$[(CF_3)_2P]_2NCH_3$.[6] Again shifts to higher energy are suggested for the pentavalent compounds perhaps indicating stronger bonding in these systems. The P–N–P asymmetric stretch in the trimethylamine adducts appears to be most reasonably assigned to the bands at 980–1000 cm^{-1}.

The notably greater reluctance of hydrogen chloride to cleave the P–N bond in pentavalent phosphorus compounds as compared to the ease of P–N bond cleavage by hydrogen halides in the trivalent phosphorus compounds may reflect a greater P–N bond strength in the pentavalent system in agreement with the infrared interpretation. The possibility of kinetic control of the cleavage of the P–N bond in pentavalent phosphorus compounds must not be overlooked.

Acknowledgment.—We thank the National Research Council of Canada for the award of a Scholarship to T. L. C. and for financial support of this research.

Notes

CONTRIBUTION FROM ROCKETDYNE,
A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Oxidation–Reduction in the Chlorine Monoxide–Arsenic Pentafluoride System[1]

BY C. J. SCHACK AND D. PILIPOVICH

Received May 5, 1969

Dichlorine oxide (or chlorine monoxide) has been reported to form a complex with AsF_5 at −78° and at about −50° to form an odd-electron molecule, $ClOAsF_5$, through elimination of Cl_2.[2] Inference of the structure as being the postulated odd-electron molecule was drawn from the observed reaction stoichiometry and the fact that the postulated odd molecule reacted with NO_2 to give $ClNO_3$. No additional data concerning the complex have appeared. Inasmuch as we had projected a reaction study based on "$ClOAsF_5$," an effort was made to verify its formation. However, it was found that the original report was erroneous in that the known $ClO_2^+AsF_6^-$ and not "$ClOAsF_5$" is produced by this reaction.

Experimental Section

Materials.—Chlorine monoxide was prepared from Cl_2 and yellow HgO using a modified procedure.[3] Arsenic pentafluoride was purchased from Ozark-Mahoning and used without purification after gas chromatography indicated a purity of better than 99.5%. Chloryl fluoride was prepared from $KClO_3$ and F_2[4] and purified by fractional condensation. Nitrogen tetroxide was purchased from the Matheson Co. and purified by fractional condensation. Phosphorus dichloride trifluoride was formed[5] from PF_3 and Cl_2.

Apparatus.—Experiments were conducted in two vacuum systems, one constructed of glass and the other of stainless steel–Teflon. Solids were handled in an inert-atmosphere glove box. Infrared spectra were taken on a Perkin-Elmer 137 Infracord using 5-cm gas cells fitted with AgCl windows and were also taken as Halocarbon oil mulls or neat solids between AgCl plates. Debye–Scherrer powder X-ray diffraction patterns were obtained with a GE XRD5 instrument using Cu Kα radiation. Vapor-phase chromatography of reactants and products was carried out on a column packed with 50% w/w of Halocarbon 4-11V oil and Kel-F low-density molding powder according to Dayan and Neale.[6]

Reactions of Cl_2O and AsF_5.—Measured quantities of Cl_2O (117 cm^3, 5.22 mmol) and AsF_5 (85.0 cm^3, 3.79 mmol) were separately condensed into the reactor (glass or Teflon tubes) at −196°. The temperature was changed to −78° and it was observed that the mixed reactants gradually developed a dark red color. Pumping on the mixture after a few hours at −78° resulted in the recovery of some of the starting materials and much Cl_2. Subsequent warming of the reaction to ambient temperature gave additional small amounts of gaseous materials and a white solid. Little or no gases not condensable at −196° were observed throughout the reaction. In all, 111 cm^3 of volatile products was obtained. Infrared and gas chromatographic analyses indicated these products to be a mixture of AsF_5 (17.5 cm^3, 0.78 mmol) and Cl_2 (93.5 cm^3, 4.17 mmol) with a trace of ClO_2 and no Cl_2O. The observed reactant:product ratio of $Cl_2O:AsF_5:Cl_2$ was 5.00:2.89:4.01. Similar reaction ratios were obtained when Cl_2O was used as the excess reagent. The solid product showed three infrared bands: 1280 (m, doublet), 1040 (w, doublet), and 690–700 cm^{-1} (s, broad).

Preparation of $ClO_2^+AsF_6^-$.—Chloryl fluoride (111 cm^3, 4.96 mmol) and AsF_5 (63.7 cm^3, 2.84 mmol) were separately condensed into a Teflon ampoule at −196°. After 1 hr at room temperature, the unreacted gases were removed and measured (48.0 cm^3, 2.14 mmol). An infrared spectrum showed only $FClO_2$. The white solid product had an infrared spectrum identical with that of the solid from the Cl_2O–AsF_5 reaction. In addition, both solids fumed in air and exploded on contact with water. Powder X-ray patterns of both solids were obtained and were identical. The observed spacings and relative intensities are given in Table I.

Reaction of $ClO_2^+AsF_6^-$ and NO.—A weighed sample of $ClO_2^+AsF_6^-$ (0.38 g, 1.48 mmol) was treated with NO (66.0 cm^3, 2.95 mmol) for approximately 1 hr at ambient temperature. The volatile products of the reaction were separated by fractional condensation and consisted of Cl_2 contaminated with a trace of ClNO (17.5 cm^3, 0.78 mmol) and NO_2 (32.2 cm^3, 1.44 mmol). Unreacted NO was not detected. The white solid product left in the reactor was identified as $NO_2^+AsF_6^-$ by its infrared spectrum.[7] A similar reaction of the $ClO_2^+AsF_6^-$ obtained from the Cl_2O reaction and NO also rapidly gave Cl_2, NO_2, and $NO_2^+AsF_6^-$ in approximately the same stoichiometry but in lower over-all yield as expected for $ClO_2^+AsF_6^-$ contaminated with $AsOF_3$.

---

[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] M. Schmeisser, W. Fink, and K. Brandle, *Angew. Chem.*, **69**, 780 (1957).

[3] C. J. Schack and C. B. Lindahl, *Inorg. Nucl. Chem. Letters*, **3**, 387 (1967).

[4] A. Engelbrecht, *Angew. Chem.*, **66**, 442 (1954).

[5] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[6] V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p 223.

[7] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $ClO_2^+AsF_6^-$

d, Å	Rel intens	d, Å	Rel intens
7.50	30	2.30	10
5.55	30	2.08	60
5.10	30	2.05	60
4.40	70	1.95	40
4.02	40	1.87	10
3.65	100	1.84	10
3.57	90	1.80	10
3.49	10	1.76	10
3.03	50	1.70	20
2.87	$\leq$10	1.59	15
2.76	$\leq$10	1.55	10
2.69	$\leq$10	1.53	10
2.54	$\leq$10		

Reaction of $ClO_2^+AsF_6^-$ and NO_2.—Weighed amounts of $ClO_2^+AsF_6^-$ and excess NO_2 gas were allowed to react for 1 hr at 0°. The expected displacement[8] of ClO_2 was achieved but in poor yield: 20% for the solid from the Cl_2O reaction and 35% for the solid from the $FClO_2$ reaction.

Reaction of PF_3Cl_2 and Cl_2O.—A 1:1 mixture of PF_3Cl_2 and Cl_2O was allowed to warm to room temperature at which point an infrared spectrum was taken. The only infrared absorbing material present was POF_3. None of the PF_3Cl_2, a strong infrared absorber, remained. The by-product Cl_2 was revealed by its color when frozen. No nonvolatile solids were observed.

Results and Discussion

The reaction of Cl_2O with AsF_5 does not give the odd molecule $ClOAsF_5$ but appears to follow the stoichiometry shown in

$$5Cl_2O + 3AsF_5 \longrightarrow 2ClO_2^+AsF_6^- + AsOF_3 + 4Cl_2 \quad (1)$$

Several experiments showed the reaction to be independent of the experimental reactant ratios and confirmed the above stoichiometry for the consumed and evolved gaseous materials. On the basis of the observed stoichiometry of the reaction and the known infrared frequencies of $Cl{=}O$[9a] and $As{-}F$[9b] compounds, it appeared the solid product might be principally $ClO_2^+AsF_6^-$. This was confirmed by preparing an authentic sample of $ClO_2^+AsF_6^-$ and comparing their infrared spectra and X-ray patterns which were found to be identical. A detailed assignment of the infrared spectrum of $ClO_2^+AsF_6^-$ has been reported.[10] The formation of $AsOF_3$ as a product was not established directly as it is a nonvolatile, X-ray-amorphous solid[11] and was present in too low a concentration to be reliably detected in the infrared spectrum of the solid product.

In the reaction of Cl_2O with AsF_5, the evolution of Cl_2 involves a much more complex process than the simple Cl–O bond rupture reported.[2] The observed oxidation–reduction of Cl_2O is a reaction typical of chlorine oxides under a variety of conditions. For example, ClO_2 gives some Cl_2O_6 on photolysis[12] and ether Cl_2O or ClO_2 reacts with SO_3 to form $(ClO)(ClO_2)S_3O_{10}$.[13] A related redox of Cl_2O initiated by AsF_5 forms a likely first step in this reaction

$$2Cl_2O + AsF_5 \longrightarrow ClO_2^+AsF_5Cl^- + Cl_2 \quad (2)$$

The complex anion shown in eq 2 would be expected to reorganize since mixed arsenic(V) halide anions are unknown.[14] A possible path is shown in the subsequent reactions

$$ClO_2^+AsF_5Cl^- + AsF_5 \longrightarrow ClO_2^+AsF_6^- + AsF_4Cl \quad (3)$$

$$2AsF_4Cl \longrightarrow AsF_5 + AsF_3Cl_2 \quad (4)$$

$$AsF_3Cl_2 + Cl_2O \longrightarrow AsOF_3 + 2Cl_2 \quad (5)$$

The sum of eq 2–5, suitably weighed, gives eq 1.

Direct verification of the formation of $AsOF_3$ as in eq 5 was not possible as AsF_3Cl_2 "goes ionic" and is formulated as $AsCl_4^+AsF_6^-$.[15] However, it was felt that a suitable test of eq 5 would be the reaction of PF_3Cl_2 and Cl_2O. Indeed, the rapid conversion of PF_3Cl_2 to POF_3 and Cl_2 as in eq 6 strongly suggests that

$$PF_3Cl_2 + Cl_2O \longrightarrow POF_3 + 2Cl_2 \quad (6)$$

"covalent" AsF_3Cl_2 would react similarly.

The original report concerning the preparation of "$ClOAsF_5$" offered the reaction of NO_2 as a proof of the radical present[2] (eq 7). The existence of NO_2AsF_5 has

$$ClOAsF_5 + 2NO_2 \longrightarrow NO_2AsF_5 + ClNO_3 \quad (7)$$

already been questioned seriously and apparently disproved.[16] However, the formation of some $ClNO_3$ could be expected from $ClO_2^+AsF_6^-$ and NO_2 inasmuch as the reaction of ClO_2 and NO_2 can give $ClNO_3$.[17] On examination, it was found that both the product of the Cl_2O–AsF_5 reaction and "authentic" $ClO_2^+AsF_6$ reacted with NO_2 without forming any $ClNO_3$. Instead, only the displacement of ClO_2 occurred accompanied by the formation of $NO_2^+AsF_6^-$.

In a final effort to detect any marked difference between the Cl_2O–AsF_5 reaction product and $ClO_2^+AsF_6^-$, their reaction with NO was tested. The reaction shown by eq 8 was obtained with both solids, indicating their essential identity. It should be noted that the reaction observed is not in agreement with that reported[8] for NO and $ClO_2^+AsF_6^-$.

$$2NO + ClO_2^+AsF_6^- \longrightarrow NO_2^+AsF_6^- + {}^1\!/_2Cl_2 + NO_2 \quad (8)$$

Thus, proof of the existence of "$ClOAsF_5$" through its reactions or its synthesis was not obtained and all the data indicate that $ClO_2^+AsF_6^-$ is the primary solid product of the reaction of Cl_2O and AsF_5.

Acknowledgment.—The authors wish to express their gratitude to the Office of Naval Research, Power Branch, for support of this work.

---

(8) M. Schmeisser and W. Fink, *Angew. Chem.*, **69**, 780 (1957).

(9) (a) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963); (b) R. Peacock and D. Sharp, *J. Chem. Soc.*, 2766 (1959).

(10) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

(11) K. Dehnicke and J. Weidlein, *Z. Anorg. Allgem. Chem.*, **342**, 225 (1966).

(12) H. J. Schumacher and G. Stieger, *Z. Physik. Chem.*, **37**, 363 (1930).

(13) H. A. Lehmann and G. Kruger, *Z. Anorg. Allgem. Chem.*, **274**, 141 (1953).

(14) L. Kolditz in "Halogen Chemistry," Vol. 2, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 115.

(15) H. M. Dess, R. W. Parry, and G. L. Vidall, *J. Am. Chem. Soc.*, **78**, 5730 (1956).

(16) S. I. Morrow and A. R. Young, *Inorg. Nucl. Chem. Letters*, **2**, 349 (1966).

(17) H. Martin and Th. Jacobsen, *Angew. Chem.*, **67**, 524 (1955).