If we combine Equations 1 and 5 of this paper with the equation for the free energy of iodine vapor,[1]

$$2I(s.) = I_2(g.);\ \Delta F^\circ_{298} = -4640$$

we obtain finally the free energy of formation of cyanogen gas,

$$2C_G + N_2 = (CN)_2(g.);\ \Delta F^\circ_{298} = 87580. \qquad (6)$$

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

REACTIONS IN NON-AQUEOUS SOLVENTS. II. THE ACTION OF CHROMYL CHLORIDE UPON PHOSPHORUS HALIDES.

BY HARRY SHIPLEY FRY AND JOSEPH L. DONNELLY.

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In the first paper of this series[2] it was shown that the dangerously explosive interaction between chromyl chloride and the phosphorus trihalides could be controlled and studied quantitatively by conducting the reactions in anhydrous carbon tetrachloride solutions. Equimolar solutions of chromyl chloride and phosphorus trichloride and tribromide were found to interact in the ratio of two volumes of the former to three volumes of the latter, *i. e.*, $2CrO_2Cl_2 : 3PX_3 (X = Cl \text{ or } Br)$, yielding new compounds of the formulas $CrOCl.POX_3$ according to the general equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2.$$

The determination of these ratios by volumetric methods was rendered possible through the use of acetyl bromide as an indicator for the detection of minute traces of chromyl chloride, the end point of the reaction depending upon the formation of the unstable but intensely colored (violet-red) chromyl bromide.[3]

This paper presents briefly the results of a further quantitative study of the action of chromyl chloride upon the following phosphorus halides: (A) Triiodide, (B) Pentachloride, (C) Pentabromide, and (D) Diiodide.

A. Interaction of Chromyl Chloride and Phosphorus Triiodide.

A volumetric study of the interaction of 0.2 *M* solutions of chromyl chloride and phosphorus triiodide in anhydrous carbon tetrachloride using acetyl bromide as an indicator (method described in Part I, Section A, *loc. cit.*) could not be effected because the slightly violet-red color of the phosphorus triiodide solution, due to inevitable traces of free iodine, invariably obscured the end point of the reaction. However, equimolar (0.2 *M*) solutions of chromyl chloride and phosphorus triiodide interacted exothermally, and instantaneously, yielding a voluminous dark brown precipitate, which, after being filtered, and repeatedly washed with carbon tetrachloride

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[1] Lewis and Randall, THIS JOURNAL, 36, 2259 (1914).

[2] Fry and Donnelly, *Ibid.*, 38, 1923 (1916).

[3] Fry, *Ibid.*, 33, 697 (1911).

and dried in a current of air free from moisture and carbon dioxide, was found to be a purple-red powder, too deliquescent and unstable for microscopic examination. The addition of a few drops of water to the compound effected violent decomposition with liberation of clouds of iodine vapor. Boiling with an excess of water gave a solution containing chromic, phosphate, chloride and bromide ions. This facilitated the quantitative analysis of the compound for the chromium and halogen content.

Determination of Chromium.—Weighed samples of the compound were dissolved in water. Boiling volatilized the free iodine. Cr^{+++} was oxidized to CrO_4^{--} by the addition of sodium peroxide. After successive treatments with sodium peroxide and dilute sulfuric acid, the percentage of chromium was determined by titration with 0.1 *N* ferrous ammonium sulfate solution, with the following results:

Compound (g.).	0.1 *N* ferrous soln. cc.	% Cr found.
0.2486	13.00	9.05
0.5984	31.15	9.02

It was naturally supposed that phosphorus triiodide and chromyl chloride would yield a compound of the formula $CrOCl.POI_3$, just as phosphorus trichloride and tribromide had previously yielded $CrOCl.POCl_3$ and $CrOCl.POBr_3$, respectively. This, however, was not the case since the percentage of chromium in the anticipated compound $CrOCl.POI_3$, 9.78 is not in agreement with the above values for chromium.

Determination of Halogens.—Since treatment of the compound in question with water involved the liberation of iodine and hydrogen halides, the following method was adopted: Weighed samples were placed in test tubes of 50 cc. capacity and covered with 10 cc. of carbon tetrachloride, which, in turn, was covered with 35 cc. of water. The tubes were securely stoppered and shaken. This procedure yielded a carbon tetrachloride solution of the liberated iodine and an aqueous solution of chlorides and iodides which were subsequently precipitated and weighed as mixed silver halides, $(AgCl)_x(AgI)_y$. Since the theoretical halogen content for the compound in question was not known, a value in the form of a factor, based upon the ratio of the quantity of the mixed halides found to the quantity of the compound taken for analysis, was determined as follows:

Compound (g.).	(AgCl)(AgBr) (g.).	Factor.
0.1098	0.1475	1.343
0.2440	0.3262	1.336

As the interaction between chromyl chloride and phosphorus triiodide did not yield the anticipated compound $CrOCl.POI_3$ the substance obtained was assumed to be an addition compound of the formula $CrO_2Cl_2.PI_3$, which would be decomposed by water according to the equation

$$2CrO_2Cl_2.PI_3 + 4H_2O \longrightarrow 4HCl + 4HI + 2CrPO_4 + I_2.$$

According to this equation, $CrO_2Cl_2.PI_3$ should yield $2AgCl + 2AgBr$ when the compound is decomposed by water and the resulting solution is treated with silver nitrate as described above. Accordingly, the theoretical ratio or factor should be $(CrO_2Cl_2.PI_3) : (AgCl)_2(AgI)_2 = 1.334$. This factor is substantiated by the experimentally determined factors given above. Moreover, the percentage of chromium in the addition compound $CrO_2Cl_2.PI_3$, namely 9.18, is checked by the percentages found: 9.05 and 9.02.

In summarizing Part A, it should be noted that while phosphorus trichloride and tribromide interact with chromyl chloride in anhydrous carbon tetrachloride according to the equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2,$$

which is an *oxidation-reduction reaction*, the behavior of phosphorus triiodide is abnormal in that it forms an *addition compound* according to the equation

$$CrO_2Cl_2 + PI_3 \longrightarrow CrO_2Cl_2.PI_3.$$

B. Interaction of Chromyl Chloride and Phosphorus Pentachloride.

When equal volumes of 0.1 *M* solutions of chromyl chloride and phosphorus pentachloride, in anhydrous carbon tetrachloride, are mixed, a brown gelatinous precipitate is formed. The reaction is exothermal but proceeds so slowly that a titrimetric study was impossible. After the reaction mixture had stood for an hour, the precipitate was filtered, repeatedly washed with carbon tetrachloride, and dried in a current of air free from moisture and carbon dioxide. The yellow-red powder thus obtained readily decomposes in the air evolving hydrogen chloride. It is vigorously decomposed by water yielding a solution containing chromic, phosphate, and chloride ions. The compound was analyzed for its chromium and chlorine contents by the methods outlined in the preceding Section A. The results of the analyses clearly indicate that an addition compound was formed according to the equation

$$CrO_2Cl_2 + PCl_5 \longrightarrow CrO_2Cl_2.PCl_5.$$

Data for Chromium Determinations:

Compound (g.).	0.1 *N* ferrous soln. (cc.).	% Cr found.	% Cr theory.
0.1487	12.05	14.04	14.08
0.2086	17.10	14.20	...

Data for Chlorine Determinations:

Compound (g.).	AgCl (g.).	% Cl found.	% Cl theory.
0.1131	0.3121	68.27	68.34
0.1470	0.4053	68.21	...

C. Interaction of Chromyl Chloride and Phosphorus Pentabromide.

Equimolar quantities of chromyl chloride and phosphorus pentabromide in carbon tetrachloride solution react exothermally yielding a gray, gelatinous precipitate which, when dried according to previously described methods, was found to be a dark purple powder, readily decomposed by atmospheric moisture with the evolution of fumes of hydrochloric and hydrobromic acids. Treatment with water gave a solution containing chromic, phosphate, chloride and bromide ions.

By analogy to the preceding reaction (B) with phosphorus pentachloride, the pentabromide should have formed a molecular compound of the formula $CrO_2Cl_2.PBr_5$, but repeated analyses of the product for chromium and halogen contents did not confirm the analogy. Repetitions of the interaction with varying concentrations of chromyl chloride and phosphorus pentabromide failed to yield a product of constant composition.

This anomaly may be explained by the fact that phosphorus pentabromide in carbon tetrachloride solution is partially dissociated and, consequently, embodies the reaction components of the equilibrium mixture

$$PBr_5 \rightleftarrows PBr_3 + Br_2.$$

Phosphorus tribromide, as previously described,[1] reacts readily with chromyl chloride to give the compound $CrOCl.POBr_3$; and a part, at least, of the phosphorus pentabromide would lend itself, presumably, to the formation of an addition compound $CrO_2Cl_2.PBr_5$, the analog of the compound $CrO_2Cl_2.PCl_5$ prepared in Section B. From this point of view, the product of the interaction of chromyl chloride and phosphorus pentabromide is a variable mixture of two compounds, $CrOCl.POBr_3$ and $CrO_2Cl_2.PBr_5$, which would not give concordant analyses for a definite addition compound.

D. Interaction of Chromyl Chloride and Phosphorus Diiodide.

The reaction between 0.1 *M* solutions of chromyl chloride and phosphorus diiodide (P_2I_4) is highly exothermal with instantaneous precipitation of a compound which, recovered by the usual method, was brown in color and very unstable in moist air. Iodine is freely evolved upon the addition of water, and subsequent boiling gives a solution containing chromic, chloride and iodide ions.

The results of the analyses for chromium indicate the formation of an addition compound according to the equation

$$2CrO_2Cl_2 + P_2I_4 \longrightarrow (CrO_2Cl_2)_2.P_2I_4.$$

Compound (g.).	0.1 *N* ferrous soln. (cc.).	% Cr found.	% Cr theory.
0.2005	13.90	12.01	11.82
0.1805	12.45	11.95	...

In the determination of the halogen content, a method was designed to precipitate all of the halogen in the compound as mixed silver halides in the ratio demanded by the assumed formula, namely 4 (AgCl.AgBr) : $(CrO_2Cl_2)_2.P_2I_4$ = 1.719.

Weighed samples were placed in test tubes of 50 cc. capacity and covered with 10 cc. of carbon tetrachloride to which was added a supernatant layer of 35 cc. of sodium thiosulfate solution. The tubes were then

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[1] Fry and Donnelly, This Journal, 38, 1926 (1916).

securely stoppered and shaken, thus bringing the samples into contact with the aqueous solution. In this manner the liberated iodine, as well as the remainder of the halogen in the compound, was converted into sodium halides. Boiling the solution with dilute nitric acid, and the subsequent addition of an excess of silver nitrate solution precipitated all of the halogen in the compound as mixed silver chloride and iodide. The results of the determinations check the theoretical factor, noted above, and confirm the formula $(CrO_2Cl_2)_2.P_2I_4$.

Compound (g.).	AgCl.AgI (g.).	Factor, found.	Factor, theory.
0.1872	0.3468	1.715	1.719
0.1169	0.2004	1.714	...

Summary.

The extended study of the interaction of chromyl chloride and phosphorus halides in anhydrous carbon tetrachloride solutions reveals the following facts:

1. While the interaction between chromyl chloride and phosphorus trichloride, or tribromide, is an *oxidation-reduction reaction* conforming to the equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2 (X = Cl \text{ or } Br),$$

the interaction with phosphorus triiodide unexpectedly gave an *addition compound* of the formula $CrO_2Cl_2.PI_3$.

2. The interaction with phosphorus pentachloride likewise resulted in the formation of an addition compound, $CrO_2Cl_2.PCl_5$.

3. The interaction with phosphorus pentabromide gave no definite compound but, presumably, a mixture of compounds, $CrOCl.POBr_3$ and $CrO_2Cl_2.PBr_5$.

4. The interaction with phosphorus diiodide gave a compound corresponding in composition to the formula $(CrO_2Cl_2)_2.P_2I_4$, or, more briefly, $CrO_2Cl_2.PI_2$. This substance is similar in composition and properties to the compound $CrO_2Cl_2.PI_3$ noted in (1).

5. None of these compounds has been prepared before. Their constitution is unknown, and they do not lend themselves to classification according to the Werner coördination formulas.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE OXIDIZING POWER OF CYANATES AND THE FREE ENERGY OF FORMATION OF CYANIDES.

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In attacking the difficult problem of free energy changes in organic reactions it has seemed at the outset necessary to determine the free energy of formation, through reversible synthesis from the elements of several