entropy of both forms determined. The entropy difference of the two forms obtained from the heat capacities agrees, within the small experimental uncertainty, with that from the heat of transition, as expected from the third law.

The heat capacity at constant volume has been calculated for rhombic sulfur, and its variation with temperature compared with the "*n* formula" of Lewis and Gibson.

BERKELEY, CALIF. RECEIVED NOVEMBER 10, 1936

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

The Reaction of Titanium Tetrachloride with Hydrogen Peroxide in Dry Ethyl Acetate

BY DOUGLAS G. NICHOLSON AND M. ANTOINE REITER

Several references concerning addition compounds of titanium tetrachloride and neutral molecules have appeared in recent chemical literature.[1–4] In view of these references, it seemed quite probable that titanium tetrachloride would unite with hydrogen peroxide in a non-aqueous medium to form a similar addition compound. Since both substances have an appreciable solubility in dry ethyl acetate, this material was selected as the solvent in the investigation.

Experimental

The solution of hydrogen peroxide in dry ethyl acetate was prepared in a manner previously described.[5] This peroxide solution was added slowly to an ice cold solution of titanium tetrachloride in ethyl acetate. As it was added, the titanium solution became orange to orange-red in color, and, with continued addition of the peroxide, a white crystalline precipitate formed. After thoroughly washing this precipitate with cold dry ethyl acetate, samples were analyzed in an effort to determine the chlorine to titanium, as well as the hydrogen peroxide to titanium, ratios present. Efforts to determine the actual composition of the white precipitated material proved unsatisfactory, because of its extremely unstable nature.

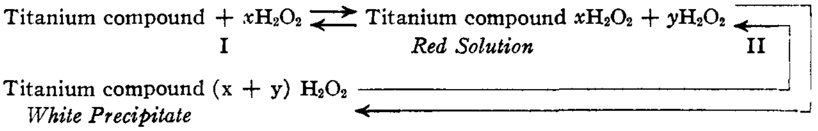
Data

Analysis of fourteen different samples of the material showed the average ratio of chlorine to titanium content to be 1 to 1.05 with an average deviation of 0.01 and a maximum deviation of 0.03. The average hydrogen peroxide to titanium ratio obtained from the same sample was 1 to 1.01 with an average deviation of 0.022 and a maximum deviation of 0.05.

Discussion

The color change encountered, as the solution of hydrogen peroxide in acetate was added to the titanium tetrachloride solution, followed by the formation of the white precipitate, seemed to indicate that more than one compound of these two substances had been formed. If some of the red colored solution was allowed to remain in an open vessel for some time the intensity of the color gradually faded.

In view of these facts the following equilibria are postulated:



The presence of a trace of moisture caused the white precipitate to become orange-red in color. Thus, it seems quite probable that moisture tends to shift the right-hand equilibrium (II) toward the left. All attempts to remove the last traces of acetate solution from the white precipitate resulted in its partial decomposition, in which the surface of the material became yellow to orange in color. This white precipitate was very soluble in water, producing the yellow to orange typical peroxytitanate solutions.

Analysis of the titanium tetrachloride used showed it to be very pure. The apparent loss of three atoms of chlorine per molecule of titanium tetrachloride can be attributed to either or both of two factors: namely, (1) oxidation to free chlorine by the hydrogen peroxide present, and

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(1) Chrétien and Varga, *Compt. rend.*, **201**, 558 (1935).

(2) Ralston and Wilkinson, THIS JOURNAL, **50**, 258 (1928).

(3) Holtje, *Z. anorg. allgem. Chem.*, **190**, 241 (1930).

(4) Karantassis, *Compt. rend.*, **194**, 461 (1932).

(5) Nicholson, THIS JOURNAL, **58**, 2525 (1936).

(2) partial decomposition of the ethyl acetate, producing ethyl chloride and titanium acetate. The second factor seems more probable, since refluxing a solution of titanium tetrachloride in ethyl acetate resulted in a partial loss of chlorine. No explanation is made concerning the fact that but three of the chlorine atoms had been replaced.

Summary

The reaction between titanium tetrachloride and hydrogen peroxide in dry ethyl acetate has been studied in some detail. A white compound containing titanium, chlorine and hydrogen peroxide in the approximate ratio of 1:1:1 can be prepared. This material is unstable toward water, as well as slightly elevated temperatures. In decomposing, it becomes yellow-orange in color. It is very soluble in water, producing orange-red clear solutions.

URBANA, ILL. RECEIVED SEPTEMBER 16, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Use of Iodine and of Potassium Iodate as Volumetric Oxidizing Agents in Solutions Containing Mercuric Salts. I. The Effect of Mercuric Salts upon the Stoichiometry of Various Oxidation–Reduction Reactions. New Procedures for the Titration of Arsenite and Antimonite with Standard Solutions of Iodine or of Potassium Iodate

BY N. HOWELL FURMAN AND CLARK O. MILLER[1]

Introduction

The stoichiometry of certain reactions between powerful oxidizing agents and halides, or between the halogens or their oxy acids and reducing agents, is modified when mercuric salts are present in excess. Several situations may arise, depending upon particular halide that is present, the total acidity and the relative concentrations of mercuric salt, halide and acid. There are two principal kinds of behavior which are of interest here: (a) the failure of free halogen to appear when a limited quantity of a halide, an excess of mercuric ion and an excess of nitric, sulfuric or perchloric acid is treated with a powerful oxidizing agent, as for example, potassium bromate or permanganate; (b) the reduction of bromate to bromide, of iodate to iodide and of iodine to iodide by various reducing agents in the presence of an excess of mercuric salt and acid. The former case will be reviewed briefly with presentation of some experimental observations, and the latter will be treated more fully, especially with regard to the reactions of potassium iodate and of iodine and the application of these reactions in volumetric analysis.

(a) The Non-appearance of Free Halogen when Mercuric Salt is Present in Excess.—G. F. Smith[2] described a series of experiments in which solutions of bromides, chlorides or iodides containing mercuric nitrate or perchlorate and the corresponding free acid were heated with an excess of potassium bromate solution. He reported that no reaction was observed and that the solution after the heating liberated an amount of iodine equivalent to the original potassium bromate when an excess of potassium iodide was added to the cold solution. He found similar results for mixtures of a bromide, mercuric salt, potassium permanganate and acid, and attributed this "preventive effect" to the formation of slightly ionized mercuric halides.

We have repeated experiments of the type described by Smith upon mixtures containing potassium iodide, excess of mercuric sulfate and sulfuric acid. Potassium bromate or permanganate was added. After heating there was no loss of oxidizing power toward potassium iodide. Reactions had occurred, however, for the potassium bromate had been reduced and an equivalent amount of iodate had been formed, as was indicated by the presence of bromide and iodate in mixtures that were examined qualitatively and by quantitative experiments. The potassium permanganate was decolorized and iodate was formed. Smith's explanation[2] of the "protective action" of mercuric salts is contradicted by these qualitative experiments.

In the case of iodide, which is of principal inter-

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[1] Present address, Case School of Applied Science, Cleveland, O.

[2] G. F. Smith, THIS JOURNAL, 45, 1417 (1923).