HCF_3, in accord with the established fact that $(CF_3)_2POOH$ yields only one HCF_3 per molecule under these conditions.[6]

The Phosphinous Esters $(CF_3)_2POR$

The methyl, ethyl and *t*-butyl phosphinous esters were made for infrared spectroscopy (leading to

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(6) H. J. Emeléus, R. N. Haszeldine and R. C. Paul, *J. Chem. Soc.*, 563 (1955).

useful correlations for the assignment of some bands) and also for a study of the tendency of such compounds to undergo Arbuzov-type rearrangements, $(CF_3)_2POR \rightarrow (CF_3)_2RPO$. In relation to these purposes it was also useful to make and characterize two of the corresponding phosphine oxides and the phosphinous acid chloride and bromide. The method chosen for the synthesis of the esters was the alcoholytic cleavage $P_2(CF_3)_4 + ROH \rightarrow (CF_3)_2POR + (CF_3)_2PH$. This process can be made quantitative, with easy isolation of the products; and it represents an attractive method of making $(CF_3)_2PH$ for other purposes.

The Methyl Ester.—The initial experiment on the methanol cleavage of $P_2(CF_3)_4$ was done in these Laboratories by Walter Mahler, who found that the reaction became inconveniently rapid (leading to undesired decompositions) if started at room temperature. In the present study, 1.767 mmoles of $P_2(CF_3)_4$ and 1.812 mmoles of CH_3OH reacted slowly during 13 hr. at 0° and then proceeded smoothly to completion at room temperature. The products were separated easily by high-vacuum fractional condensation, followed by removal of methanol from the ester by contact with P_4O_{10}. The empirical equation (with mol. wt. of the products) was

$$1.767P_2(CF_3)_4 + 1.79CH_3OH \longrightarrow 1.67(CF_3)_2POCH_3 + 1.85(CF_3)_2PH$$

mol. wt. obsd.	200.1	170.7
calcd.	200.0	170.7

An attempt to make the ester by the reaction of $(CF_3)_2PI$ with $NaOCH_3$ led to detonation in a static system and to unresolvable mixtures when a vapor-flow method was tried.

The purified ester $(CF_3)_2POCH_3$ melted sharply at −78.5° and exhibited the consistent set of vapor tensions given with an equation in Table V; normal b.p., 55.4°; Trouton constant, 21.1 cal./deg. mole. Such evidences of purity, taken with the nearly quantitative synthesis and the mol. wt., would be enough to prove the formula, but for further confirmation a 21.9 mg. sample was hydrolyzed in 10% NaOH (36 hr. at 100°), to give 15.3 mg. of HCF_3, just as calculated for $2HCF_3$ per mole.

TABLE V

VAPOR TENSIONS OF LIQUID $(CF_3)_2POCH_3$

$(\log P_{\text{mm.}} = 7.5975 + 1.75 \log T - 0.00800T - 2133/T)$

t (°C.)	−63.8	−45.3	−27.0	0.00	7.0	12.1	15.8
$P_{\text{mm.}}$ (obsd.)	0.63	3.42	14.06	73.68	106.1	136.6	162.2
$P_{\text{mm.}}$ (calcd.)	0.62_5	3.43_5	14.05	73.68	106.1	136.4	162.5

The ester $(CF_3)_2POCH_3$ proved to be inert toward boron trifluoride and equally indifferent to trimethylamine. The lack of base action is attributed to delocalization of the oxygen lone-pair electrons toward phosphorus; and this is more effective for weakening the electron-acceptor character of phosphorus than is the three-atom delocalization of the oxygen lone-pair electrons in $(CF_3)_2POP(CF_3)_2$.

The Ethyl Ester.—The compound $(CF_3)_2POC_2H_5$, previously made by the alcoholysis of $(CF_3)_2PCl$,[7] was obtained in 98.5% yield by the biphosphine cleavage method; empirical equation

$$0.718P_2(CF_3)_4 + 0.739C_2H_5OH \longrightarrow 0.719(CF_3)_2PH + 0.707(CF_3)_2POC_2H_5$$

mol. wt. obsd.	169.3	214.0
calcd.	170.0	214.0

The reaction began during 12 hr. at 0°, continued through 27 hr. at 25°, and was brought surely to completion during 4 hr. at 60°. Again, the products were isolated by fractional condensation, with removal of the last of the alcohol by contact with P_4O_{10}. Since this ester was made only for spectroscopic purposes, it was not more fully characterized.

The *t*-Butyl Ester.—An exploratory experiment, performed in these Laboratories by Walter Mahler, showed that the cleavage of $P_2(CF_3)_4$ by *t*-butanol was far slower than the methanolysis, presumably on account of steric hindrance. In the present work, the reaction was only moderately advanced after 80 hr. at 25°, but 98.8% complete after 11 days. Allowing for the recovery of unused $P_2(CF_3)_4$, but not correcting for probable losses of the ester during the P_4O_{10} treatment and final purification, the empirical equation is given as

$$2.936P_2(CF_3)_4 + 2.973C_4H_9OH \longrightarrow 2.937(CF_2)_2PH + 2.826(CF_3)_2POC_4H_9$$

mol. wt. obsd.	170.7	242.0
calcd.	170.0	242.0

A well purified sample of $(CF_3)_2POC_4H_9$ melted very sharply at −26.1° and exhibited the vapor tensions given with the equation in Table VI; normal b.p., 110.3°; Trouton constant, 20.3 cal./deg. mole.

TABLE VI

VAPOR TENSIONS OF LIQUID $(CF_3)_2POC_4H_9$

$(\log P_{\text{mm.}} = 7.3142 + 1.75 \log T - 0.00688T - 2422/T)$

t (°C.)	0.00	11.5	25.0	30.0	41.7	56.7	67.0
$P_{\text{mm.}}$ (obsd.)	6.79	13.82	29.53	38.21	67.18	128.7	192.4
$P_{\text{mm.}}$ (calcd.)	6.79	13.88	29.51	38.21	67.20	128.6	192.4

Isomerization Reactions.—Both the methyl and *t*-butyl phosphinites in pure form seemed to be permanently stable against the Arbuzov rearrangement $R_2POR' \rightarrow R_2\overset{\text{O}}{\text{P}}R'$; but with methyl iodide as a catalyst the *t*-butyl ester isomerized easily to form $(CF_3)_2\overset{\text{O}}{\text{P}}C_4H_9$, instead of converting to $(CF_3)_2\overset{\text{O}}{\text{P}}CH_3$ and C_4H_9I in typical Arbuzov manner. It was noted also that $(CF_3)_2POCH_3$ in the presence of methyl iodide could be forced to isomerize only at elevated temperatures and pressures. It is supposed that the relative ease of moving a *t*-butyl group from oxygen to phosphorus is in some way related to the relatively low energy required to detach a $t\text{-}C_4H_9^+$ group in the stabilized $(CH_3)_3C^+$ planar form,[8] but the catalytic function of the methyl iodide is not obvious.

In one experiment 0.515 mmole of $(CF_3)_2POC_4H_9$ and 0.516 mmole of CH_3I were heated together in a small sealed tube for 2 hr. at 70–80°. The mixture now was resolved into three fractions: 0.513 mmole of CH_3I (99.4% recovery, by passage through a high-vacuum trap at −78°; mol. wt. 141.6 *vs.* calcd. 141.9), 0.0777 mmole of $(CF_3)_2POC_4H_9$ (15.1% recovery, by passage through a trap at −30°; vapor tension 6.8 mm. at 0°, as calcd.), and 0.400 mmole of the less volatile isomeric phosphine oxide (77.7% yield; trapped at −30°), having mol. wt. 242.0, as calcd.

A 0.797 mmole sample of $(CF_3)_2POCH_3$ with 0.803 mmole of CH_3I in a 5 ml. sealed tube (ensuring the presence of a liquid phase) was heated for 22 hr. at 130° without appreciable change. During a further 196 hr. period at 130°, the extent of the isomerization was 3.8%. Continued heating for 144 hr. at 148° brought the yield of the isomeric phosphine oxide to 19.5 mg. (0.0975 mmole), representing 12.2%

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[7] H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 380 (1959).

[8] V. Mark, *Tetrahedron Letters*, 298 (1961), has shown that such relatively easy detachment of $(CH_3)_3C^+$ occurs also in the alkylation of hexachlorocyclopentadiene by $P(OR)_3$.

conversion. The phosphine oxide was identified by comparison with a sample made by an independent synthesis, as next described.

Characterization of the Phosphine Oxides.—The independent synthesis of methyl-bis-(trifluoromethyl)-phosphine oxide was done by the reaction (16 hr. at 80°) between 1.246 mmoles of dry HgO and 1.557 mmoles of $CH_3P(CF_3)_2$, the latter having been made in these Laboratories by Dr. K. K. Joshi, using $(CF_3)_2PI$ with $Zn(CH_3)_2$. The yield of the desired phosphine oxide was 1.10 mmoles, representing 97.5% of the consumed $CH_3P(CF_3)_2$. A trace of a sublimable solid probably was $Hg(CF_3)_2$, the low yield of which contrasts with its major formation from $(CF_3)_3P$ with HgO.[9] Further heating of the phosphine oxide with the residues led to no change, indicating no tendency for the reverse-Arbuzov isomerism which was observed for $(CF_3)_2\overset{H}{P}O$. Indeed, one would expect to remove a fluorocarbon group from phosphorus far more easily than to detach a hydrocarbon group.

The phosphine oxide $(CF_3)_2\overset{O}{P}CH_3$ was easily purified by high-vacuum fractional condensation and melted in the range −27.0 to −26.8°. Its formula was confirmed by the molecular weight (201.2 *vs.* calcd. 200.0) and by an infrared spectrum which showed a sharp P=O stretching band at 1320 cm.$^{-1}$. Its vapor tensions, shown with the equation in Table VII, indicated the normal b.p. as 129.7° and the Trouton constant as 20.6 cal./deg. mole.

TABLE VII

VAPOR TENSIONS OF LIQUID $(CF_3)_2\overset{O}{P}CH_3$

$(\log P_{mm.} = 8.7837 + 1.75 \log T - 0.00836T - 2858/T)$

t (°C.)	0.00	15.8	29.5	40.1	44.6	50.2	59.5
$P_{mm.}$ (obsd.)	2.01	6.08	14.24	25.8	32.6	43.2$_5$	66.5
$P_{mm.}$ (calcd.)	2.00	6.08	14.36	25.7	32.5	43.0$_5$	66.8

The vapor tensions of the purified sample of $(CF_3)_2\overset{O}{P}C_4H_9$ (from the isomerization reaction) are presented in Table VIII, with an equation which gives the normal b.p. as 177° and the Trouton constant as 23.4 cal./deg.mole. With a normal Trouton constant (21.0) the b.p. estimate would be nearer to 185°.

TABLE VIII

VAPOR TENSIONS OF LIQUID $(CF_3)_2\overset{O}{P}C_4H_9$

$(\log P_{mm.} = 7.9940 - 2302/T)$

t (°C.)	0.00	13.8	25.0	35.5	43.3	49.9	78.1
$P_{mm.}$ (obsd.)	0.37	0.94	1.88	3.43	5.24	7.39	27.6
$P_{mm.}$ (calcd.)	0.37	0.94	1.88	3.43	5.25	7.39	27.6

The alkaline hydrolysis of this phosphine oxide during 65 hr. at 100° gave only 1.38HCF$_3$ per mole. Such slow HCF_3 formation from CF$_3$-phosphines having a P-hydrocarbon linkage has been noticed before,[10] and the terminal P=O bond also may have some inhibiting effect. This oxygen atom seems to have little base action, for the compound failed to form any adduct with boron trifluoride. Presumably the lone-pair electrons are far more effectively delocalized toward phosphorus than in the analogous phosphine oxide $(CH_3)_3PO$, which holds BF_3 fairly well.[11]

The Phosphinic Acid Halides.—The phosphinyl chloride $(CF_3)_2\overset{O}{P}Cl$ was formed by a direct chlorination of the diphosphoxane in a sealed tube (80 hr. at −78° and 16 hr. at 80°). The products were isolated by high-vacuum fractional condensation; empirical equation: $0.540(CF_3)_2POP(CF_3)_2 + 0.540Cl_2 \rightarrow 0.513(CF_3)_2\overset{O}{P}Cl + 0.527(CF_3)_2PCl$. The formula $(CF_3)_2\overset{O}{P}Cl$ was demonstrated by this virtually quantitative process, taken with the mol. wt. (220.4 *vs.* calcd. 220.5) and an infrared spectrum (Table XIII) indicating purity. This spectrum also shows P=O and P–Cl bonds, and the right multiplicity of C–F stretching to show a $(CF_3)_2P$ group. The hydrolysis of a 0.265 mmole sample (2 ml. of 1% NaOH, 36 hr. at 100°) gave 0.258 mmole of HCF_3, in accord with removal of half of the CF$_3$ groups as HCF$_3$ from $(CF_3)_2POOH$.[6]

The m.p. of this phosphinyl chloride could not be observed because of its strong tendency to supercool. Its vapor tensions are shown with an equation in Table IX. The extrapolated b.p. is 52.6° and the Trouton constant 20.9 cal./deg. mole.

TABLE IX

VAPOR TENSIONS AT LIQUID $(CF_3)_2\overset{O}{P}Cl$

$(\log P_{mm.} = 6.8443 + 1.75 \log T - 0.00700T - 1980/T)$

t (°C.)	−45.0	−30.9	−24.1	0.0	12.5	20.4
$P_{mm.}$ (obsd.)	5.1	14.1	22.1	90.5	162.8	230.3
$P_{mm.}$ (calcd.)	5.0	14.1	22.1	88.6	162.6	230.5

The phosphinyl bromide $(CF_3)_2\overset{O}{P}Br$ was obtained as the most intelligible result of an investigation of the action of bromine on the *t*-butyl phosphine oxide $(CF_3)_2\overset{O}{P}C_4H_9$. There was no cleavage of CF$_3$ groups from phosphorus (such as occurs when CF$_3$-phosphines are attacked by bromine),[12] presumably because the formally pentavalent phosphorus could not receive bromine in order to initiate such a reaction. Instead, there was some bromination of C–H bonds when a mixture of 0.1632 mmole of the phosphine oxide and 0.949 mmole of bromine was heated in a sealed tube for 20 hr. at 100° (forming 0.340 mmole of HBr), and then for a further six days at 130°. The yield of HBr now was 0.611 mmole (total) and a non-volatile black tar had formed. The yield of $(CF_3)_2\overset{O}{P}Br$ amounted to 0.0844 mmole, or 51.7%. It was purified by shaking with mercury, followed by a slow high-vacuum fractional condensation through a trap at −78°.

The melting point of the phosphinyl bromide was observed as −35.5 ± 0.3°. Its vapor tensions (given with the equation in Table X) indicated the normal b.p. to be 78.3° and the Trouton constant 21.4 cal./deg. mole. The molecular formula was confirmed by the molecular weight (264.3 *vs.* calcd. 264.9) and by an alkaline hydrolysis of the 0.0844 mmole sample to give 0.086 meq. of Br$^-$ and 0.0834 mmole of HCF$_3$. The infrared spectrum showed the P=O stretching mode at 1312 cm.$^{-1}$.

TABLE X

VAPOR TENSIONS OF LIQUID $(CF_3)_2\overset{O}{P}Br$

$(\log P_{mm.} = 5.0476 + 1.75 \log T - 0.003833T - 1854/T)$

t (°C.)	−23.8	−5.3	0.0	6.1	10.2	16.5
$P_{mm.}$ (obsd.)	7.1	22.2	29.9	41.6	51.2	70.0
$P_{mm.}$ (calcd.)	7.1	22.2$_5$	29.9	41.5	51.2	69.9

The Reaction of the Diphosphoxane with Dimethylphosphine

The diphosphoxane $(CF_3)_2POP(CF_3)_2$ seems to be the only known member of its class, which doubtless will include many other stable R_2POPR_2 compounds in which R represents various higher fluorocarbon groups. However, there remains the

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(9) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 5759 (1960).

(10) L. R. Grant, Ph.D. Dissertation, University of Southern California Libraries, 1960, pp. 36, 60 and 67; *cf.* also R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3880 (1957).

(11) A. B. Burg and W. M. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951).

(12) A. B. Burg and J. E. Griffiths, *ibid.*, **82**, 3514 (1960).

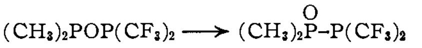
large question whether there can be stable diphosphoxanes in which some of the R groups are considerably less electronegative. As an initial step toward answering this question, we have tried the action of dimethylphosphine on the diphosphoxane, seeking to obtain $(CH_3)_2POP(CF_3)_2$ either by the following series of reactions (all analogous to effects already here described), or by any other sequence leading to the same result.

$$(CF_3)_2POP(CF_3)_2 + (CH_3)_2PH \longrightarrow (CF_3)_2POP(CF_3)_2\cdot(CH_3)_2PH \quad (1)$$

$$\longrightarrow (CF_3)_2POH + (CH_3)_2PP(CF_3)_2 \quad (2)$$

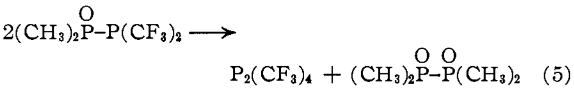
$$\longrightarrow (CF_3)_2PH + (CH_3)_2POP(CF_3)_2 \quad (3)$$

However, the desired unsymmetrical diphosphoxane would conform to the type $(CH_3)_2POR$, where R = $P(CF_3)_2$, and so might be very unstable in the sense of the Arbuzov isomerization:



$$(CH_3)_2POP(CF_3)_2 \longrightarrow (CH_3)_2\overset{O}{P}\text{–}P(CF_3)_2 \quad (4)$$

Then the biphosphine monoxide could well disproportionate:



$$2(CH_3)_2\overset{O}{P}\text{–}P(CF_3)_2 \longrightarrow P_2(CF_3)_4 + (CH_3)_2\overset{O}{P}\text{–}\overset{O}{P}(CH_3)_2 \quad (5)$$

Finally, the whole process would be complicated by the phosphinolytic redistribution

$$(CF_3)_2PP(CF_3)_2 + (CH_3)_2PH \longrightarrow (CF_3)_2PH + (CH_3)_2PP(CF_3)_2 \quad (6)$$

The sequence of equations (1–5) serves as an argument for the expectation of the products actually observed, although it does not necessarily describe the true or exclusive mechanism of a course of events which might occur more easily otherwise, or through intermediate stages not here indicated. Equation (1) is like the formation of the trimethylamine adduct, while (2) would be a normal continuation of an S_N2 cleavage. Equation (3) is predictable from the known cleavage of $(CH_3)_2P$-$P(CF_3)_2$ by HCl and by water,[13] whereby a proton always attaches to the $(CF_3)_2P$ moiety. The isomerization (4) would be aided by the high base strength of the $(CH_3)_2P$ group, and the disproportionation (5) should lead to stronger P–P bonding. Reaction (6) is closely analogous to the alcoholytic cleavages of $P_2(CF_3)_4$, whereby the phosphinous esters were made.

The Actual Experiments.—The reaction of $(CH_3)_2PH$ with $(CF_3)_2POP(CF_3)_2$ was tried in sealed tubes, first directly at 25° during 14 hr., whereas in the second experiment the mixture was warmed slowly from −78° before standing 4 days at 25°. The results are summarized in Table XI.

TABLE XI

THE $(CH_3)_2PH$–$(CF_3)_2POP(CF_3)_2$ REACTION

Reactants (mmole)		Recovered	Products (mmole)			
Me_2-PH	$(CF_3)_2$-POP-$(CF_3)_2$	Me_2PH (mmole)	$(CF_3)_2$-PH	$P_2(CF_3)_4$	Me_2P-$P(CF_3)_2$	$Me_4P_2O_2$
1.19	0.722	0.15	1.005	0.011[a]	0.337[a]	0.386[b]
0.508	0.512	nil	0.534	0.183[a]	0.064[a]	0.29[b]

[a] Estimated from mol. wt. of mixture; components proved by distinctive infrared and ultraviolet spectra; *cf.* ref. 13. [b] Calcd. as total weight of the sublimable residue.

Both of these experiments deviate from quantitative recovery of each group present in the original mixture; for example in the first experiment the listed products are short by 0.08 mmole of $(CF_3)_2P$ groups and 0.035 mg. atom of H but show excesses of 0.07 mmole of $(CH_3)_2P$ groups and 0.05 mg. atom of oxygen. One reason might be minor side reactions; another could be the difficulty of estimating the proportions of the diphosphines solely by the mol. wt. of the mixtures. However, the spectroscopic identification of these diphosphines was not doubtful, and the $(CH_3)_2P$-$P(CF_3)_2$ was further recognized by the approach toward its known m.p. and vapor tensions[13] as the more volatile $P_2(CF_3)_4$ was gradually removed by repeated high-vacuum fractional condensation.

The stoichiometry of these two experiments taken together would seem adequate to establish the empirical formula of the least volatile product as $[(CH_3)_2PO]_x$ if some small allowance is made for the missing $(CF_3)_2P$ material as part of the residue. Nearly all of this residue could be sublimed under high vacuum at 100°, and the purity of the sublimate was indicated by its sharp melting range: for both samples, 132.5–132.7°. It was strictly inert toward pure oxygen even above the m.p., showing that its phosphorus all must be pentavalent. Thus the most reasonable molecular formula would be that of the diphosphine dioxide $(CH_3)_2\overset{O}{P}\text{–}\overset{O}{P}(CH_3)_2$. A higher polymer (such as a cage-type tetramer) is eliminated by the infrared spectrum, showing an intense P=O stretching band at 1220 cm.$^{-1}$ but no band assignable to a P–O–P linkage. The usual CH_3 bands were present, and C–F stretching was absent.

Intermediate Processes.—A separate experiment showed that the same over-all results are obtained if one begins with reaction (3) instead of (1). A mixture containing 0.108 mmole of $(CH_3)_2PP(CF_3)_2$ and about 0.13 mmole of $(CF_3)_2POH$ showed a gradual formation (16 hr., 25°) of a white solid appearing to be the same diphosphine dioxide: m.p. 132.5–132.7°; same manner of sublimation and same crystalline appearance. Also found were 0.14 mmole of $(CF_3)_2PH$ and 0.09 mmole of vapor which was spectroscopically identified as $P_2(CF_3)_4$ with a trace of $(CH_3)_2PP(CF_3)_2$.

Reaction (6) also was tried directly, in a sealed tube during 3 days at 25°, and proved to be virtually quantitative: $0.323(CH_3)_2PH + 0.324P_2(CF_3)_4 \rightarrow 0.326(CF_3)_2PH + 0.315(CH_3)_2PP(CF_3)_2$. Both products were easily isolated as pure samples agreeing well with the known vapor tensions.

Infrared Spectra

The frequency assignments for the vibrational modes of the trifluoromethyl halides[14,15] recently have been successfully extended to include a variety of compounds containing the CF_3S-group.[16] Similar spectra are found for $(CF_3)_2P$- compounds, so that the synthesis of a number of closely related compounds containing the $(CF_3)_2PO$ group affords an opportunity to extend further the existing correlations of group frequencies in CF_3–P compounds. Moreover, there has been such a lack of infrared spectral data for oxyphosphines having

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(13) L. R. Grant and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 1834 (1962).

(14) E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

(15) W. F. Edgell and C. E. May, *J. Chem. Phys.*, **22**, 1808 (1954).

(16) S. N. Nabi and N. Sheppard, *J. Chem. Soc.*, 3439 (1959).

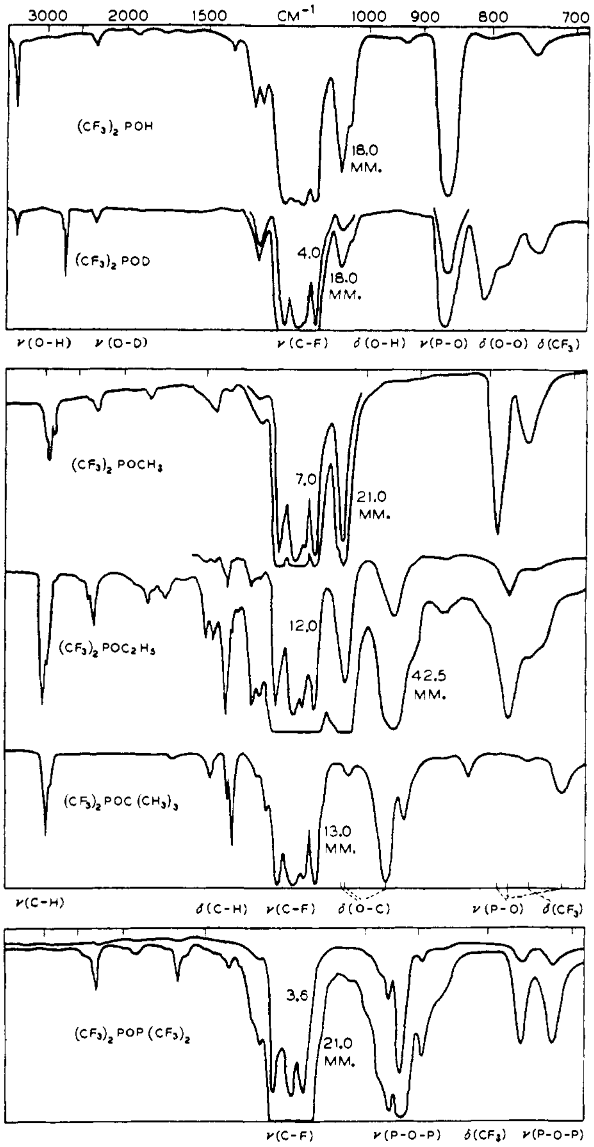

Fig. 1.—Infrared spectra of $(CF_3)_2P$-O-R compounds, corresponding to Table XII. The numbers within the charts refer to pressures (mm.) of the vapors in the 71 mm. cell.

a reasonably isolated P-O single bond, that such a correlation seems quite valuable.

The spectra of such compounds were obtained either with a Perkin-Elmer Infracord instrument with sodium chloride optics, or with a Perkin-Elmer Model 13 spectrophotometer, permitting extension into the potassium bromide region. All samples were in the vapor phase, in a cell with KBr windows 71 mm. apart. The pressures in mm. are shown by the numbers accompanying the curves in Figs. 1 and 2. These tracings from the Infracord charts show some trends of frequency due to varying substituents, while some group frequencies remain almost constant. The full data for the oxyphosphine derivatives are given with the probable assignments in Table XII, while the phosphinyl halides and phosphine oxides (having the P=O bond in common) are covered by Table XIII. This

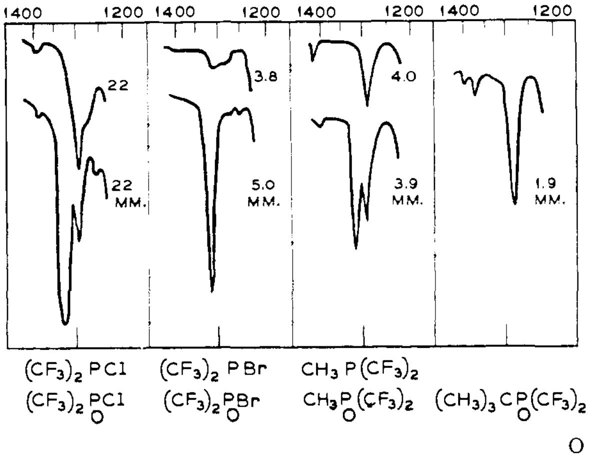

Fig. 2.—Comparison spectra of $(CF_3)_2P$- and $(CF_3)_2P$-compounds in the P=O stretching region. The numbers at the top represent frequencies (cm.$^{-1}$) while those within the chart indicate pressures (mm.) of the vapors in the 71-mm. cell.

table omits frequencies above 1500 cm.$^{-1}$, as these represent only the usual C–H stretching modes and the persistent C–F stretching overtones or combinations.

Vibrations of the $(CF_3)_2P$ Group.—The C–F vibrational modes seem not to be much affected by the P–O or P=O bond, for there is good correlation with compounds containing no oxygen. In the C–F stretching region (1100–1225 cm.$^{-1}$) one usually finds four very intense bands, one of which may be difficult to observe when it occurs as a shoulder (*e.g.* at 1135 cm.$^{-1}$ in the methyl phosphinite) on the central C–F band, as shown in Fig. 1. In the P=O compounds the C–F bands on the lower-frequency side are less intense. The CF_3-deformation modes are easily assigned by analogy with similar situations.[5,16] For the oxyphosphines the symmetric deformation mode occurs uniformly near 745 cm.$^{-1}$, but it is mostly a little higher for the P=O compounds. Also the asymmetric deformation mode appears uniformly near 570 cm.$^{-1}$ for the oxyphosphines but varies more among the P=O compounds.

In alkyl phosphines the P–C stretching vibration occurs in the 650–750 cm.$^{-1}$ range,[17] but the analogous modes for $(CF_3)_2P$- and CF_3S- compounds appear below 500 cm.$^{-1}$.[16] Hence the C–P–C asymmetric stretching vibration evidently is represented by the strong band near 460 cm.$^{-1}$ for three $(CF_3)_2PO$- compounds, but at 495 and 498 cm.$^{-1}$ for two $(CF_3)_2P$=O compounds. The corresponding C–P–C symmetric stretching modes, which are expected to be weaker and at lower frequencies, would explain the weak bands near 410 and at 430 cm.$^{-1}$, respectively. The P–C bending modes must occur at still lower frequencies, beyond the range of our instruments.

Vibrations of the P–O–R Linkages.—The good agreement of the six $(CF_3)_2P$–O–R compounds in regard to $(CF_3)_2P$ group modes implied that the assignments were trustworthy, so that the task of interpreting the remaining bands became rela-

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(17) M. Halman, *Spectrochim. Acta*, **16**, 407 (1960), and other references there cited.

TABLE XII

INFRARED SPECTRA OF $(CF_3)_2P–O–R$ COMPOUNDS[a]

Assignment	H	D	CH_3	C_2H_5	t-C_4H_9	$P(CF_3)_2$
O–H, ν	3620s	3620vw	...	...	...	...
C–H, ν	...	...	...	3000m	3008s	...
	...	...	2935m	2915m	...	...
	...	...	2850w	2860vw	...	...
O–D, ν	...	2680vw	...	...	...	...
	...	2640m	...	...	...	...
c	2365vw	...	2365vw	2350vw	2385vw	...
c	2270vw	2270vw	...	2280vw	...	2240vw
c	...	...	...	1820vw	...	...
c	...	...	...	1710vw	1655vw	1630vw
CH_3, δ-a	...	...	1475w	1490w	1475w	...
	...	...	1458w	1455w	...	...
CH_3, δ-e	...	...	1380w	1400m	1395w	...
	...	...	...	...	1375w	...
c	1305w	1295w	...	1305m	...	...
c	1282w	...	1280w	1275w	1255w	1280w
C–F, ν	1203vs	1210vs	1222vs	1225vs	1218vs	1222vs
	1170vs	1170vs	1172vs	1175vs	1172vs	1181vs
	1137vs	1140vs	1135vs	1145vs	1135vs	1140vs
	1103vs	1120vs	1105vs	1115vs	1103vs	...
O–H, δ	1054s	1055w	...	...	...	...
	1033s,sh	1040w,sh	...	...	...	...
C–O, ν	...	...	1044vs	1040vs	952s	...
C–C, ν; CH_3–ρ	...	...	...	939m	917m	...
P–O–P, ν-a	...	...	...	...	...	950w
	...	...	...	...	...	925s
	...	...	...	...	...	885w
C–C, ν ?	...	...	...	860vw	850vw	...
t-C_4H_9 effect ?	...	...	...	...	819vw	...
	...	...	...	...	767vw	...
P–O, ν	854vs	858vs	780s	770m	705w	...
O–D, δ	...	805ms	...	...	...	...
	...	780m,sh	...	...	...	...
CF_3, δ-e	743w	742w	745m	745m,sh	744w	745w
P–O–P, ν-e	...	...	...	...	...	715w
CF_3, δ-a	572m	ni	574m	ni	568ms	ni
	546w		549w		550w	
C–C, δ	...	...	...	ni	489w	ni
C–P–C, ν-a	465	ni	459s	ni	458s	ni
C–P–C, ν-e ?	407vw	ni	407vw	ni	415vw	ni

[a] s = strong, m = medium, w = weak, v = very, sh = shoulder, c = combination or overtone, ν = stretching, δ = deformation, ρ = rocking, a = asymmetric, e = symmetric, ni = not investigated. Frequencies (cm.$^{-1}$) are listed under R groups designating the respective compounds.

tively easy. For $(CF_3)_2POH$ the decrease of frequency from 3620 to 2640 cm.$^{-1}$ on deuteriation left no doubt of the O–H stretching mode, which could scarcely be misinterpreted anyway. Similarly, 1054 *vs.* 805 cm.$^{-1}$ would be normal for the O–H *vs.* O–D bending vibrations. Thus the only remaining frequency, 854 cm.$^{-1}$ for $(CF_3)_2POH$ or 858 cm.$^{-1}$ for $(CF_3)_2POD$, must represent the P–O stretching vibration. For the diphosphoxane, a similar argument by elimination makes the identification of the P--O-P symmetric and asymmetric stretching modes quite certain. Since the asymmetric mode in this case is expected to have both a higher frequency and a higher intensity than the symmetric mode, the present result supports the argument for the 970–930 rather than the 710 cm.$^{-1}$ region for asymmetric stretching in the pyrophosphates.[18–20]

For the esters, the frequencies of the P–OR stretching vibrations show the expected decrease as O is weighted with heavier groups. Similarly, there is a sharp decrease in the C–O stretching frequency when R becomes t-butyl. In these esters the recognition of the C–H stretching and bending modes is routine; however, it is very difficult to distinguish the C–C stretching modes from C–CH_3 rocking, or possibly more complex modes in the case of the t-butyl group.

P=O Stretching and CF_3-Group Electronegativity.—The P=O stretching frequencies for the compounds indicated in Table XIII were relatively easy to identify on account of their high relative intensity and the availability of most of the related phosphines for comparison. Figure 2 shows three

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(18) E. D. Bergmann, U. Z. Littauer and S. Pinchas, *J. Chem. Soc.*, 847 (1952).

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, p. 318.

(20) B. Holmstedt and L. Larsson, *Acta Chem. Scand.*, **5**, 1179 (1951).

TABLE XIII

INFRARED SPECTRA OF $(CF_3)_2\overset{O}{P}-R$ COMPOUNDS[a]

Assignment	Cl	Br	CH_3	t-C_4H_9
CH_3, δ-a	...	...	1411vw	1470w
t-C_4H_9	...	...	...	1400vw
				1270s
P=O, ν	1330s	1312s	1316s	1282s
c	1295m	1250w	...	...
c or CH_3, δ-e	...	...	1295w	...
C–F, ν	1204vs	1202vs	1205vs	1197vs
	1143s	1162s	1180vs	1172vs
	1122m,sh	...	1135vs	1150s
	1098w	...	1098vw	1128s
...		1047w(?)		1026vw(?)
CH_3	...	...	887s	...
t-C_4H_9	...	...	...	812w
CF_3, δ-e	759m	753m	775m	745w
CH_3, ρ or P–CH_3, ν	...	...	732m	...
P–Cl, ν	615s	...	...	...
CF_3, δ-a	581sh		581sh	
	563s	ni	543m	ni
	536sh		...	
C–P–C, ν-a	498s	ni	495s	ni
C–P–C, ν-e (?)	...	ni	430m	ni

[a] All symbols are as in Table XII, and again the R groups (including Cl and Br) head the columns for the respective compounds.

comparisons in the pertinent range (1250–1350 cm.$^{-1}$); for the t-butyl phosphine oxide, however, the comparison could not be made for lack of the spectrum of the corresponding phosphine, t-C_4H_9-$P(CF_3)_2$.

The shift in the frequency of the P=O stretching band with substitution of groups or atoms on phosphorus has been used to calculate the effective electronegativity of the CF_3 group.[21] The result, 3.3 on the Pauling scale, seemed to be in the right range and its agreement with other spectral and thermochemical data also lent confidence. Thus we use the available data for POF_3, $POCl_3$, $POBr_3$ and $(CF_3)_3PO$ to derive the empirical equation $\nu = 918 + 41.3\Sigma x$ (where Σx is the sum of the electronegativity values for the groups attached to P=O and ν is the P=O stretching frequency) to determine the electronegativity of any group on phosphorus from the known values for the other groups. However, this equation was based upon compounds having C_{3v} symmetry and required testing for less symmetrical situations such as our new $(CF_3)_2P{=}O$ compounds, of symmetry no higher than C_s.

The calculated values shown in Table XIV are based upon the equation and our P=O stretching frequencies, using the accepted Pauling electronegativities for Cl and Br, and an x value for CH_3 calculated from the P=O stretching frequency in $(CH_3)_3PO$.[22]

TABLE XIV

CALCULATED ELECTRONEGATIVITIES OF THE CF_3 GROUP

Compound	$(CF_3)_2\overset{O}{P}Cl$	$(CF_3)_2\overset{O}{P}Br$	$(CF_3)_2\overset{O}{P}CH_3$
$\nu_{P=O}$ (cm.$^{-1}$)	1330	1312	1316
x calcd. for CF_3	3.5	3.4	3.6

Although these new electronegativity values for the CF_3 group, averaging 3.5, deviate appreciably from the value 3.3 given by Lagowski, the difference seems to be within the uncertainty of the electronegativity concept itself.[23]

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An Electron Impact Study of 1,1,1-Trifluoroethane, 1,1,1-Trifluoropropane and 3,3,3-Trifluoropropene[1]

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The appearance potentials of the major positive ions in the mass spectra of 1,1,1-trifluoroethane, 1,1,1-trifluoropropane and 3,3,3-trifluoropropene have been measured. The R–CF_3 bond dissociation energy and the heat of formation are reported for each compound. The various processes for dissociation under electron impact are discussed.

In recent years the chemistry of organic fluorine compounds has been studied extensively. However, our knowledge of the thermochemistry[3] of these compounds has been somewhat limited by the experimental difficulties associated with calorimetric work. Another means of obtaining thermodynamic data is the electron impact method, which can lead directly to such important properties as bond dissociation energies and heats of formation.[4] An electron impact study of 1,1,1-trifluoroethane, 1,1,1-trifluoropropane and 3,3,3-trifluoropropene, undertaken in order to determine the effect of the CF_3 group on the thermodynamic properties of hydrocarbons, is described in this paper. The only previous electron impact investigation of small partially fluorinated hydrocarbons, containing more than one carbon atom, involved 1,1,1-trifluoroethane and hexafluoroethane.[5]

Experimental

The appearance potentials were measured using a Consolidated Electrodynamics Corporation Model 21-103 C mass spectrometer, modified to allow magnetic scanning. The data were evaluated from semilog plots of the ionization efficiency curves[6] when parallelism with the standard curve

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[2] Postdoctoral Fellow, Harvard University.

[3] For a recent review see C. R. Patrick, "Advances in Fluorine Chemistry" (Eds. M. Stacey, J. C. Tatlow and A. G. Sharpe), **2**, 1 (1961), Butterworths, London.

[4] Mass spectrometry of fluorine compounds has recently been reviewed by J. R. Majer, *ibid.*, p. 55.

[5] V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Chem. Phys.*, **20**, 761 (1952).

[6] See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.