CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Kinetic and Equilibrium Studies of Halogen Exchange on Trivalent Phosphorus

BY A. D. JORDAN AND R. G. CAVELL*

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The PCl_3–PBr_3 redistribution in the neat liquid was studied by ^{31}P nmr spectroscopy. Although previous work indicated that the system attains equilibrium within 15 min at 25°, the reaction was found to have a half-life of at least 10.7 days at 70°. A kinetic study of the reaction was complicated by nonreproducible results, which appeared to originate from catalysis by traces of water. It was shown, however, that the rate of production or disappearance of a given species in the catalyzed reaction was first order. A study of the temperature dependence of the equilibrium distribution of the species indicated that the reorganization is essentially random. The CF_3PCl_2–CF_3PBr_2 redistribution in the neat liquid was studied by ^{19}F nmr spectroscopy. The reaction attains equilibrium with a half-life of at least 48 hr at 40°, and it is catalyzed by traces of water. The temperature dependence of the equilibrium distribution of the species indicated that the reorganization is random. The gas-phase redistribution of PF_2Cl, studied by infrared spectroscopy, was found to take place only to a limited extent after 24 hr at 300°. The hydrolysis of PF_2Cl was investigated and a path for the reaction proposed.

Introduction

The redistribution reactions of trivalent phosphorus halides have been known for some time.[1-8] Similar reactions between halogen and organic substituents on phosphorus have been used to prepare mixed substituents.[9] Little is known, however, about the kinetics and mechanism of these redistribution reactions. Kinetic studies of the halogen exchange in PX_3 and CF_3PX_2 (X is Cl or Br) were undertaken, the latter system providing the simpler case of two rather than three exchanging substituents. While our study was not wholly successful, some insight into the nature of these reactions has been provided as well as an explanation for the discrepancy with previous studies.

Experimental Section

1. **Instrumentation.**—Infrared spectra were recorded with Perkin-Elmer 337 and 421 spectrophotometers. The appropriate salt windows were sealed on the cell flanges with a thin layer of paraffin wax. Mass spectra were recorded with an AEI MS-9 double-focusing spectrometer. Proton and fluorine nmr spectra were recorded with a Varian A-56/60 spectrometer. Some phosphorus nmr spectra were recorded on a Varian HA-60 spectrometer at 24.3 MHz; however, the majority was recorded on a Varian HA-100 spectrometer at 40.5 MHz. The nmr instruments were equipped with variable-temperature probes and the Varian V6040 temperature controller. The temperature in the probe was accurately measured with a copper–constantan thermocouple in an nmr tube containing ethanol. The temperature was constant to ±1°.

2. **Preparation and Purification of Compounds.**—All preparations, purifications, and subsequent handling of compounds were carried out either in a standard vacuum apparatus constructed with glass stopcocks which were lubricated with KEL-F 90 grease or in a grease-free apparatus constructed with Fisher & Porter 1.25-mm Teflon stopcocks. The compounds PF_3, PCl_3, PBr_3, and HCl were obtained from commercial sources and purified by fractional condensation under vacuum before use. The chlorophosphine, PF_2Cl, was prepared from $(CH_3)_2NPF_2$[10] as described in the literature.[3] The trifluoromethyl compounds CF_3PCl_2 and CF_3PBr_2 were prepared from CF_3PI_2[11,12] as described.[12,13]

3. **Procedure.**—Samples for the study of the PCl_3–PBr_3 redistribution in the liquid phase were prepared by vacuum distilling the two compounds into an nmr tube. Small amounts of water were added to the trihalides by allowing water vapor to expand into a chamber of known volume and then condensing into the nmr tube. A more quantitative method was achieved by heating a known weight of $[Co(NH_3)_5H_2O]Br_3$, contained in a sealed side arm, and condensing the water which is liberated quantitatively into the nmr tube. The course of the reaction was followed by recording the ^{31}P nmr spectrum[14] of the sample as a function of time. The variation of the equilibrium distribution of species with temperature was determined from the nmr spectra of samples kept at the desired temperature over a period of at least 10 half-lives, as determined from their kinetic results. An internal standard was not employed for fear of contamination, and since external standards decreased the signal intensity, spectra were recorded in HR mode. The mole fraction of each species in a scan was obtained by fitting the observed spectra to standard Lorentzian curves generated with an analog curve resolver (Du Pont 310) equipped with an integrator.

The CF_3PCl_2–CF_3PBr_2 redistribution was studied in the liquid phase by ^{19}F nmr spectroscopy[15] using procedures identical with those used for the PCl_3–PBr_3 system except that the integrated nmr signal was used to obtain the mole fraction of each species.

The gas-phase disproportionation of PF_2Cl, its hydrolysis, and the PF_3–PCl_3 redistribution were studied by analyzing the contents of sealed tubes, allowed to react at a particular temperature for a prescribed period, by infrared spectroscopy. Although there is considerable overlap in the infrared spectra[4,16-18] of PF_3, PF_2Cl, $PFCl_2$, and PCl_3, it was found that the strong bands at 892 and 487 cm^{-1} in the spectrum of PF_3, which obey Beer's law, would be suitable for monitoring the redistribution reactions. Samples were prepared by condensing weighed amounts of the compounds into reaction tubes in a standard grease-lubricated system. Initial results on the PF_2Cl disproportionation indicated that hydrolysis was taking place; therefore the reaction tubes were dehydrated by heating with $SOCl_2$ at 300° for 24 hr. Since no hydrolysis products were detected when PF_2Cl was heated in such "dehydrated" tubes for several hours at 100°, this dehydrating procedure was used for all the PF_3–PCl_3 samples.

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(14) The ^{31}P chemical shifts of PBr_3, PBr_2Cl, $PBrCl_2$, and PCl_3 in an equilibrium mixture at 40° are 115.4, 114.6, 111.4, and 106.0 ppm, respectively, downfield from P_4O_6.

(15) The ^{19}F chemical shifts of CF_3PBr_2, CF_3PBrCl, and CF_3PCl_2 in an equilibrium mixture at 40° are 67.8, 70.0, and 72.0 ppm, respectively, upfield from $CFCl_3$, and their corresponding P–F coupling constants are 69.5, 74.5, and 80.5 Hz.

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Results and Discussion

I. Kinetic Studies. 1. PCl_3–PBr_3 System.—The reorganization of a mixture of PCl_3 and PBr_3 has been

$$PCl_3 + PBr_3 \rightleftarrows PBr_2Cl + PBrCl_2 \qquad (1)$$

reported to attain equilibrium in 1–1.5 hr at room temperature[5] and in less than 15 min at 25°.[6] In the present case, initial studies of samples prepared in the standard greased vacuum system gave erratic results with the half-life of the reaction ranging from 5 to 140 min at 41° for a particular concentration mixture. Samples prepared under grease-free conditions showed a marked decrease in rate, the longest half-life obtained being 10.7 days at 70° for a sample of PCl_3 and PBr_3 containing 0.55 mol fraction of the former. Compared to previous results this represents about 1000-fold decrease in the rate of the reaction, ignoring the expected effects of the temperature difference. However, the reaction was not yet free of catalytic impurities, as demonstrated by the continuing nonreproducibility of the rate results.

It was shown that trace amounts of water greatly accelerated the redistribution. Since phosphorus halides hydrolyze[19] in excess water to phosphorous acid and the corresponding hydrohalic acid, either product or water itself could be the catalyst. Addition of anhydrous HCl or HBr did not yield an increased rate of exchange. The effect of added H_3PO_3 could not be tested because of the difficulty in obtaining it free of water. Known amounts of water were added to a series of samples containing a constant concentration of the two halides in an attempt to determine the order of the catalyzed reaction with respect to water. No quantitative conclusions can be made since the results were not in consistent agreement, as demonstrated by a half-life of 16–125 min for samples containing 0.05 *M* added water to 10.3 *M* total halide (0.62 mol fraction of PCl_3). This is not surprising considering the difficulties of achieving quantitative transfer of minute amounts of water (1.46×10^{-2} mmol in the above case).

Although the order of the reaction with respect to the catalyst is unknown, the overall reaction process is pseudo first order with respect to the change of the concentration of each of the four individual species with time, since linear first-order plots were obtained over at least 90% of the course of the reaction for each species in 30 of the 34 samples studied.

It is not likely[20] that the catalyst for the redistribution is pure water but rather one of the hydrolysis products. In addition to the hydrohalic acids and H_3PO_3 previously mentioned, other hydrolysis products, such as $H_4P_2O_5$, have been reported.[21–24] Evidence for the stepwise hydrolysis of PCl_3 to H_3PO_3 has also been reported and the intermediates PCl_2OH and $PCl(OH)_2$ have been postulated.[25] This is not unreasonable since there is evidence for similar intermediates in the hydrolysis of PF_3.[26,27] Thus halogen-containing intermediates such as PCl_2OH, $PCl(OH)_2$, PBr_2OH, and $PBr(OH)_2$ could be proposed as catalysts for the PCl_3–PBr_3 redistribution.

2. CF_3PCl_2–CF_3PBr_2 System.—No previous investigation of the redistribution reaction

$$CF_3PCl_2 + CF_3PBr_2 \rightleftarrows 2CF_3PBrCl \qquad (2)$$

has been reported. The results of kinetic studies on samples, prepared under grease-free conditions, with a mole fraction of 0.53 of CF_3PCl_2 were irreproducible; the half-life of the reaction ranged from 1.7 to 48.3 hr at 42°. Small amounts of water were found to catalyze the redistribution, but no further attempts to study the reaction were made. Catalysts of a similar nature to those of the PCl_3–PBr_3 system could be involved, since the products of the hydrolysis of CF_3PCl_2 and CF_3PBr_2 are $CF_3P(H)(O)OH$ and the corresponding hydrohalic acids.[28]

3. PF_3–PCl_3 System.—Preliminary results with PF_2Cl contained in nontreated reaction tubes indicated that some reaction had occurred, the only products being PF_3, OPF_2H, F_2POPF_2, HCl, and SiF_4 (presumably due to hydrolysis) and unreacted PF_2Cl. Analysis of several samples of PF_2Cl, contained in carefully "dehydrated" tubes at temperatures of 70–200° for 12–40 hr, gave no indication of redistribution products. However, a sample of PF_2Cl at 300° for 24 hr indicated the presence of small amounts of PF_3, $PFCl_2$, and PCl_3 and traces of the hydrolysis products. Equimolar quantities of PF_3 and PCl_3 gave no redistribution products after 24 hr at 100°, detectable amounts of PF_2Cl after 24 hr at 200°, and both PF_2Cl and $PFCl_2$ after 24 hr at 300°. Larger quantities of the redistribution products together with SiF_4 and OPF_3 were observed at higher temperatures, in agreement with previous results.[1] Since the disproportionation of PF_2Cl and the redistribution of PF_3 and PCl_3 are slow, little can be said about the thermodynamic stability of the mixed species with respect to the parent halides.

The reaction of PF_2Cl (0.95 mmol) and H_2O (1.1 mmol) at room temperature for 24 and 48 hr yielded PF_3, HCl, SiF_4, and H_3PO_3. The reaction of PF_2Cl (0.79 mmol) with H_2O (0.33 mmol) yielded OPF_2H and unreacted PF_2Cl in addition to the above products, while the hydrolysis of PF_2Cl with traces of water also yielded F_2POPF_2. It seems reasonable to suggest that the reaction of PF_2Cl with limited amounts of water yields OPF_2H which may then react with excess PF_2Cl to yield F_2POPF_2 or decompose[29] to H_3PO_3 (see eq 3–5). The presence of SiF_4 may be explained by the

$$PF_2Cl + H_2O \longrightarrow OPF_2H + HCl \qquad (3)$$

$$OPF_2H + PF_2Cl \longrightarrow F_2POPF_2 + HCl \qquad (4)$$

$$3OPF_2H \longrightarrow 2PF_3 + H_3PO_3 \qquad (5)$$

hydrolysis of OPF_2H[29] to H_3PO_3 and HF, the latter attacking the glass.

II. Equilibrium Studies. 1. PCl_3–PBr_3 System.—

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[20] In two separate experiments in which a small amount of water was allowed to react with large amounts of PCl_3 and PBr_3 in a sealed tube, the reaction seemed to occur within a few minutes, and a distinct, oily liquid was formed as a separate phase.

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The redistribution in this system can be fully described by the equilibria

$$2PCl_3 + PBr_3 \rightleftarrows 3PBrCl_2 \qquad K_1 \qquad (6)$$

$$2PBr_3 + PCl_3 \rightleftarrows 3PBr_2Cl \qquad K_2 \qquad (7)$$

The values of K_1 and K_2 and their respective enthalpy ($\Delta H°$) and entropy ($\Delta S°$) are given in Table I. The value of $\Delta S°$ for the random reorganization in eq 6 calculated[30] from the statistical distribution of all species is 6.55 cal mol^{-1} deg^{-1}, and the values of $\Delta H°$ and $\Delta S°$ computed from the thermodynamic functions[31] of the species on the basis of a rigid rotator–harmonic oscillator model are 51 cal mol^{-1} and 7.32 cal mol^{-1} deg^{-1}, respectively. Similarly, the value of $\Delta S°$ for the random reorganization in eq 7 is 6.55 cal mol^{-1} deg^{-1}, while the corresponding $\Delta H°$ and $\Delta S°$ from the thermodynamic functions[31] are 66 cal mol^{-1} and 7.20 cal mol^{-1} deg^{-1}, respectively. The experimental values of $\Delta H°$ and $\Delta S°$ agree with the theoretical values, within the experimental error. It should be noted that in a previous study of these equilibria at 25° the values of K_1 and K_2 were determined to be 40 and 10, respectively.[6]

TABLE I

VARIATION OF THE EQUILIBRIUM CONSTANTS WITH TEMPERATURE FOR THE PCl_3–PBr_3 SYSTEM

Temp, °C	Av $K_{1,\text{obsd}}$[a]	$K_{1,\text{calcd}}$[b]	Av $K_{2,\text{obsd}}$[a]	$K_{2,\text{calcd}}$[b]
35.0	8.56(6.27→10.48)	9.01	7.90(5.67→10.21)	8.18
37.0	8.67(5.55→10.68)	9.11	8.04(5.86→10.49)	8.33
40.5	9.60(5.96→12.02)	9.28	8.98(6.43→10.89)	8.59
50.0	10.82(9.62→12.50)	9.74	9.68(7.53→10.49)	9.29
60.0	10.07(6.04→11.57)	10.23	9.98(8.28→11.87)	10.06
70.0	10.35(7.60→12.43)	10.71	10.69(7.09→13.39)	10.83

$\Delta H° = 1039(-1134 \rightarrow 2829)$[c] cal mol^{-1} $\qquad$ $\Delta H° = 1683(-1665 \rightarrow 5174)$[c] cal mol^{-1}

$\Delta S° = 7.74(0.98 \rightarrow 13.27)$[c] cal mol^{-1} deg^{-1} $\qquad$ $\Delta S° = 9.64(-0.40 \rightarrow 20.26)$[c] cal mol^{-1} deg^{-1}

[a] Values in parentheses are the lower and upper values on the basis of all the determinations. [b] From a least-squares fit of the data to $K = \exp(-\Delta H°/RT)\exp(\Delta S°/R)$. [c] Values in parentheses are the lower and upper limits, calculated from the worst possible fits encompassing the entire range of equilibrium constants.

2. **CF_3PCl_2–CF_3PBr_2 System.**—The values for the equilibrium constant of this system, described by eq 2, together with the corresponding $\Delta H°$ and $\Delta S°$, are given in Table II. The near thermoneutrality of the reaction, together with the value of $\Delta S°$, which is in excellent agreement with the statistical[30] value of 2.76 cal mol^{-1} deg^{-1}, indicates that the redistribution is random.

TABLE II

VARIATION OF THE EQUILIBRIUM CONSTANT WITH TEMPERATURE FOR THE CF_3PCl_2–CF_3PBr_2 SYSTEM

Temp, °C	Av K_{obsd}[a]	K_{calcd}[b]
25.0	2.70(2.58→2.79)	2.75
30.0	2.77(2.76→2.78)	2.77
40.0	2.96(2.76→3.29)	2.82
42.0	2.81(2.64→2.99)	2.83
50.0	2.83(2.70→3.08)	2.85
60.0	2.86(2.54→3.06)	2.90

$\Delta H° = 2.86(-39 \rightarrow 715)$[c] cal mol^{-1}

$\Delta S° = 2.97(0.72 \rightarrow 4.25)$[c] cal mol^{-1} deg^{-1}

[a] Values in parentheses are the lower and upper values on the basis of all the determinations. [b] From a least-squares fit of the data to $K = \exp(-\Delta H°/RT)\exp(\Delta S°/R)$. [c] Values in parentheses are the lower and upper limits, calculated from the worst possible fits encompassing the entire range of equilibrium constants.

Conclusion

The major conclusion derived from this study is that the redistribution of halogens on trivalent phosphorus is much slower than had been previously reported. This observation could be extended to apply to similar redistribution reactions on other group Va central atoms. It may be generally concluded that redistribution reactions involving halogens may be more susceptible to catalysis by moisture because of the ease of hydrolysis. Investigations of the catalyzed reaction could be of use in future preparative work on mixed-ligand–phosphorus compounds.

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