Redox in the Cl_2O-AsF_5 System

C. J. Schack and D. Pilipovich

Rocketdyne, a Division of North American Rockwell Corporation
Canoga Park, California 91304

Dichlorine oxide (or chlorine monoxide) has been reported to form a complex with AsF_5 at -78° and at about -50° formed an odd molecule, $ClOAsF_5$, through elimination of Cl_2.[1] Inference of the structure as being the postulated odd molecule was drawn from the observed reaction stoichiometry and the fact that the postulated odd molecule reacted with NO_2 to give $ClNO_3$.

We were interested in studying various aspects of the proposed odd molecule particularly as a ready source of the ClO radical. However, we felt that, prior to utilizing $ClOAsF_5$ as an intermediate, a more complete characterization was in order.

Experimental

Materials. Chlorine monoxide was prepared from Cl_2 and yellow HgO using a modified procedure.[2] 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[3] and purified by fractional condensation. Nitrogen tetroxide was purchased from the Matheson Co. and purified by fractional condensation. Phosphorus dichloride trifluoride was formed[4] from PF_3 and Cl_2.

Apparatus. Experiments were conducted in two vacuum systems, one constructed of glass, 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 or Halocarbon oil mulls between AgCl plates. Debye-Scherrer powder X-ray diffraction patterns were obtained with a G. E. XRD5 instrument using CuKα radiation.

Vapor phase chromatography of reactants and products was carried out on a column packed with 50% w/w of Halocarbon Oil 4-11V and Kel-F low density molding powder according to Dayan and Neale.[5]

---

(1) M. Schmeisser, W. Fink and K. Brandle, Angew. Chem. 69, 780 (1957).

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

(3) A. Engelbrecht, Angew. Chem., 66, 442 (1954).

(4) R. R. Holmes and W. P. Gallagher, Inorg. Chem., 2, 433 (1963).

Reactions of Cl_2O and AsF_5. Measured quantities of Cl_2O (117 cc, 5.22 mmoles) and AsF_5 (85.0 cc, 3.79 mmoles) 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 -196° non-condensable gases were observed throughout the reaction. In all, 111 cc of volatile products were obtained. Infrared and gas chromatographic analysis indicated these products to be a mixture of AsF_5 (17.5 cc, 0.78 mmole) and Cl_2 (93.5 cc, 4.17 mmoles) 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 two infrared bands 1280 cm^{-1} (m, doublet) and 690 to 700 cm^{-1} (s. broad). Based on the observed stoichiometry of the reaction and the known infrared frequencies of Cl-O[6] and AsF[7] compounds, it appeared the solid might be principally ClO_2AsF_6. Accordingly, an authentic sample was prepared.

Preparation of ClO_2AsF_6. Chloryl fluoride (111 cc, 4.96 mmoles) and AsF_5 (63.7 cc, 2.84 mmoles) were separately condensed into a Teflon ampoule at -196°. After 1 hour at room temperature, the unreacted gases were removed and measured (48.0 cc, 2.14 mmoles). An infrared spectrum showed only $FClO_2$. The white solid product had an infrared spectrum identical to 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 1.

Reaction of ClO_2AsF_6 and NO_2. Weighed amounts of ClO_2AsF_6 and excess NO_2 gas were reacted for 1 hour 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.

---

(5) V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p. 223.
(6) E. A. Robinson, Can. J. Chem., 41, 3021 (1963).
(7) R. Peacock and D. Sharp, J. Chem. Soc., 2766 (1959).
(8) M. Schmeisser and W. Fink, Angew. Chem., 69, 780 (1957).

TABLE 1

X-RAY POWDER DIFFRACTION DATA FOR ClO_2AsF_6

d, Å	Relative Intensity	d, Å	Relative Intensity
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	≤ 10	1.59	15
2.76	≤ 10	1.55	10
2.69	≤ 10	1.53	10
2.54	≤ 10		

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 non-volatile solids were observed.

Results and Discussion

The reaction of Cl_2O with AsF_5 does not give the odd molecule $ClOAsF_5$ but gives instead the salt ClO_2AsF_6. Further, the reaction appears to follow the stoichiometry shown in equation 1:

$$5Cl_2O + 3AsF_5 \longrightarrow 2ClO_2AsF_6 + 4Cl_2 + AsOF_3 \qquad (1)$$

The reaction stoichiometry does not appear to be dependent on the experimental reactant ratios. The formation of ClO_2AsF_6 was confirmed by preparing an authentic sample and comparing their X-ray patterns.

$$FClO_2 + AsF_5 \longrightarrow ClO_2AsF_6 \qquad (2)$$

In the reaction of Cl_2O with AsF_5, the evolution of Cl_2 apparently involves a much more complex process than a simple Cl-O bond rupture. The equation reported[1] for this process at -50° is shown in equation 3:

$$Cl_2O{\cdot}AsF_5 \longrightarrow ClOAsF_5 + 1/2\ Cl_2 \qquad (3)$$

We would prefer to propose an initial step that infers an ionization of Cl_2O, i.e., an ionic complex is obtained, perhaps $ClO^+AsF_5Cl^-$:

$$Cl_2O + AsF_5 \longrightarrow ClOAsF_5Cl \qquad (4)$$

The oxidation of the ClO^+ species could then proceed with additional Cl_2O:

$$Cl_2O + ClOAsF_5Cl \longrightarrow ClO_2AsF_5Cl + Cl_2 \qquad (5)$$

This step (equation 4) should not be considered unusual inasmuch as other chlorine oxides are capable of redox (e.g., ClO_2 gives some Cl_2O_6 on photolysis[9]).

The most difficult rationale is the formation of the AsF_6^- in the reaction. Admittedly a multiplicity of diverse reaction sequences could be proposed most of which would be difficult to experimentally verify. One possible path offered involves the dissociation of ClO_2AsF_5Cl into its components with the subsequent reactions noted:

$$ClO_2AsF_5Cl \longrightarrow FClO_2 + AsF_4Cl \quad (6)$$

$$2AsF_4Cl \longrightarrow AsF_3Cl_2 + AsF_5 \quad (7)$$

$$AsF_5 + FClO_2 \longrightarrow ClO_2AsF_6 \quad (8)$$

$$AsF_3Cl_2 + Cl_2O \longrightarrow AsF_3O + 2Cl_2 \quad (9)$$

It is readily seen that the sum of equations 4 through 9, suitably weighted, gives equation 1.

The identity of $AsOF_3$ was not established as a product since it is a non-volatile[10] X-ray amorphous solid. In addition, we did not wish to further complicate matters by studying the reaction of AsF_3Cl_2 with Cl_2O as a test of equation 8 inasmuch as AsF_3Cl_2 "goes ionic" and is formulated as $AsCl_4^+AsF_6^-$[11]. We did feel, however, that a suitable test of equation 8 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 equation 10:

$$PF_3Cl_2 + Cl_2O \longrightarrow POF_3 + 2Cl_2 \quad (10)$$

strongly suggests that "covalent" AF_3Cl_2 would react similarly. The reaction conditions are such that the reorganization of AsF_4Cl, postulated as an intermediate in equation 6, would give initially the covalent structure.

The initial report on the preparations of "$ClOAsF_5$" did offer the reaction of NO_2 as a proof of the radical present[11]:

$$ClOAsF_5 + 2NO_2 \longrightarrow NO_2AsF_5 + ClNO_3 \quad (11)$$

The existence of NO_2AsF_5 has already been questioned seriously and apparently disproved[12]. Further, the formation of some $ClNO_3$ should be expected from ClO_2AsF_6 and NO_2 inasmuch as the reaction of ClO_2 and NO_2 gives $ClNO_3$[13]. It is quite likely that the reaction observed by Schmeisser et al.

(9) H. J. Schumacher, and G. Stiezer, Z. Physik, Chem., 37, 363 (1930).
(10) K. Dehnicke and J. Wiedlein, Z. Anorg. allg. chem., 342, 225 (1966).
(11) H. M. Dess, R. W. Parry, and G. L. Vidall, J. Am. Chem. Soc., 78, 5730 (1956).
(12) S. I. Morrow and A. R. Young, Inorg. and Nucl. Chem. Letters, 2, 349 (1966).
(13) H. Martin and Th. Jacobsen, Angew. Chem., 67, 524 (1955).

was the initial displacement of ClO_2 from ClO_2AsF_6 by NO_2 followed by a reaction of ClO_2 with NO_2, the overall reaction being:

$$ClO_2AsF_6 + 2NO_2 \longrightarrow NO_2AsF_6 + ClNO_3 + 1/2\ O_2 \qquad (12)$$

Except for the formation of the oxygen, the reaction in equation 12 has the same stoichiometry of NO_2 to "solid" as that reported in equation 11. Thus, the proof of "$ClOAsF_5$" through its reactions or its synthesis is not conclusive.