have values of ΔH^0_{vap} and ΔS^0_{vap} agreeing reasonably well with the Barclay–Butler equation.[18] Certainly ammonia and water both interact strongly with water and the present comparison suggests that $HgCl_2$ also does. In this connection, it is to be noted that Allen and Warhurst,[19] in their correlation with dielectric constant of the frequency of the Raman line associated with the symmetrical vibration of $HgCl_2$ in various solvents, did not feel compelled to suggest specific bonding between $HgCl_2$ and water; of the solvents they studied, only pyridine and dioxane were suggested to form bonds of appreciable strength with $HgCl_2$. Their results were, however, taken to indicate a stronger interaction of the polar Hg–Cl bonds with water than exists with many solvents of lower dielectric constants (*e.g.*, benzene, certain esters, certain alcohols, acetone and acetonitriles).

The Latimer and Jolly approach[10] to the prediction of ΔS^0 values for complex ion formation reactions has not been tested adequately for reactions involving charged ligands, for in such cases the manner in which the "charge effect" should be handled has not been solved. Latimer and Jolly consider the "charge effect" to be small, but the evidence they cite for this is marred by their consideration of reactions with $\Delta n \neq 0$. By combining the values of ΔS^0 for certain reactions studied in the present work and in the mercury(II)-bromide studies of Scaife and Tyrrell[9,20] one can check, using reactions with $\Delta n = 0$, the Latimer and Jolly prediction regarding reactions involving complexes with charged ligands but in which the value of ΔZ^2 is zero. These reactions are

$$Br^- + \frac{1}{a}\,HgCl_a{}^{+2-a} = Cl^- + \frac{1}{a}\,HgBr_a{}^{+2-a}$$

with $a = 2$, 3 and 4, and

$$I^- + {}^1/_4HgCl_4{}^= = Cl^- + {}^1/_4HgI_4{}^=$$

The Latimer and Jolly approach predicts ΔS^0 values of -3.3 e.u. for the bromide reactions and -7.4 e.u. for the iodide reaction.[21] The experimental values are -5.2, -4.2 and -4.2 e.u. for the bromide reactions with $a = 2$, 3 and 4, respectively, and -8.3 e.u. for the iodide reaction. The agreement is probably within the total uncertainty, that of the experimental values of ΔS^0 and of the experimentally determined quantities which went into the predicted values. (Since the value of ΔZ^2 for each reaction is zero, it is expected that the value of ΔS^0 will be approximately independent of I between $I = 0.5$ and $I = 0$.) The correlation is good enough in any case to suggest that the mercury(II)–bromide and mercury(II)–iodide species involved have the same coördination number as the corresponding mercury(II)–chloride species.[22]

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[18] Professor H. S. Frank pointed this out to us.

[19] G. Allen and E. Warhurst, *Trans. Faraday Soc.*, **54**, 1786 (1958).

[20] The values of ΔS^0 for reactions 3 and 4 in the bromide series at $I = 0.5$ M are -0.5 and ~ 0 e.u., respectively.

[21] In making the predictions, the entropy values used were: $\bar{S}^0_{Cl^-} = 13.2$, $\bar{S}^0_{Br^-} = 19.3$, $\bar{S}^0_{I^-} = 26.1$, $S_{Cl^-(bound)} = 8.1$, $S_{Br^-(bound)} = 10.9$ and $S_{I^-(bound)} = 13.6$ e.u. (These values were taken from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice–Hall, Inc., New York, N. Y., 1952).

[22] ADDED IN PROOF.—Scaife and Tyrrell[9] have suggested, however, that tribromomercury(II) ion is the tetrahedral species $Hg(OH_2)Br_3{}^-$

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, UNIVERSITY PARK, LOS ANGELES, CALIFORNIA]

Trifluoromethyl-bromo-phosphines and Phosphoranes[1]

BY ANTON B. BURG AND JAMES E. GRIFFITHS

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The removal of CF_3 groups from phosphorus(III) by the action of bromine is understood in terms of formation of the phosphoranes $(CF_3)_nPBr_{5-n}$, which lose CF_3Br in reverting to phosphorus(III) compounds. A number of intermediate and parallel processes are recognizable. The transfer of Br_2 from $(CF_3)_3PBr_2$ to $(CF_3)_2PBr$, from $(CF_3)_2PBr_3$ to CF_3PBr_2 and from CF_3PBr_4 to PBr_3 correlates with greater stability for phosphoranes having more Br and fewer CF_3 groups.

The cleavage of the P–CF_3 bond by halogens has been known for some time; for example the biphosphine $P_2(CF_3)_4$ heated with excess iodine or bromine eventually yields all of the CF_3 groups as CF_3I or CF_3Br, or $(CF_3)_3P$ with I_2 gives CF_3I, $(CF_3)_2PI$, CF_3PI_2 and PI_3.[2] However, these reactions have been carried on only at relatively high temperatures and little has been known of their intermediate stages.

Our initial studies of the $P_2(CF_3)_4$–Br_2 reaction indicated the formation of the phosphorane $(CF_3)_2PBr_3$ and suggested that the loss of CF_3Br from this and other phosphoranes might be the chief mechanism for removing the highly electronegative CF_3 group from its bond to phosphorus. This bromine reaction seemed best for further study, since iodophosphoranes cannot be prepared at convenient temperatures, if at all, and chlorophosphoranes tend to be either too stable—*e.g.*, CF_3PCl_4[3]—or explosive under certain conditions—*e.g.*, $(CF_3)_3PCl_2$.[2] However, the intermediate bromophosphoranes proved to be both recognizable and subject to decomposition under mild conditions.

The first step of the action of bromine upon $P_2(CF_3)_4$ is the virtually quantitative P–P bond cleavage

$$(CF_3)_2P\text{–}P(CF_3)_2 + Br_2 \longrightarrow 2(CF_3)_2PBr \qquad (1)$$

This is followed by the almost quantitative conver-

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-5435 (Subcontract No. 1) monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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

[3] W. Mahler and A. B. Burg, THIS JOURNAL, **80**, 6161 (1958).

sion of the $(CF_3)_2PBr$ to the phosphorane $(CF_3)_2PBr_3$ (m.p. 6.0–9.4°), which cannot be characterized quite satisfactorily on account of the slow decomposition

$$2(CF_3)_2PBr_3 \longrightarrow 2CF_3Br + PBr_3 + (CF_3)_2PBr \qquad (2)$$

A reasonable hypothesis concerning this decomposition, to account for the various experimental observations as well as the over-all stoichiometry, would be this set of component processes

$$(CF_3)_2PBr_3 \longrightarrow CF_3Br + CF_3PBr_2 \qquad (3)$$

$$(CF_3)_2PBr_3 + CF_3PBr_2 \longrightarrow (CF_3)_2PBr + CF_3PBr_4 \qquad (4)$$

$$CF_3PBr_4 \longrightarrow CF_3Br + PBr_3 \qquad (5)$$

complicated by

$$CF_3PBr_4 + PBr_3 \longrightarrow CF_3PBr_2 + PBr_5 \qquad (6)$$

$$PBr_5 \longrightarrow PBr_3 + Br_2 \qquad (7)$$

$$CF_3PBr_2 + Br_2 \longrightarrow CF_3PBr_4 \qquad (8)$$

Reactions (5), (6) and (8) were verified by individual experiments. The completion of reaction (7) above 65° has been demonstrated elsewhere.[4] Reactions (3) and (4) could not be separated: when (3) was tried, it supplied CF_3PBr_2 for the similarly rapid reaction (4), and when (4) was tried, the stoichiometry could be balanced only by assuming some occurrence of (3). It seems highly probable that (3) is the first step in the over-all process (2); the alternative disproportionation

$$2(CF_3)_2PBr_3 \longrightarrow (CF_3)_3PBr_2 + CF_3PBr_4 \qquad (9)$$

is not a probable part of the process, for $(CF_3)_3PBr_2$ decomposes more easily than $(CF_3)_2PBr_3$, and would have produced $(CF_3)_3P$, which could not be found among the products. Certainly process (2) is well represented by the sum of reactions (3), (4) and (5); and it seems that the complicating effect of (6) (which we have found to be complete in 30 min. at 35°) is overcome by (7), occurring appreciably only at higher temperatures.[4]

The foregoing discussion suggests also a reasonable scheme of reactions whereby a halogen acts upon $(CF_3)_3P$ to form $(CF_3)_2PX$ and CF_3PX_2 compounds. In particular, the action of bromine on tris-(trifluoromethyl)-phosphine can be represented by the sequence

$$4(CF_3)_3P + 4Br_2 \longrightarrow 4(CF_3)_3PBr_2 \qquad (10)$$

$$2(CF_3)_3PBr_2 \longrightarrow 2(CF_3)_3P + 2Br_2 \qquad (11)$$

$$2(CF_3)_3PBr_2 \longrightarrow 2CF_3Br + 2(CF_3)_2PBr \qquad (12)$$

$$2(CF_3)_2PBr + 2Br_2 \longrightarrow 2(CF_3)_2PBr_3 \qquad (13)$$

$$2(CF_3)_2PBr_3 \longrightarrow 2CF_3Br + PBr_3 + (CF_3)_2PBr \qquad (2)$$

Thus some of the $(CF_3)_3P$ would be regained by reaction (11), which would supply bromine for reaction (13). The formation of CF_3PBr_2 can be ascribed to reaction (3). The elimination of CF_3Br from $(CF_3)_3PBr_2$ (eq. 12) was not proved directly, but it seems more probable than the disproportionation of $(CF_3)_3PBr_2$, in the light of arguments already presented.

It is interesting that reactions (4) and (6) and the sum of (11) and (13) all imply that the trifluoromethylbromophosphoranes are stabler with more Br and less CF_3. Evidently the P–Br bond in $(CF_3)_nPBr_{5-n}$ becomes weaker with increasing *n*. In fact, reaction (10) could be recognized only by the complete fading out of the bromine color, whereas the more brominated phosphoranes could be obtained as more distinctly recognizable compounds.

A primary reason for the weakening of P–Br bonding by CF_3 groups probably is steric interference; more subtle effects such as different hybridization for maximum overlap in P–CF_3 *vs.* P–Br bonds, or the induction of greater electronegativity for P, so that the P–Br bonds become less polar, are difficult to evaluate.

The above discussion is supported by the following experimental details.

Apparatus, Techniques and Materials

Various experiments involving mercury-reactive substances were performed in a mercury-free high-vacuum manifold, with the stopcocks lubricated by a chloro-fluorocarbon grease.[5] When mercury manometers could not be used directly, pressure measurements were done by means of a null-indicating Pyrex-glass sickle gauge,[6] placed with the pointer vertically upward so that the sample could be completely immersed in a constant-temperature bath for vapor tensions above room temperature. Above −25°, temperatures were measured by mercury-in-glass thermometers, and for lower temperatures the appropriate vapor-tension thermometers[7] were employed.

Infrared absorption spectra were recorded by means of a Perkin–Elmer Infracord instrument with sodium chloride optics, using a gas-cell 71 mm. long and having potassium bromide windows fastened by Apiezon W wax.

Bromine was purified by repeated contact with P_4O_{10} and high-vacuum distillation through one trap at −45° to another at −78°. The CF_3–P–I phosphines were made by known methods,[2,8] as was also the biphosphine $P_2(CF_3)_4$.[2] This showed 22.0 mm. pressure at 0°, as found earlier by W. Mahler in these Laboratories.

The Compound Bis-(trifluoromethyl)-bromophosphine

Synthesis.—A mixture of 0.306 mmole of $P_2(CF_3)_4$ with 0.227 mmole of Br_2 reacted at room temperature, with immediate fading of the bromine color. For certain completion of the reaction, the mixture was heated for 40 hr. in a sealed tube at 90° and then resolved by high-vacuum fractional condensation. The resulting 0.435 mmole of $(CF_3)_2PBr$ (mol. wt. 249.8; calcd., 248.9) represented 96% of the Br_2. It condensed out at −105°, having passed a trap at −78°, which retained the unused $P_2(CF_3)_4$ (21.9 mm. at 0°; 0.072 mmole of calcd. 0.079). The only other component was 0.016 mmole of CF_3Br (mol. wt. 145; calcd., 148.6).

If a large excess of bromine is used for reaction with $P_2(CF_3)_4$, all CF_3 groups are removed at temperatures as low as 90°. The experiment was not tried directly, but the conclusion can be argued from the above synthesis and reactions (2) and (13). With a Br_2:$P_2(CF_3)_4$ ratio between 2 and 1, the products are more various, as described later.

An alternative synthesis was by the reaction of $(CF_3)_2PI$ with silver bromide, 10 g. of which was kept in a sealed tube with 11.28 mmoles of $(CF_3)_2PI$ (44.0 mm. at 0°, in accord with the known value[8]) for 96 hr. The yield of $(CF_3)_2PBr$ was 11.03 mmoles, or 97.8%. However, it was not possible to remove a trace of unused $(CF_3)_2PI$, which was detectable by its action upon mercury. The pure sample of $(CF_3)_2PBr$, made by the cleavage of $P_2(CF_3)_4$, proved to be inert toward mercury at 25° and showed 140.0 mm. pressure at 0°. The sample from the AgBr–$(CF_3)_2PI$ reaction showed 132.3 mm. pressure at 0°.

Confirmation of the Formula.—Alkaline hydrolysis of 100.7 mg. of the product gave 0.811 mmole of HCF_3 (calcd., 0.810; mol. wt. 70.0, as calcd.; vapor tension 93.5 mm. at −111.6° *vs.* calcd. 94.0 mm.). The gas-phase mol. wt. was determined as 248.9, exactly as calcd. for $(CF_3)_2PBr$.

Volatility.—The tensiometrically uniform product from the bromine-cleavage of $P_2(CF_3)_4$ had the vapor-tension

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[4] G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 3732 (1958).

[5] Halocarbon Stop-Cock Grease, from Halocarbon Products Corporation, Hackensack, New Jersey.

[6] T. E. Phipps, M. L. Spealman and T. G. Cooke, *J. Chem. Ed.*, **12**, 321 (1935).

[7] A. Stock, *Z. Elektrochem.*, **29**, 354 (1923).

[8] A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, THIS JOURNAL, **79**, 247 (1957).

values shown in Table I. These determined the equation log $p_{\text{mm.}} = 5.8940 - 0.00566\ T + 1.75 \log T - 1766.5/T$, giving the normal b.p. as 42.2° and the Trouton constant as 21.0 cal./deg. mole. The m.p. could not be observed because the material formed a glass at low temperatures.

TABLE I

VAPOR TENSIONS OF LIQUID $(CF_3)_2PBr$

t (°C.)	$p_{\text{mm.}}$ (obsd.)	$p_{\text{mm.}}$ (calcd.)	t	p (obsd.)	p (calcd.)
−45.6	9.86	9.89	0.0	140.0	140.0
−31.0	25.23	25.23	7.9	200.9	201.6
−23.2	39.7	40.6	14.8	270.9	271.7
−10.3	84.5	83.5	23.4	382.2	382.2

The Compound Trifluoromethyl-dibromophosphine

Synthesis.—A 4.92 mmole sample of CF_3PI_2 (slightly contaminated with iodine) was shaken periodically with silver bromide (8.0 g.) in a sealed tube at room temperature, during one week. The product was subjected to high-vacuum fractional condensation, passing a trap at −35° and condensing at −78°. The yield was 4.55 mmoles (92.5%).

Confirmation of Formula.—The mol. wt. of the product was determined in the vapor phase, as 260.0 (calcd., 259.8). The alkaline hydrolysis of an 89.1 mg. sample gave 0.347 mmole of authenticated HCF_3 (calcd., 0.343 mmole). The infrared spectrum (see Table III) corresponded to expectations for CF_3PBr_2.

Volatility.—The vapor tensions of a tensiometrically uniform sample of CF_3PBr_2 were obtained by means of the sickle gauge. The results, shown in Table II, determined the equation log $p_{\text{mm.}} = 3.8579 - 0.00206\ T + 1.75 \log T - 1694.74/T$, according to which the normal b.p. would be 86.7° and the Trouton constant 21.7 cal./deg. mole.

TABLE II

VAPOR TENSIONS OF LIQUID CF_3PBr_2

t (°C.)	$p_{\text{mm.}}$ (obsd.)	$p_{\text{mm.}}$ (calcd.)	t	p (obsd.)	p (calcd.)
−23.2	5.8	5.8	14.2	47.2	46.8
− 9.7	12.9	13.1	22.8	70.2	70.3
0.0	22.6	22.6	30.4	98.5	98.5
6.7	32.3	32.2	37.3	131.5	131.9

This substance also formed a glass at low temperatures, so that the m.p. could not be observed.

Infrared Spectra

The infrared spectra of $(CF_3)_2PBr$ and CF_3PBr_2 in the sodium-chloride region are summarized in Table III. They are similar to those of other CF_3–P-halides of P(III), conforming to the general observation that the frequencies of C–F stretching vibrations in CF_3–P compounds are split into $n + 1$ bands, where n is the number of CF_3 groups on each phosphorus atom.[2,3]

TABLE III

VIBRATION FREQUENCIES OF $(CF_3)_2PBr$ AND CF_3PBr_2

$(CF_3)_2PBr$		CF_3PBr_2	
Freq. (cm.$^{-1}$)	Assignment	Freq. (cm.$^{-1}$)	Assignment
2275 w.	2 × 1145	2265 vw.	2 × 1135
1425 vw.	overtones or combinations	1410 vw.	Overtones or combinations
1315 s.		1300 m.	
1282 s.		1270 w.	
1220 vs.	C–F stretching	1190 vs.	C–F stretching
1177 vs.		1135 vs.	
1145 vs.			
755 s.	C–F bending	745 s.	C–F bending
728 vw.			

The Trifluoromethyl-Bromo-Phosphoranes

The Tribromophosphorane; Reaction (2).—An equimolar mixture (1.03 mmoles each) of $(CF_3)_2PBr$ and Br_2 was warmed to room temperature, with immediate fading of the bromine color. The product was subjected to high-vacuum fractional condensation at −55° (removing 0.08 mmole of CF_3Br) and then appeared as a white solid melting to a pale yellow liquid in the range 6.0–9.4°. It was not appreciably volatile at 0°. A 0.414 mmole sample of this product, presumed to be $(CF_3)_2PBr_3$, decomposed slowly at room temperature and completely at 90°, with transient appearance of two solids. The first of these had the m.p. (28°) and bright orange color of CF_3PBr_4. The second, having the lemon-yellow color of PBr_5 (per reaction 6) disappeared with rising temperature, to form a bromine-like vapor.

After the decomposition was complete (as judged by the absence of color) high-vacuum fractional condensation was used to isolate and purify the products, which could be identified by their molecular weights. The yields and molecular weights are shown in relation to equation (2) as

	$2(CF_3)_2PBr_3 \longrightarrow$	$2CF_3Br\ +$	$PBr_3\ +$	$(CF_3)_2PBr$
Amount (mmole)	0.414	0.412	0.188	0.210
Mol. wt. (obsd.)	...	148.7	271.7	252.5
(calcd.)	...	148.9	270.7	248.9

The 9% deficiency in the yield of PBr_3 is attributed to its tendency to dissolve in the halocarbon stopcock grease—an effect which could not be entirely overcome. For further identification its vapor tension was measured as 4.0 mm. at 29° (calcd. from literature equations, 3.9 mm.).

The Tetrabromophosphorane; Reaction (5).—A bright-orange-colored solid, melting almost completely in the range 28.3–28.5°, was formed from 0.537 mmole of CF_3PBr_2 and 0.406 mmole of Br_2, slowly warmed together from −196°. No free Br_2 could be recovered by distillation at −64° but it was possible to isolate 0.075 mmole of CF_3Br and 0.128 mmole of CF_3PBr_2 (mol. wt. 258.8; calcd., 259.8), leaving a product having the composition of 0.40 mmole of CF_3PBr_4. On heating for 30 min. at 90°, the sample became colorless; and after 16 hr. at that temperature, the products were separated and measured. The over-all process (corrected for the initial excess of CF_3PBr_2) is expressed by the following equation, with quantities and evidences of identity.

	$CF_3PBr_2\ +$	$Br_2 \longrightarrow$	$CF_3PBr_4 \longrightarrow$	$CF_3Br\ +$	PBr_3
Amount (mmole)	0.402	0.405	(orange)	0.404	0.403
Mol. wt. (obsd.)	260.7	159.3		147.6	......
(calcd.)	259.8	159.8		148.6	......
M.p. (obsd.)	.....	.....		.....	−39.2°
(known)	.....	.....		.....	−40.0°

Evidence of Reactions (3) **and** (4).—The reaction between $(CF_3)_2PBr_3$ and CF_3PBr_2 was most reasonably explained in terms of equations (3) and (4), neither of which could be separately verified to the exclusion of the other. A sample of $(CF_3)_2PBr_3$ was made from 0.312 mmole each of $(CF_3)_2PBr$ and Br_2 at room temperature and treated with 0.311 mmole of CF_3PBr_2. After 66 hr. at 27° the yield of CF_3Br (0.05 mmole) indicated only 16% completion of the reaction, but a 12-hr. heating in a sealed tube at 95° brought the process to completion, as shown by the following tabulation of products and evidences of identity.

Compound	CF_3Br	$(CF_3)_2PBr$	CF_3PBr_2	PBr_3
Mmoles (obsd.)	0.307	0.206	0.208	0.140
(calcd.)	0.312	0.206	0.211	0.206
Mol. wt. (obsd.)	...	248.9	261.4	...
(calcd.)	...	248.9	259.8	...

Volatility of CF_3Br: 251.8 mm. at −78.5 (calcd. 252.0 mm.); volatility of PBr_3 judged qualitatively.

The calculated quantities here are based upon the assumption that 0.106 mmole of $(CF_3)_2PBr_3$ went to form CF_3Br and CF_3PBr_2 (eq. 3), so that the use of the remaining 0.206 mmole of $(CF_3)_2PBr_3$ for the transfer of Br_2 to CF_3PBr_2 (eq. 4) required only 0.100 mmole of the 0.311 mmole initial sample of CF_3PBr_2. The low yield of PBr_3 again is to be ascribed to the condition of the stopcocks: with time there is an increase in the amount of grease squeezed out into the space available to the vapors, and a trace of bromine in the grease makes it especially effective for absorbing PBr_3.

The Bromine-transfer Reaction (6).—A 0.242 mmole sample of CF_3PBr_4 was made by mixing equimolar portions of CF_3PBr_2 and Br_2, which reacted completely within a few minutes at 0°. Then 0.311 mmole of PBr_3 (m.p. $-39.2°$; reported value, $-40.0°$) was added and the mixture was heated for 30 min. at 35°. Now it was possible to isolate 0.03 mmole of CF_3Br and 0.212 mmole of CF_3PBr_2 (volatility 22.8 mm. at 0°; known, 22.6 mm.). The remaining mixture weighed 118.2 mg.; calcd. as $PBr_3 + PBr_5$, 118.7 mg. The PBr_5 appeared as a lemon-yellow solid even at 45° and could be sublimed *in vacuo* at room temperature, along with the distilling PBr_3.

Tris-(trifluoromethyl)-phosphine with Bromine.—Equimolar samples of $(CF_3)_3P$ and Br_2 were brought together by condensation at $-196°$ and warmed to room temperature. The initially immiscible liquids reacted slowly to form a single colorless liquid, having the composition of the formula $(CF_3)_3PBr_2$. In the initial experiment this product was heated for 18 hr. at 80°, with results roughly summarized by the over-all empirical equation

$$8(CF_3)_3PBr_2 \longrightarrow 8CF_3Br + CF_3PBr_2 + 3(CF_3)_2PBr + 3(CF_3)_3P + PBr_3$$

This experiment was regarded as tentative because the fraction representing the $(CF_3)_2PBr$ and $(CF_3)_3P$ was not fully resolved; however, the weight of this fraction, taken with the accurately observed yields of CF_3Br and CF_3PBr_2, required this equation for a correct material balance.

A considerably more accurate experiment began with 1.008 mmole of $(CF_3)_3P$ and 1.005 mmole of Br_2. A 9-hr. heating at 90° yielded a mixture which was resolved, by high-vacuum fractional condensation, into the four fractions:

(a) CF_3Br, 150.0 mg. (1.007 mmoles); mol. wt. 148.8 (calcd., 148.9); 252.3 mm. at $-78.5°$ (calcd., 252.0 mm.).

(b) $CF_3PBr_2 + PBr_3$, 43.7 mg. (0.165 mmole by rough volume msmt.). This was hydrolyzed in 15% NaOH (30 hr. at 100°) to give 11.1 mg. of HCF_3 (0.159 mmole; mol. wt. 69.8 *vs.* calcd., 70.0); then a Volhard determination of bromide in acid solution showed 0.338 meq. Hence the fraction seemed to consist of 0.159 mmole of CF_3PBr_2 with 0.007 mmole of PBr_3.

(c) $(CF_3)_2PBr + (CF_3)_3P$, 180.5 mg. (0.749 mmole by volume). An analysis as in (b) gave 1.752 mmoles of HCF_3 and 0.320 meq. of Br^-; however, these results would imply only 0.371 mmole of $(CF_3)_3P$ and 0.320 mmole of $(CF_3)_2PBr$, falling short of the observed 0.749 mmole for the two together.

(d) PBr_3, 26.8 mg. (0.099 mmole by volume); mol. wt. 271 (calcd., 270.7); 2.7 mm. at 23.5° (calcd., 2.7).

This analysis is summarized by an empirical equation, with calculated and observed results (in mmoles) attached to the formulas, as follows:

$$\begin{array}{lccccc} & 32(CF_3)_3PBr_2 & \longrightarrow & 32CF_3Br & +\ 5CF_3PBr_2 & +\ 3PBr_3 \\ \text{calcd.} & 1.005 & & 1.005 & 0.157 & 0.094 \\ \text{obsd.} & 1.005 & & 1.007 & 0.159 & 0.106 \end{array}$$

$$\begin{array}{lc} & +\ 12(CF_3)_2PBr + 12(CF_3)_3P \\ \text{calcd.} & \underbrace{0.377 \qquad\qquad 0.377} \\ \text{obsd.} & 0.749 \end{array}$$

Although much of this process may have gone according to equation (12), processes (11), (13) and (2) also would account for the equimolar yield of CF_3Br and seem necessary to explain the formation of $(CF_3)_3P$, CF_3PBr_2 and PBr_3. The alternative idea that these formed by disproportionation of $(CF_3)_2PBr$ seems to require that CF_3Br be reabsorbed by $(CF_3)_2PBr$ to form $(CF_3)_3PBr_2$. Such a step would contradict the whole trend of individually observed reactions favoring the more highly brominated phosphoranes.

Reactions Involving Mercury

Bis-(trifluoromethyl)-bromophosphine and Mercury.—Although $(CF_3)_2PBr$ seems to be quite inert toward mercury at room temperature, a 0.321 mmole sample, heated with mercury for 16 hr. at 100° (without shaking) was 80% converted to $P_2(CF_3)_4$ (0.128 mmole), with recovery of 0.067 mmole of the original $(CF_3)_2PBr$.

The Tribromophosphorane with Mercury.—The existence of $(CF_3)_2PBr_3$ made possible an experiment to determine whether the room-temperature inertness of $(CF_3)_2PBr$ toward mercury would persist even when this bromophosphine is being formed by a chemical reaction. A 144.3 mg. sample of $(CF_3)_2PBr_3$ (only slightly contaminated by the decomposition products CF_3PBr_4 and PBr_3) reacted rapidly with mercury in a sealed tube at room temperature. After some shaking, the mixture yielded 0.321 mmole of $(CF_3)_2PBr$ (calcd., 0.354 mmole; mol. wt. 248.6 *vs.* calcd., 248.9) as the only volatile product. Thus 91% of the expected $(CF_3)_2PBr$ withstood the action of mercury during formation.

Trifluoromethyl-dibromophosphine with Mercury.—Unlike $(CF_3)_2PBr$, the dibromophosphine CF_3PBr_2 reacts easily with mercury, to form CF_3P-polymers at room temperature. A 66.2 mg. sample of CF_3PBr_2 (0.255 mmole) was shaken briefly with excess mercury and the products separated. The main component was the equilibrium mixture of $(CF_3P)_4$ and $(CF_3P)_5$,[3] altogether amounting to 15.7 mg. and representing 70% of the CF_3PBr_2. The recovery of this dibromophosphine was 11.0 mg. (17%). The remaining CF_3P units (13%) presumably were aggregated as involatile higher polymers.

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The Effect of Fluorine Substitution on the Rate of Hydrolysis of Chloromethane[1]

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Rate constants for the hydrolysis of CH_3Cl, CH_2FCl and CHF_2Cl in neutral aqueous solution are reported as a function of temperature. The activation energies decrease slightly with increasing temperature and range between 21 and 23 kcal./mole for all three substances. The rate constants decrease regularly with increasing fluorination.

There is much qualitative evidence available to indicate that the reactivity of a halogen atom in an aliphatic compound is markedly reduced by the presence of one or more fluorine atoms attached to the same carbon atom. There have been, however, relatively few quantitative investigations from which the extent of the reduction might be judged.

The problem is of special interest in connection with the relationships between bond length, bond dissociation energy and force constants in the carbon–halogen bonds involved. For carbon–carbon bonds, a shortened bond length is associated with

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