

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

REACTIONS IN NON-AQUEOUS SOLVENTS. I. THE ACTION OF CHROMYL CHLORIDE UPON THE PHOSPHORUS TRIHALIDES.

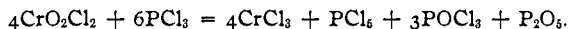
BY HARRY SHIPLEY FRY AND JOSEPH L. DONNELLY.

Received July 21, 1916.

A. Interaction of Chromyl Chloride and Phosphorus Trichloride.

The action of chromyl chloride upon phosphorus trichloride has received very little attention. This may be due to the explosive nature of the reaction, concerning which A. Michaelis has written:¹

"Chromacichlorid darf man wegen der Heftigkeit der Einwirkung nur tropfenweise zu stark abgekühlten Phosphorchlorür fließen lassen. Jeder Tropfen verursacht lebhaftes Zischen und Feuerscheinung, die jedoch nur zuerst sichtbar ist, indem sich die Retorte bald mit einem undurchsichtigen blaugrünen Anflug beschlägt. Die letzten Tropfen verursachen zuweilen Detonation. Die Reaction verlief nach der Gleichung:



"Indem aber das Phosphorsuperchlorid theilweise auf das Anhydrid einwirkte, entstand noch mehr Oxychlorid:



Since these equations have not been substantiated by quantitative data, a study of the interaction of chromyl chloride and phosphorus trichloride under new and safer conditions is of moment.

When solutions of chromyl chloride and phosphorus trichloride in *anhydrous carbon tetrachloride* are mixed there is formed at once a dark brown gelatinous precipitate which, when filtered off, washed with carbon tetrachloride and dried in a current of air free from moisture and carbon dioxide, was a finely divided gray-green powder, too deliquescent to be examined microscopically. It reacted with water (exothermic reaction) and the dark green aqueous solutions gave reaction for the following ions: H^+ , Cl^- , Cr^{+++} and PO_4^{---} .

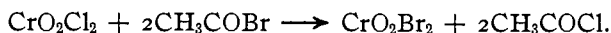
If the carbon tetrachloride solution of phosphorus trichloride is added slowly to the carbon tetrachloride solution of chromyl chloride, the volume of the precipitate increases but the color of the red chromyl chloride gradually fades to yellow and eventually becomes colorless when an excess of the phosphorus trichloride has been added. Then, of course, further additions of the trichloride yielded no more precipitate. These facts suggested the possibility of studying the reaction volumetrically provided that the end point of the reaction could be determined satisfactorily.

An accurate determination of the end point was made possible by applying a new reaction² for the detection of minute traces of chromyl

¹ *Jahresb. Chem.*, 1871, 248.

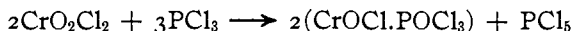
² Fry, "Notes on the Preparation of Chromyl Compounds," *THIS JOURNAL*, 33, 697 (1911).

chloride in carbon tetrachloride solution which depended upon the formation of the unstable but intensely colored *chromyl bromide* according to the equation¹

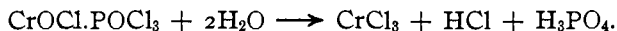


Fry found that the addition of one drop of acetyl bromide to a 0.001 molar solution of chromyl chloride in carbon tetrachloride gave an intense violet-red coloration permanent for about five minutes. Thus it is possible to titrate standard solutions of chromyl chloride and phosphorus trichloride in carbon tetrachloride to an accurate end point which is conveniently determined by removing a small drop of the reaction mixture on the end of a stirring rod and mixing it with a drop of the indicator, acetyl bromide, on a tile plate. The excessive fuming of the acetyl bromide may be modified by diluting it with carbon tetrachloride. This dilution does not interfere with the violet-red end point coloration.

In order to ascertain the molecular ratios in which chromyl chloride and phosphorus trichloride interact, 0.2 molar solutions of these compounds in carbon tetrachloride were prepared and immediately titrated from burets into 300 cc. Erlenmeyer flasks containing 100 cc. of carbon tetrachloride. An average of four titrations gave the interesting ratio in which 2 volumes of 0.2 molar CrO_2Cl_2 solution were equivalent to 3.02 volumes of 0.2 molar PCl_3 solution. This is practically a 2:3 ratio, *i. e.*, $2\text{CrO}_2\text{Cl}_2:3\text{PCl}_3$. The following equation, based upon this ratio, was assumed to represent the reaction in question:



The properties of the compound formed, and its analysis (described below) indicated that its composition may be represented by the formula $\text{CrOCl}.\text{POCl}_3$. It is decomposed by atmospheric moisture with evolution of hydrochloric acid fumes. Its decomposition by water, yielding a solution containing hydrogen-, chlorine-, chromic- and phosphate-ions, indicates that the hydrolysis may be represented by the equation



The ready and complete hydrolysis of the compound facilitated the analysis for its chromium and chlorine contents.

Determination of Chromium.—Weighed samples of the compound were dissolved in water. Cr^{+++} was oxidized to CrO_4^{--} by addition of sodium peroxide. Titration with standard ferrous ammonium sulfate solution gave the following results:

Substance (g.).	0.1 N ferrous soln. (cc.).	% Cr. Found.	% Cr. Theory.
0.3587	41.79	20.12	20.26
0.7100	82.70	20.14

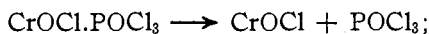
¹ The existence of chromyl bromide has been indicated in three other reactions, namely: $\text{CrO}_3 + 2\text{HBr} \longrightarrow \text{CrO}_2\text{Br}_2 + \text{H}_2\text{O}$; $\text{CrO}_2\text{Cl}_2 + 2\text{HBr} \longrightarrow \text{CrO}_2\text{Br}_2 + 2\text{HCl}$; $(\text{HO})_2\text{CrO}_2 + 2\text{CH}_3\text{COBr} \longrightarrow \text{CrO}_2\text{Br}_2 + 2\text{CH}_3\text{COOH}$. (Fry, *Loc. cit.*)

(The chromium was also determined by the sodium peroxide fusion method with equally concordant results.)

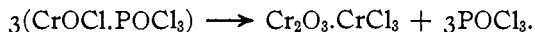
Determination of Chlorine.—Weighed samples were dissolved in water. After addition of nitric acid the chlorine was precipitated and weighed as silver chloride with the following results:

Substance (g.).	AgCl (g.).	% Cl. Found.	% Cl. Theory.
0.3938	0.8680	54.53	54.98
0.2372	0.5247	54.72

Invariably, minute quantities of hydrogen chloride were lost when the compound was decomposed with water, which accounts for the slightly lower percentage of chlorine than that demanded by the theory. Nevertheless, the preceding analysis for the contents of chromium and chlorine indicate that the composition of the compound may be represented by the formula $\text{CrOCl} \cdot \text{POCl}_3$. Further confirmation of this formula was afforded by igniting weighed samples of the compound in porcelain crucibles, assuming that decomposition proceeded according to the equation



or to the equivalent equation



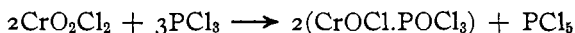
Accordingly, the residue obtained after ignition should correspond in composition to the formula CrOCl or $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$, the volatile component of the original compound being POCl_3 . This is indicated by the following data:

Substance.	Residue, CrOCl .	% CrOCl . Found.	% CrOCl . Theory.
0.3102	0.1228	39.52	40.23
0.5702	0.2252	39.48

The dark green residue was insoluble in water and in concentrated acids. It was analyzed for its chromium content by the sodium peroxide fusion method with the following results:

Substance.	0.1 N ferrous soln., cc.	% Cr. Found.	% Cr. Theory.
0.2789	80.40	49.84	50.26
0.3509	100.55	49.78

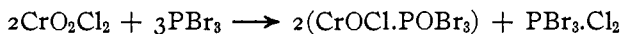
The amount of the residue left upon ignition and the percentage of chromium in the residue indicates that the insoluble product of the interaction of chromyl chloride and phosphorus trichloride in carbon tetrachloride solution may be represented by the formula $\text{CrOCl} \cdot \text{POCl}_3$. Furthermore, the reaction for its formation has been shown to involve 2 molecules of CrO_2Cl_2 to 3 molecules of PCl_3 . Hence the equation for the reaction



is warranted by the quantitative study herewith presented in Part A.

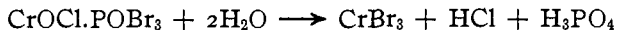
B. Interaction of Chromyl Chloride and Phosphorus Tribromide.

Nothing was found in the literature relative to the interaction of chromyl chloride and phosphorus tribromide. When minute quantities of the pure substances are brought together the reaction takes place with explosive violence. Therefore, it is desirable to modify the reaction by dissolving the chromyl chloride and the phosphorus tribromide in anhydrous carbon tetrachloride, and to study quantitatively the interaction in the same way that the interaction of chromyl chloride and phosphorus trichloride was investigated in the preceding Part A. Here also, upon titration, one-fifth molar solutions of chromyl chloride and the phosphorus trihalide were found to interact completely in the ratio of two volumes of the former to three volumes of the latter, *i. e.*, $2\text{CrO}_2\text{Cl}_2 : 3\text{PBr}_3$. The end point of the reaction was readily determined by the formation of *chromyl bromide* using acetyl bromide as the indicator reagent on the porcelain tile as previously described. On the basis of the above ratio (2 : 3) the following equation was assumed for the reaction in question:



This equation is perfectly analogous to the equation for the interaction of CrO_2Cl_2 and PCl_3 in Part A.

The product of the interaction (presumably CrOCl.POBr_3) after being filtered, washed repeatedly with carbon tetrachloride and dried in a current of air free from moisture and carbon dioxide, was a finely divided purple-gray powder. Its extremely deliquescent properties made it difficult to handle and prevented, with the resources at hand, a much desired microscopic examination. Its exothermic decomposition with water proceeded vigorously and the resulting green solution gave reactions for hydrogen-, chlorine-, bromine-, chromic- and phosphate-ions. Accordingly the hydrolysis may be represented by the following equation:



The solubility of the products of hydrolysis of the compound in question (CrOCl.POBr_3) facilitated its analysis (according to methods described in Part A) for the chromium and halogen contents. The data for the chromium determinations are as follows:

Substance (g.).	0.1 N ferrous soln. (cc.).	% Cr. Found.	% Cr. Theory.
0.2310	18.45	13.83	13.34
0.3167	25.15	13.75

The determination of the halogens in the compound involved the simultaneous precipitation of silver bromide and silver chloride in the molecular ratio $3\text{AgBr} : \text{AgCl}$. This is the ratio demanded by the assumed formula of the compound and by the equation for its hydrolysis. The assumption and formula are verified by the following analysis:

Substance (g.).	Found AgCl.3AgBr (g.).	Theory AgCl.3AgBr (g.).
0.5607	1.0238	1.0122

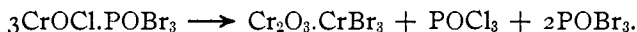
The results of the chromium and halogen determinations indicate that the composition of the compound may be represented by the formula $\text{CrOCl} \cdot \text{POBr}_3$, but its behavior upon ignition was not altogether similar to that of the preceding compound, $\text{CrOCl} \cdot \text{POCl}_3$, which yielded a residue corresponding in composition to the formula CrOCl or its equivalent $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$. The compound now in question, $\text{CrOCl} \cdot \text{POBr}_3$, yielded on ignition a purple residue which corresponded in quantity to a compound of the formula CrOBr or its equivalent, $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$, as shown by the following data:

Substance (g.).	Residue (g.).	% CrOBr. Found.	% CrOBr. Theory.
0.5002	0.1878	37.55	37.90
0.4546	0.1708	37.57

This purple residue, insoluble in water and in concentrated acids, was analyzed for its chromium content by the sodium peroxide fusion method. The results of this analysis also indicate that the composition of the residue may be represented by the formula CrOBr or $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$.

Substance (g.).	0.1 N ferrous soln. (cc.).	% Cr. Found.	% Cr. Theory.
0.2076	42.25	35.37	35.16
0.2542	52.05	35.40

Therefore, in conformity with the preceding analyses, the decomposition of the compound upon ignition may be represented by the equation



In conclusion, it may be noted that the reactions for the formation and the reactions for the decomposition of the compounds $\text{CrOCl} \cdot \text{POCl}_3$ and $\text{CrOCl} \cdot \text{POBr}_3$ are analogous.

Summary.

1. The dangerously explosive interaction between chromyl chloride and the phosphorus trihalides can be controlled and investigated quantitatively by conducting the reactions in the anhydrous solvent carbon tetrachloride.

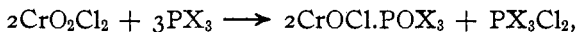
2. Equimolar solutions (0.2 molar) of chromyl chloride and phosphorus trihalide were found to interact in the ratio of two volumes of the former to three volumes of the latter, *i. e.*, $2\text{CrO}_2\text{Cl}_2 : 3\text{PX}_3$ ($\text{X} = \text{Cl}$ or Br).

3. The determination of this ratio 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*.¹

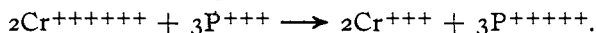
4. The new compounds thus prepared correspond in composition to the formulas $\text{CrOCl} \cdot \text{POCl}_3$ and $\text{CrOCl} \cdot \text{POBr}_3$. They yielded on ignition compounds corresponding to the formulas CrOCl (or $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$) and CrOBr (or $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$), respectively.

¹ Fry, *THIS JOURNAL*, 33, 697 (1911).

5. The interactions between chromyl chloride and the phosphorus trihalides are essentially oxidation-reduction processes as shown by the composition and properties of the compounds formed. The general equation for the reactions, namely,



indicates reduction of the hexavalent chromium compound to trivalent chromic compounds and the oxidation of trivalent phosphorus halides to pentavalent phosphorus compounds. Thus, on the basis of the established 2 : 3 ratio, the above equation reduced to its simplest term becomes



CINCINNATI, O.

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

THE INFLUENCE OF THE POTASSIUM ION AND OF THE CALCIUM ION UPON THE FERRI-FERRO-CYANIDE POTENTIAL.

BY EUGENE P. SCHOCH AND WILLIAM A. FELSING.

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OUTLINE.—1. Review of Previous Investigations. 2. Outline of Work Done and Results Attained. 3. Experimental Details and Calculation of Results. 4. Theoretical Considerations: (a) Significant Values of n and k for Ferricyanides and Ferrocyanides. (b) The Relation between the Activities and the Concentrations of the Ferricyanides and Ferrocyanides. 5. Summary.

Review of Previous Investigations.

The earliest measurements of the potential of the ferri-ferrocyanide¹ electrode were made by Schaum² and showed a dependence of the potential upon the concentration represented by Peters' modification of the Nernst formula

$$E_{\text{obs.}} = E_k + 0.0002 T \log \frac{[\text{total ferricyanide}]}{[\text{total ferrocyanide}]}$$

A little later (1902) Fredenhagen³ obtained the same result.

However, the result announced by these investigators is not true in general but it is only true for a series of solutions in which the total ion concentration is constant. This was shown conclusively by Lewis and Sargent,⁴ who made a rigorous test of the rule of mixtures by making up mixtures with constant potassium ion concentrations, but different ferri-ferrocyanide concentrations, and measuring their potentials. These

¹ The term "ferri-ferrocyanide" is used in this paper to denote any mixture containing both potassium (or calcium) ferricyanide and potassium (or calcium) ferrocyanide with or without the chloride of the same metal.

² *Z. Elektrochem.*, 5, 316 (1899); see also *Ibid.*, 9, 406 (1903).

³ *Z. anorg. Chem.*, 29, 398 (1902).

⁴ *THIS JOURNAL*, 31, 355 (1909).