[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction of Hydrogen Peroxide with Chromic Anhydride in Dry Ethyl Acetate

BY DOUGLAS G. NICHOLSON

The chemical literature contains many references to the deep blue colored metastable compound formed when acidified chromate solutions are treated with hydrogen peroxide. Many of these references[1–6] imply that the chromium in this compound is in a valence state higher than six; while others[7–10] show quite conclusively that the chromium is present in the hexavalent state.

An investigation was undertaken to prepare and, if possible, study the properties of this peroxychromic compound in a non-aqueous medium. The solubility of chromic anhydride and hydrogen peroxide in dry ethyl acetate led to the selection of this material as the solvent for this work.

Experimental

A solution of hydrogen peroxide in ethyl acetate was prepared by shaking a mixture of 100 ml. of 30% hydrogen peroxide, 3–5 ml. of water, and 900 ml. of ice cold ethyl acetate for about fifteen minutes, allowing the liquids to separate, then carefully pouring off the acetate layer. This acetate solution of hydrogen peroxide was then dried over anhydrous copper sulfate for at least thirty minutes. After filtration, to remove the cupric sulfate, a small portion of this solution was titrated (in dilute aqueous sulfuric acid solution) with standard permanganate solution. This titration showed the peroxide content of the ethyl acetate solution to be between 0.95–0.99 normal. Upon standing for several days this solution showed no material loss in peroxide content.

From one-half to one gram of solid chromic anhydride was added to the remaining bulk of the ethyl acetate peroxide solution. The resulting intensely blue colored solution was maintained at the temperature of the ice-bath, while a solution of ammonia in absolute alcohol was added in slight excess. This alcoholic ammonia solution was prepared by adding liquid ammonia to absolute alcohol. Upon the addition of the ammonia, the intensely blue color faded leaving a water clear solution and a tan colored precipitate.

The peroxide solution was maintained in excess at all times in order to retain the chromic anhydride in combination as the blue colored peroxy compound.

The tan precipitate was carefully washed with cold ethyl acetate and dried in an atmosphere of nitrogen while retained in a vessel jacketed with dry ice. Samples of the dry material were analyzed for ammonia as well as for the chromium content.

Discussion

Since chromic anhydride unites with water forming chromic acid, it seems likely that the anhydride may unite with hydrogen peroxide in a non-aqueous medium to form a peroxy acid analogous to Caro's acid in the case of sulfur trioxide. Addition of the alcoholic ammonia solution should form an ammonium salt of this acid. The tan precipitate which formed upon addition of the ammonia was studied to evaluate some of its physical and chemical properties.

The ammonia content of the tan precipitate was determined using the standard method of absorbing the ammonia in a known volume of standard acid, then back titrating with standard alkali solution.

The chromium was determined by reduction and precipitation of chromic hydroxide, with subsequent ignition to chromic oxide; as well as by oxidation to chromate, precipitation of mercurous chromate, and ignition to chromic oxide.

On the basis that hydrogen peroxide would unite with chromic anhydride forming a peroxychromic acid thus: $H_2O_2 + CrO_3 \longrightarrow H_2CrO_5$, and that the tan precipitate would have the formula $H_2CrO_5 \cdot 2NH_3$, the calculated chromium content would be 30.95% while the ammonia content would be 20.23%. The average chromium content found by analysis was 30.93%, and the average ammonia content 20.15%.

Considerable difficulty was encountered in the analysis of the tan material due to its extremely unstable nature. Several samples took fire spontaneously during the course of weighing. Other samples gave poor results due to absorption of moisture and subsequent decomposition.

The tan colored ammonium salt dissolves in water with evolution of oxygen, forming a yellow-orange chromate solution. When added to acidic solutions it evolves oxygen with the formation of the unstable blue peroxychromic acid, and the resulting decomposition gives rise to a green chromic salt. At temperatures slightly above room temperature, the salt decomposes spontaneously

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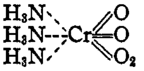
(1) Riesenfeld, *Ber.*, **41**, 3941–51 (1908).
(2) Riesenfeld, *ibid.*, **38**, 4068 (1905).
(3) Riesenfeld, *ibid.*, **47**, 548, 553 (1914).
(4) Schwarz and Giese, *ibid.*, **65B**, 871–76 (1932).
(5) Rumpf, *Compt. rend.*, **198**, 1694–7 (1934).
(6) Riesenfeld, *Chem.-Ztg.*, **32**, 914 (1908).
(7) Moissan, *Compt. rend.*, **97**, 96 (1883).
(8) Schwarz and Giese, *Ber.*, **66**, 310 (1933).
(9) Rosenheim, *Z. anorg. Chem.*, **209**, 175 (1932).
(10) Bancroft and Murphy, *J. Phys. Chem.*, **39**, 377–397 (1935).

and bursts into flame. This decomposition takes place in two stages—swelling and ignition. The particles appear to swell considerably, and finally flash rapidly leaving a residue of finely divided chromic oxide. If struck a sudden blow the material decomposes with explosive violence. If allowed to remain for some time below, or at room temperature, the material becomes more stable and behaves in much the same manner as does ammonium dichromate. X-Ray diffraction patterns show the tan colored material to have a structure quite different from that of ammonium chromate or ammonium dichromate.

The physical and chemical properties of this material resemble those described by Riesenfeld[11] for the compound chromic tetroxide triammine. The formula given this compound is



Since the molecular weight of this material would be 167, and that of $H_2CrO_5{\cdot}2NH_3$ 168, it follows that the chromium content would not be a deciding factor in the determination of structure. Since but two ammonia groups could be accounted for by accurate ammonia analysis in the case of the material prepared in this study; it is assumed that these compounds are different in chemical constitution although very similar in chemical properties.

Summary

The reaction between hydrogen peroxide and chromic anhydride has been studied using dry ethyl acetate as the solvent. A tan ammonium salt of the blue colored peroxychromic acid has been prepared. Analyses of this salt are in accord with the formula $H_2CrO_5{\cdot}2NH_3$. From this information the formula of the blue peroxychromic acid probably is H_2CrO_5 or $CrO_3{\cdot}H_2O_2$. Some physical and chemical properties of the ammonium salt have been determined.

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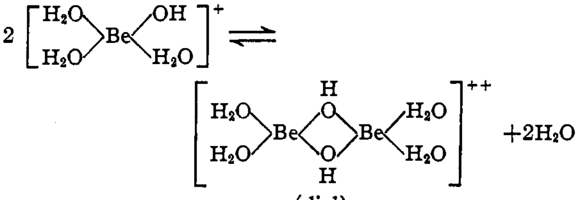
[11] Riesenfeld, *Ber.*, 41, 3536–52 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Basic Beryllium and Complex Beryllate Hydrosols; an Additional Contribution to the Concept of Polyolated and Polyoxolated Structures

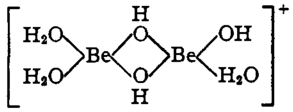
BY ARTHUR W. THOMAS AND HOKE S. MILLER

In previous publications from this Laboratory the properties of certain colloidally dispersed metallic "oxides" have been readily explained according to the concept that the micelles are polyolated and/or polyoxolated structures.[1] Application of this theory which involves the Werner–Pfeiffer ideas of hydrolysis and olation together with Stiasny's concept of the oxolation of ol groups, has produced a new and fundamental knowledge of beryllium "oxide" hydrosols.[2] Accepting the coördination number of 4 usually assigned to beryllium, the formation of a diol from triaquo monohydroxo beryllium ion would be



(diol)

The dissociation of an aquo group in this dinuclear diol ion, or the replacement of one of its aquo groups by OH would produce an ion such as



According to the theory, two of these in turn can olate, the result in this case being a tetranuclear olated ion. Since removal of H^+ ion favors olation, one would expect increase in size of the olated ions when a solution of a beryllium salt is made increasingly basic. Increases in basicity, however, and especially elevation of temperature

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[1] (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, 35, 27 (1931); (b) A. W. Thomas and A. P. Tai, THIS JOURNAL, 54, 841 (1932); (c) A. W. Thomas and F. C. von Wicklen, *ibid.*, 56, 794 (1934); (d) A. W. Thomas and R. D. Vartanian, *ibid.*, 57, 4 (1935); (e) A. W. Thomas and C. B. Kremer, *ibid.*, 57, 1821, 2538 (1935); (f) A. W. Thomas and H. S. Owens, *ibid.*, 57, 1825, 2131 (1935).

[2] For convenience, those hydrosols in which the beryllium is in the cationic micelle will be called *basic beryllium* hydrosols and the name *complex beryllate* will signify hydrosols in which the beryllium exists in the form of an anionic micelle.