The writer found that the auric hydroxide of preparation *G* did not attain constant weight on heating 52 hours at 160–178°; that preparations, *H*, *I* and *J* after heating for 72, 44 and 68 hours respectively to 157–172° were essentially auric oxide with 2.5 to 2.7 per cent. of water; *H* and *J* at higher temperatures lost oxygen but did remain constant in weight at any temperature, nor become anhydrous at 200–210°, that is, none of the preparations gave on heating auric oxide, Au_2O_3, indicated by the one experiment by Schottländer, or the auroauric oxide, Au_2O_2, derived from the data of one experiment by Krüss. The former did not heat, as Krüss[1] suggests, a sufficient length of time to expel the water from the hydrate. Moreover, the writer has shown, as stated, that water is retained at 210°. Krüss's result would have been more satisfactory if he had measured the oxygen given off by what he regarded as Au_2O_2 instead of calling the loss in weight oxygen. While he did the work with great care the existence of Au_2O_2 is doubtful.

The compound formed on a gold anode is auric hydroxide with varying amounts of water, three molecules or less. When potassium sulfate is the electrolyte a notable quantity of potassium is retained by the hydroxide, presumably as an acid potassium aurate. With sulfuric acid for an electrolyte the product contains a little basic auric sulfate which is not removed by cold water. Since ozone does not attack gold, the corrosion of the metal is not due to the ozone formed in the electrolysis, and it is probable that auric sulfate is formed by the union of sulfate ions with gold, the auric sulfate hydrolyzing at once in the dilute acid solution. The auric hydroxide formed on a gold anode under the microscope is ruby-red in color, translucent, and appears to be an aggregation of minute particles with curved surfaces. Some flat surfaces are seen which indicate crystallin structure. The anodic hydroxide and the amorphous form obtained by hydrolysis of auric nitrate or sulfate behave essentially alike when heated and neither yields auroauric oxide, Au_2O_2, or auric oxide, Au_2O_3. Auric hydroxide is reduced to the metal by hydrogen peroxide and by a solution of sodium peroxide. It may be mentioned that a fulminate forms on a gold anode in a solution of ammonium carbonate.

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

NOTES ON THE PREPARATION OF CHROMYL COMPOUNDS.

BY HARRY SHIPLEY FRY.

Received February 24, 1911.

The present paper is a résumé of some work, the object of which was the preparation of the unknown compounds, chromyl bromide and chromyl iodide. While it was only partially successful in this respect, certain note-

---

[1] *Loc. cit.*

worthy results were obtained, namely: a new reaction for the preparation of chromyl chloride; a reaction for the detection of minute traces of chromyl chloride (0.00001 g. per 1 cc. of solvent) depending upon the formation and color of chromyl bromide; the preparation and identification of the new compounds, anhydrous chromic acetate and chromyl acetate.

The interaction of the halide and the dichromate of a metal with an excess of concentrated sulfuric acid constitutes the general method of preparing either chromyl fluoride or chloride. The chromyl halide thus prepared is specifically a product in the reversible reaction represented by the equation

$$(HO)_2CrO_2 + 2HX \rightleftarrows CrO_2X_2 + 2H_2O. \quad (X = Cl \text{ or } F.)$$

The appropriation of the water by the excess of concentrated sulfuric acid prevents hydrolysis and thus renders possible the recovery of the chromyl halide by distillation.

This method cannot be extended to the preparation of chromyl bromide or iodide, since the intermediately formed hydrobromic or hydriodic acid is susceptible to oxidation by chromic and by sulfuric acid and thereby yields free bromine or iodine respectively. It follows, therefore, that a general reaction for the preparation of the chromyl halides should be conducted in anhydrous solvents and avoid the formation of halogen acids in the presence of oxidizing agents. The first reaction investigated from this standpoint was that of anhydrous potassium chromate upon acetyl chloride dissolved in carbon disulfide.

Interaction of Potassium Chromate and Acetyl Chloride.—Several reactions are theoretically possible as indicated in the following equations:

$$(1) \quad 2CH_3COCl + (KO)_2CrO_2 = 2CH_3COOK + CrO_2Cl_2;$$

$$(2) \quad 2CH_3COOK + CrO_2Cl_2 = (CH_3COO)_2CrO_2 + 2KCl;$$

$$(3) \quad 2CH_3COCl + (KO)_2CrO_2 = (CH_3COO)_2CrO_2 + 2KCl.$$

The feasibility of the first reaction would warrant its extension to the preparation of chromyl bromide or iodide by employing acetyl bromide or iodide respectively. The interaction of the products of equation (1), according to equation (2), would result in the production of a new compound, acetyl chromate or chromyl acetate, the name respectively depending upon whether the substance is regarded as a derivative of chromic acid or of acetic acid. The possibility of the direct formation of chromyl acetate is indicated in equation (3).

One-half gram-molecular quantities (according to equation 1) of anhydrous potassium chromate and acetyl chloride, in 500 cc. of anhydrous carbon disulfide, were heated to boiling upon a water-bath in a flask provided with reflux condenser. Apparently no reaction took place until a few drops (1 cc.) of glacial acetic acid were added, whereupon the mixture immediately assumed a deep red color (due to the formation of chromyl chloride) and boiled spontaneously for an hour. The contents of the flask were then poured into a Büchner filter and thoroughly washed with carbon disulfide. Aliquot portions of the filtrate, when shaken with water, yielded aqueous solutions of chromic acid which upon titration with standard ferrous ammonium sulfate solution gave the equivalent content of chromyl chloride. The quantity of chromyl chloride in the distillate was thus found to equal 3.83 per cent. of the theoretical yield required by equation (1).

The contents of the filter consisted almost entirely of unaffected potassium chromate completely covered over with a brown substance insoluble in carbon disulfide. Consequently its formation prevented complete interaction between the potassium chromate and the acetyl chloride, thereby accounting for the low yield of chromyl chloride. An aqueous solution of this brown substance gave reactions for hydrogen, acetate, and chromate ions, which would be the naturally expected products of the hydrolysis of chromyl acetate as indicated in the equation

$$(CH_3COO)_2CrO_2 + 2HOH = 2CH_3COOH + (HO)_2CrO_2.$$

Either of the above noted equations, (2) or (3), would account for the formation of chromyl acetate. The preparation of chromyl acetate through the interaction of silver acetate and chromyl chloride (to be described later) is analogous to the reaction represented by equation (2), and serves to substantiate the above assumption.

It has been noted that the interaction between acetyl chloride and potassium chromate did not occur until a few drops of acetic acid were added. Hence it is possible that the acetic acid functions catalytically according to the equations:

$$2CH_3COOH + (KO)_2CrO_2 \longrightarrow 2CH_3COOK + (HO)_2CrO_2,$$
$$(HO)_2CrO_2 + 2CH_3COCl \longrightarrow CrO_2Cl_2 + 2CH_3COOH.$$

The generation of free chromic acid would, accordingly, precede and condition the formation of chromyl chloride. Furthermore, the interaction of any given acetyl halide with chromic acid should result in the formation of the corresponding chromyl halide.

Interaction of Chromic Acid and Acetyl Chloride.—When a solution of acetyl chloride in carbon tetrachloride is added to dry pulverized chromic anhydride no change is apparent; but when a few drops of glacial acetic acid are added, the chromic anhydride dissolves with the evolution of heat, and a dark red solution of chromyl chloride is formed. The equations for the reactions involved are presumably as follows, the acetic acid functioning as a catalytic agent:

$$CrO_3 + 2CH_3COOH \longrightarrow (HO)_2CrO_2 + (CH_3CO)_2O;$$
$$(HO)_2CrO_2 + 2CH_3COCl \longrightarrow CrO_2Cl_2 + 2CH_3COOH.$$

One-eighth gram-molecular quantities of chromic anhydride and acetyl chloride, plus an excess of 10 grams of the latter reagent, in 100 cc. of carbon tetrachloride, to which was added 1 cc. of glacial acetic acid, were heated together upon a water-bath in a half-liter flask equipped with reflux condenser. When the chromic anhydride was dissolved the condenser was turned down and the contents of the flask subjected to distillation. For every 50 cc. of distillate collected there was added to the distilling flask 50 cc. of carbon tetrachloride. In this manner the chromyl chloride was completely driven over into the distillate, the total volume eventually amounting to 500 cc. Aliquot portions of the distillate on treatment with water and subsequent titration with standard ferrous sulfate solution gave data calculating to a yield of 15.96 grams of chromyl chloride, or 82.43 per cent. of the theoretical based upon the ratio CrO_3: CrO_2Cl_2. The separation of chromyl chloride from the solvent carbon tetrachloride by fractional distillation is practically impossible. The solid dark green residue in the distilling flask, weighing 8.50 grams, consisted chiefly of chromic acetate and chloride.

The interaction of chromic acid and acetyl chloride thus affords a new method of producing chromyl chloride. Analogously, chromic acid and acetyl bromide should, presumably, yield chromyl bromide.

Interaction of Chromic Acid and Acetyl Bromide.—When 12.5 grams of chromic anhydride were added to a solution of 41.0 grams of acetyl bromide in 100 cc. of carbon tetrachloride, containing 1.0 cc. of glacial acetic acid, a singular transition of colors was noted. An intense permanganate-red coloration appeared and then faded rapidly to red-brown. Treatment of the reaction mixture as described in the above preparation of chromyl chloride yielded a red distillate, the color of which vanished upon treatment with potassium hydroxide solution. The red color of the distillate was therefore due to bromine and not to any volatil chromyl compound. The quantity of bromine was determined by titrating aliquot portions of the distillate with standard sodium arsenite solution and thus found to equal 4.98 grams, or 25 per cent. of the theoretical yield based upon the assumption that chromyl bromide was formed intermediately, thereby producing the permanganate-red coloration, and then decomposed yielding the red-brown solution of free bromine. The solid green residue remaining in the distilling flask weighed 30 grams and upon analysis was found to contain 27.72 per cent. of unaffected chromic anhydride; 12.78 per cent. of chromium, combined as acetate and bromide; and 25.60 per cent. of combined bromine.

Chromyl Bromide.—The possibility of the production of chromyl bromide as an unstable compound yielding solutions of characteristic color is supported by four different reactions:

(1) If a solution of anhydrous hydrogen bromide in carbon tetrachloride is added to a small quantity of dry chromic anhydride the solution immediately assumes a permanganate-red color, which slowly fades to orange-red:

$$CrO_3 + 2HBr = CrO_2Br_2 + H_2O.$$

(2) The addition of a carbon tetrachloride solution of hydrogen bromide to a very dilute solution of chromyl chloride produces an intense permanganate-red coloration which gradually fades to orange-red:

$$CrO_2Cl + 2HBr = CrO_2Br_2 + 2HCl.$$

(3) The interaction of chromic anhydride and acetyl bromide in the presence of glacial acetic acid, as described above, may be represented by the equation

$$(HO)_2CrO_2 + 2CH_3COBr = CrO_2Br_2 + 2CH_3COOH.$$

(4) The addition of one drop of acetyl bromide to five cc. of a solution prepared by dissolving one drop of chromyl chloride in 500 cc. of carbon tetrachloride is also productive of the permanganate-red color, which vanishes in the course of five minutes:

$$CrO_2Cl + 2CH_3COBr = CrO_2Br + 2CH_3COCl.$$

The delicacy of this last reaction as a color test for minute traces of chromyl chloride (0.00001 gram per 1 cc. of solvent) was determined as follows: Solutions of chromyl chloride in carbon tetrachloride were prepared containing, per cubic centimeter, 0.01, 0.001, 0.0001 and 0.00001 gram of chromyl chloride, and numbered 1 to 4 respectively. Twenty-nine cubic centimeters of each of these solutions were placed in Eggertz tubes and to each was added one cubic centimeter of pure acetyl bromide. The colors of the solutions in the Eggertz tubes both before and after the addition of acetyl bromide are tabulated in terms of Mulliken's Color Standards[1] as follows:

Concentration of CrO_2Cl_2 solution.	Color before addition of CH_3COBr.	Color after addition of CH_3COBr.
(1) 1 cc. = 0.01 g.	Normal O R.	Violet-black.
(2) 1 cc. = 0.001 "	" R O.	Normal R.
(3) 1 cc. = 0.0001 "	" O Y.	Tint 1, V R.
(4) 1 cc. = 0.00001 "	Tint 2, Y.	" 2, O R.

Solutions of chromyl chloride have the color of bromine solutions while solutions of chromyl bromide are identical in color with solutions of iodine in such solvents as carbon disulfide, chloroform, and carbon tetrachloride.

Interaction of Chromic Acid and Acetyl Iodide.—The interaction of chromic acid and acetyl iodide was investigated in precisely the same manner as were the reactions with acetyl chloride and bromide. There was no direct evidence of the formation of chromyl iodide. The distillate contained free iodine in quantity equivalent to a yield of 19 per cent.

---

[1] S. P. Mulliken, "The Identification of Pure Organic Compounds."

of the theoretical based upon the ratio $CrO_3 : I_2$. The residue in the distilling flask contained 82.61 per cent. of the original quantity of chromic anhydride.

The quantitative results of the preceding interactions indicate that acetyl chloride is far more reactive with chromic acid than is acetyl bromide, and in turn the acetyl bromide is more reactive than acetyl iodide.

Interaction of Chromic and Acetic Anhydrides.—It has been noted that the solid residues obtained in the preceding reactions were soluble in water, the resulting solutions giving reactions for high concentrations of chromium and acetate ions. The presence of chromic acetate is accordingly inferred. Its formation may be explained thus: Since the interaction between chromic anhydride and the acetyl halide may produce acetic anhydride according to the equation

$$CrO_3 + 2CH_3COX = CrO_2X_2 + (CH_3CO)_2O,$$

and since chromic anhydride does not react with glacial acetic acid, it is possible that chromium acetate owes its formation to a secondary interaction between chromic anhydride and acetic anhydride as produced in the above equation. Chromic anhydride is soluble in acetic anhydride without decomposition, but if the resulting red solution is heated to boiling, a violent reaction ensues, the solution becomes green, and cooling is necessary. The addition of carbon tetrachloride causes the precipitation of a finely divided, light green powder. After filtration and washing with carbon tetrachloride the substance was dried at 100°, and upon analysis was found to contain 22.96 per cent. of chromium, the theoretical for anhydrous chromium acetate being 22.73 per cent.

According to the above method a given amount of chromic anhydride can be converted quantitatively to the acetate. For example, 1.6282 grams of chromic anhydride gave 3.7546 grams of anhydrous chromium acetate, the calculated yield being 3.7313 grams. Anhydrous chromium acetate is slightly deliquescent, soluble in water, alcohol, and hot acetic anhydride.

Interaction of Chromyl Chloride and Silver Acetate.—The failure to obtain a satisfactory yield of chromyl chloride through the interaction of potassium chromate and acetyl chloride was attributed to a secondary reaction between chromyl chloride and potassium acetate yielding chromyl acetate and potassium chloride. The production of the new compound, chromyl acetate or acetyl chromate, may be accomplished through the similar interaction of chromyl chloride and silver acetate, presumably according to the equation

$$CrO_2Cl_2 + 2AgC_2H_3O_2 \longrightarrow (C_2H_3O_2)_2CrO_2 + 2AgCl.$$

When a solution of chromyl chloride in carbon tetrachloride is added to powdered silver acetate, suspended in carbon tetrachloride, the red color of chromyl chloride immediately vanishes and a brown precipitate is formed. The end point of the reaction is conveniently determined by the permanency of the red color of chromyl chloride upon the addition of an excess of that reagent. The brown precipitate, after being filtered, washed with carbon tetrachloride, and dried in a vacuum desiccator, was found to be an intimate mixture of silver chloride and a brown, lustrous powder, presumably chromyl acetate. An analysis of this mixture for the content of silver chloride and of chromic anhydride, the latter being calculated as chromyl acetate, gave the following results which substantiate the formation of chromyl acetate:

	Per cent.
Silver chloride	68.79
Chromyl acetate	31.08
Total	99.87

Chromyl acetate is a deliquescent substance and is readily hydrolyzed by water, yielding chromic and acetic acids. A suitable solvent for effecting its complete separation from silver chloride has not yet been found.

A further investigation of the properties of chromyl bromide and of chromyl acetate, and an extension of the reactions herein noted to the preparation of other chromyl compounds, is in progress.

THE PREPARATION OF AMMONIUM SELENATE: A NEW METHOD.[1]

By Frank C. Mathers and Roy S. Bonsib.

Received March 1, 1911.

Introductory Statement.

The object of this research was to determin the best conditions for the preparation of ammonium selenate by the treatment of either barium selenate or lead selenate with an excess of ammonium carbonate. This reaction forms insoluble barium carbonate or lead carbonate, with the ammonium selenate and the excess of ammonium carbonate in solution. This mixture is filtered and the filtrate is evaporated. During the heating, the excess of ammonium carbonate volatilizes and any barium or lead selenate which is in solution is precipitated. This precipitate is filtered off and the pure ammonium selenate allowed to crystallize.

The only method described[2] for the preparation of ammonium selenate is the saturation of selenic acid with ammonia. This method is undesirable because pure selenic acid, itself, is difficult to prepare.

In a method[3] similar to the one described in this paper, barium selenate

---

[1] From a thesis to be submitted to the Faculty of Indiana University, for the degree of Master of Arts, by Roy S. Bonsib, 1911.

[2] Gmelin-Kraut, *Handbuch*, 1, 785 (1907).

[3] Gerichten, *Ann.*, 168, 214.