Reaction of Hydrogen Peroxide with Titanium (IV) at Different pH Values*

By Motoshichi MORI, Muraji SHIBATA, Eishin KYUNO and Syu ITO

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Titanium (IV) gives the well-known orange coloration by the action of hydrogen peroxide on an acidified solution, and the production of color has been shown by Jahr and his co-workers[1] to be due to the $(TiO_2 \cdot aq)^{2+}$ ion. On the other hand a yellow compound is formed when ammoniacal hydrogen peroxide is added to a solution of a titanyl salt, and this compound has been regarded by Schwarz and Giese[2] as ortho-pertitanic acid, $Ti(OH)_3(OOH)$. Recently, Babko and Valkova[3] found that the orange color in an acidified solution faded away with the decreasing of the acidity and assumed the existence of different ion-species in solutions with different pH values.

$$\text{pH below 3,}\quad Ti^{4+}+H_2O_2 \rightleftarrows \underset{\text{(orange)}}{Ti(H_2O_2)^{4+}}$$

$$\text{pH 3–6,}\quad Ti^{4+}+H_2O_2 \rightleftarrows \underset{\text{(colorless)}}{Ti(HO_2)^{3+}}+H^+ \text{ or}$$

$$Ti^{4+}\quad H_2O_2 \rightleftarrows Ti(O_2)^{2+}+2H^+$$

We have carried out a series of experiments with a view to finding out whether this assumption is correct.

Early in this work, our attention was attracted by a noteworthy fact that at least four different ion-species exist in solutions whose pH range 1 to 13. The first species, orange in color, appears in solutions of high acidity ($pH<2$), the second, the bright yellow kind, in solutions of lower acidity (pH 3–6), the third, the pale yellow kind, in slightly alkaline solutions ($pH<9$), and the fourth, which is colorless, exists in more strongly basic solutions ($pH>10$). Proceeding with our experiments we obtained various kinds of information about the behavior of these ions, and also devised a new method of volumetric analysis of titanium.

Experimental

Materials.—Stock solution of titanyl sulfate was prepared by carbonate-fusion and acid-digestion of titanium dioxide free from iron. Other reagents used were of analytical grade.

Measurement.—A Beckman Model DU Spectrophotometer and an Ito Spectrophotometer were used to obtain the absorptiometric data and all the measurements were made in matched 1.0 cm. cells. The Molar extinction coefficient was calculated from the titanium content of the solution.

Adjustment of pH was made with a buffer solution and the measurement of pH was made with a Mitamura pH meter. The content of structural water in the solid sample was estimated from the loss of weight of the sample by drying at 400°C by using a Shimazu Thermano Balance. The titanium content was determined by the usual gravimetric or colorimetric method depending upon the sample taken. Active oxygen was volumetrically estimated by using a standard permanganate solution. Molar ratio of hydrogen peroxide to titanium in colored solution was determined by the method of continuous variation. The analysis of the sulfate ion was made gravimetrically and that of potassium ion, alkalimetrically.

Results and Discussion

Appearances of Different Species of Ion with Changes of pH.—When an aliquot of the yellowish solution obtained by neutralizing titanyl sulfate solution with potassium carbonate and then adding a few drops of hydrogen peroxide was introduced into each of a number of buffer solutions, the resulting mixtures showed different colors ranging from orange to colorlessness according to the pH of each solution. The optical density of the colors was measured at 415 mμ, and the values were plotted against the pH (Fig. 1). The curve has its first point of inflexion in the range of pH 1 to 2, its second in that of pH 6 to 7 and the third, which is not so clear as the others, near pH 9. This information indicates the probability that there are at least four different ion-species, each of which exists in solutions having pH value within a certain range. Additional evidence for this was obtained through the measurement of absorption spectra of the solutions (Fig. 2). As shown in Fig. 2 the maximum on each absorption curve is shifted to the short wavelength side with increase of pH. Namely, the species arising from solutions with pH 1.5, 4.2 and 8.6 show the absorption maximum at 400, 330 and 313 mμ respectively. This may be attributed to co-ordination binding

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[1] H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry", D. Van Nostrand Co., Inc., N.Y., (1952), p. 375.

[2] Schwarz und Giese, *Z. anorg. Chem.*, 176, 209 (1928).

[3] *C. A.*, 42, 44836 (1948).

of the peroxide ion, O_2^{2-}, with the titanium ion since a certain μ-peroxo-cobalt (III) complex has a similar maximum at 330 mμ[4]. In a strongly alkalified solution (pH 13.0), the absorption band lies in far shorter region and has no maximum. This may be considered to be due to weaker co-ordination binding of the peroxide ion. Thus, it may be said that at least four different species exist separately in specified pH regions (i. e. pH<2, 3–6, 7–9 and 10<pH). Hereafter these species will be denoted by "A", "B", "C" and "D" respectively.

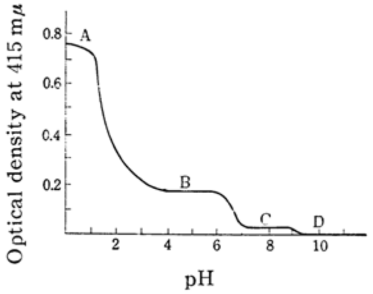

Fig. 1. Light absorption of the Ti(IV)-H_2O_2 system vs. pH. Concentration of Ti, approximately 1×10^{-3} mol./l.

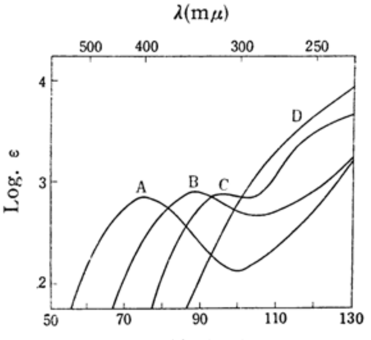

Fig. 2. Absorption spectra of various species.

A. at pH 1.5	B. at pH 4.2
C. at pH 8.6	D. at pH 13.0

Types of Behavior and Formulas.—In order to determine the chemical compositions of "B" and "C", continuous variation studies were carried out, and the results are shown in Fig. 3. In both species, titanium appears to combine with only one molecule of hydrogen peroxide. By the way, it has been well known that in highly acidified solutions they react in the one-to-one molar proportion[5].

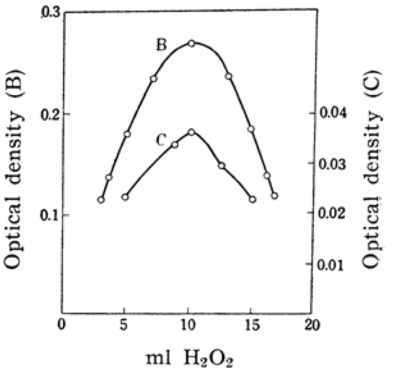

Fig. 3. Curves for graphical determination of ratio of H_2O_2 to Ti (λ=415 mμ). Concentrations of $TiOSO_4$ and H_2O_2, 7.2×10^{-3} M. Total volume, 20 ml.

Further experiments were conducted to isolate solids from the solutions containing each species of ions. Addition of a large amount of alcohol resulted in precipitation of solids. Namely, in the presence of potassium sulfate an orange-colored solid was isolated from the solution containing "A", and a yellow solid, from the solution containing "B". From solutions containing "C" and "D" a pale yellow and a white compound were isolated respectively in the absence of sulfate. After being washed with water, alcohol and finally ether, each precipitate was dried over sulfuric acid and kept for analyses. For convenience' sake they are denoted by A_1, B_1, C_1 and D_1. A_1 and D_1 were easily soluble, B_1 was slightly soluble in water, but C_1 was insoluble in water. All the solids were soluble in mineral acids. C_1 was stable at room temperature but B_1 underwent gradual decomposition. A_1 and D_1 were hygroscopic. Molar ratios of the various components to titanium were as follows.

For A_1: O, 1; H_2O, 3; SO_4, 2; K, 2; assumed composition, $K_2O\cdot TiO_3\cdot 2SO_3\cdot 3H_2O$. For B_1: O, 1; H_2O, 2.5; SO_4, 2.5; K, 4; $4K_2O\cdot Ti_2O_6\cdot 5SO_3\cdot 5H_2O$. For C_1: O, 1; H_2O, 2; $TiO_3\cdot 2H_2O$. For D_1: O, 2; H_2O, 1; K, 2; $K_2O\cdot TiO_4\cdot H_2O$.

On standing at room temperature the solution containing "A" acquired no turbidity, but pale yellow precipitates appeared in the solution containing "C" after standing for a little while, and on standing for several days the solutions containing "B" and "D" yielded a bright yellow and a pale yellow precipitate respectively. On heating them to about 70°C, however, the precipitation was quickly completed. After being washed with water, alcohol and ether, they were dried over sulfuric acid and kept in a vacuum desiccator for analysis. These are denoted

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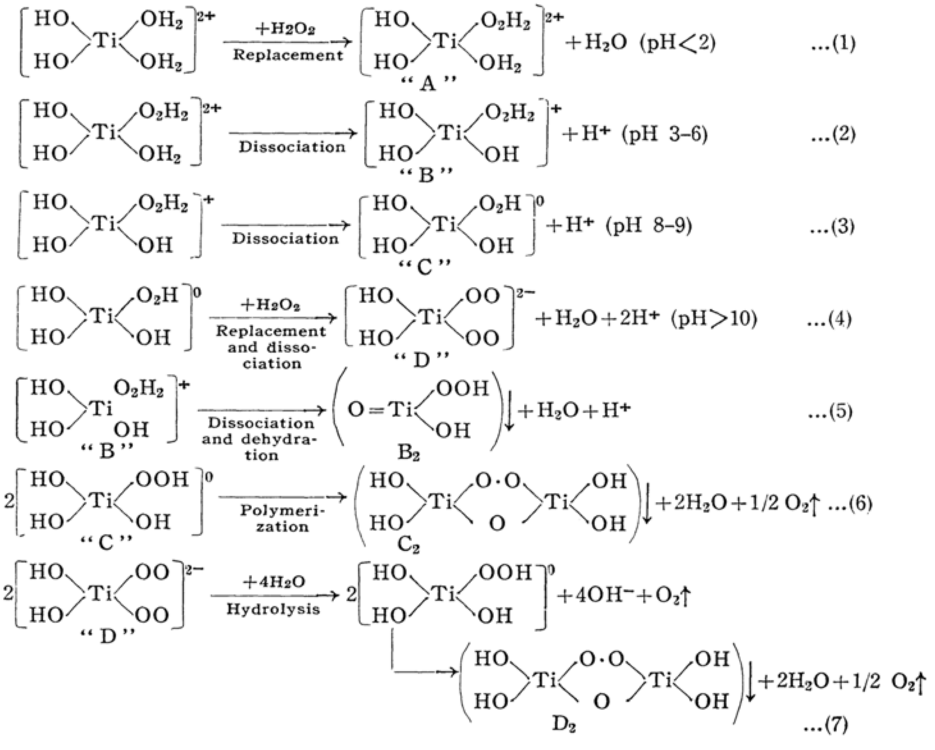
[4] S. Yamada, Y. Shimura and R. Tsuchida, This Bulletin, **26**, 72 (1953).

[5] Y. Shaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

by B_2, C_2 and D_2. All the precipitates were insoluble in water and soluble in 3 N sulfuric acid. The analytical results were as follows.

For B_2: O, 0.9; H_2O, 1; assumed composition $TiO_3 \cdot H_2O$. For C_2 and D_2: O, 0.5; H_2O, 1; assumed composition, $Ti_2O_5 \cdot 2H_2O$.

Now, we are in a position to discuss the reactions taking place in solutions consisting of the titanium (IV)-hydrogen peroxide system. In addition to the absorptiometric and analytical results, the types of behavior of the species toward ion-exchangers are also useful for this discussion. Namely, "A" and "B" were held on a cation exchanger in Na-form (i. e. positively charged) and "D" was held on an anion exchanger in Cl-form (i. e. negatively charged), but "C" passed through both exchangers (i. e. uncharged). Thus, assuming that the co-ordination number of tetravalent titanium is four and that a hydrogen peroxide molecule can unite with the central ion through co-ordination linkage, the reactions involved may be represented as follows:



Among the hypothetical formulae, $[Ti(OH)_2(H_2O)(H_2O_2)]^{2+}$ is substantially identical with $(TiO_2 \cdot aq)^{2+}$, and its double salt $K_2SO_4 \cdot [Ti(OH)_2(H_2O)(H_2O_2)]SO_4$ is also identical with $K_2(TiO_2)(SO_4)_2 \cdot 3H_2O$[1]. The chemical formulae of B_1, C_1 and D_1 are presumed to be $4K_2SO_4 \cdot [Ti(OH)_3(H_2O_2)]_2SO_4$, $[Ti(OH)_3(O_2H)]$ and $K_2[Ti(OH)_2(O_2)_2]$ respectively.

Furthermore, the precipitation reactions taking place during the standing or heating of the solutions, may be represented by the following equations.

New Volumetric Analysis of Titanium

Procedure.—By means of a pipet, transfer a 10 ml. portion of the sample solution containing about 10 mg. of titanium (IV) to each of 300-ml. Erlenmeyer flasks, dilute them to about 150 ml. with distilled water and then add a saturated solution of potassium bicarbonate until each solution becomes alkaline and a white precipitate appears. Carefully add a few drops of 30% hydrogen peroxide; then the precipitate will be redissolved and the solution will become yellowish in color. Stand them on a water-bath in the neighborhood of 80°C until effervescence ceases (about two hours). During the time a pale yellow precipitate will separate out. Cool the contents to room temperature and dissolve the precipitate by adding about 50 ml. of 6 N sulfuric acid and standing the mixture about half an hour. Finally, titrate each of the orange-colored solutions with a 0.1 N permanganate solution by using a microburette. One ml of the 0.1 N solution corresponds to 0.00479 g. of titanium.

Discussion

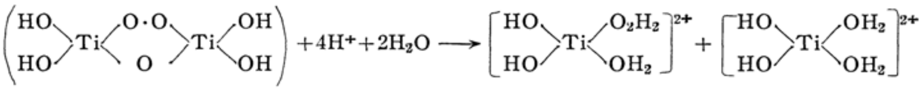
Some of the results obtained by the procedure described above are given in Table I, which clearly shows that the procedure is

TABLE I

ANALYSIS OF TITANIUM

Expt. No.	0.1 N $KMnO_4$ (f=0.9763) ml.	Ti Found mg.	Ti Present mg.	Expt. No.	0.1 N $KMnO_4$ (f=0.9763) ml.	Ti Found mg.	Ti Present mg.
1	1.630	7.62	7.48	6	10.02	46.84	48.15
2	1.610	7.53	〃	7	10.54	49.27	〃
3	1.605	7.50	〃	8	10.19	47.64	〃
4	1.625	7.60	〃	9	10.40	48.62	〃
5	1.610	7.53	〃	10	11.30	52.83	〃

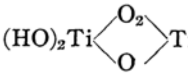
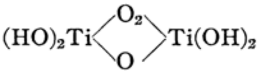
suited for the determination of titanium in quantities of the order of 10 mg. This method is based on the fact that when an alkaline solution containing a titanyl salt and hydrogen peroxide is heated, a pale yellow compound is formed in which the molar ratio of active oxygen to titanium is one to two. (Reaction (6)). By being dissolved with sulfuric acid, this compound decomposes into two components;


...(8)

Accordingly, it may be said that the reaction of hydrogen peroxide with a permanganate is applied to this method. Incomplete removal of the oxygen produced by reaction (6) and further decomposition of $[Ti(OH)_2(H_2O)(H_2O_2)]^{2+}$ into the hydrous oxide may interfere with the accuracy of the analysis and long and gentle heating on a water-bath and dissolution of the precipitates without heating should be resorted to in order to avoid these sources of error.

Summary

Reaction of hydrogen peroxide with titanium(IV) has been investigated over the range of pH 0 to 13. Below pH 2 this reaction gives orange-colored ion-species, $[Ti(OH)_2(H_2O)(H_2O_2)]^{2+}$ or $(TiO_2\cdot aq)^{2+}$. In the range of pH 3 to 6 formation of a yellow species is observed and its chemical formula is presumed to be $[Ti(OH)_3(H_2O_2)]^+$. Existence of a species different from the above is indicated by the pale yellow color observed in the region of pH 7 to 9. This species is very unstable unless a large excess of hydrogen peroxide is present, and its chemical formula is presumed to be $[Ti(OH)_3(OOH)]^0$. At higher pH values (10<pH), the reaction mixture is colorless, and presumably contains $[Ti(OH)_2(O_2)_2]^{2-}$. All the tentative formulae of these species are based on the composition of isolated salts, the absorption spectra of the solutions etc. A solution containing $[Ti(OH)_2(H_2O)(H_2O_2)]^{2+}$ remains unchanged but a solution containing $[Ti(OH)_3(H_2O_2)]^+$ gives a yellow precipitate $TiO(OH)(OOH)$, and one containing $[Ti(OH)_3(OOH)]^0$ or $[Ti(OH)_2(O_2)_2]^{2-}$ gives a pale yellow compound


$(HO)_2Ti{<}\genfrac{}{}{0pt}{}{O_2}{O}{>}Ti(OH)_2$, when left for a while at room temperature or more quickly when heated on a water-bath. The precipitation reaction of 
$(HO)_2Ti{<}\genfrac{}{}{0pt}{}{O_2}{O}{>}Ti(OH)_2$ is taken advantage of in a new volumetric analysis suited for determination of titanium in quantities of the order of 10 mg.

Department of Chemistry, Faculty of
Science, Kanazawa University
Kanazawa