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## Hydrolysis Products of Tungstates

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Aqueous suspensions, containing 0.2 *M* ammonium or sodium tungstate and different amounts of one of HCl, HNO<sub>3</sub>, or H<sub>2</sub>SO<sub>4</sub>, were subjected to aging at room temperature. The resulting products were examined by means of X-ray powder diffraction. The formation of 5(NH<sub>4</sub>)<sub>2</sub>O·12WO<sub>3</sub>·11H<sub>2</sub>O and hydrates of tungstic oxide takes place, depending mainly on the pH. The presence of sulfate was found to hinder the crystal growth of hydrates of tungstic oxide except for that of H<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O.

### INTRODUCTION

When alkaline solutions of normal tungstates (R<sub>2</sub>WO<sub>4</sub>), such as Na<sub>2</sub>WO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub>, are made neutral or acidic, the tungsten (VI) ions are hydrolyzed to form precipitates. It is known that hydrates of paratungstates (3R<sub>2</sub>O·7WO<sub>3</sub> or 5R<sub>2</sub>O·12WO<sub>3</sub>),<sup>1-3</sup> metatungstates (R<sub>2</sub>O·4WO<sub>3</sub>)<sup>3</sup> and tungstic oxide (WO<sub>3</sub>)<sup>4</sup> are obtained by selecting the pH, temperature and W(VI) ion concentration.

When aqueous suspensions, containing different amounts of HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> and either 0.2 *M* ammonium or sodium tungstate, were subjected to aging at room temperature, various precipitates, such as 5(NH<sub>4</sub>)<sub>2</sub>O·12WO<sub>3</sub>·11H<sub>2</sub>O, and different hydrates of oxide, were formed as a crystalline one. The chemical compositions and crystal structures of the aging products formed at various pH values will be reported.

### EXPERIMENTAL

Two stock solutions were prepared by dissolving 1.0 mol of H<sub>2</sub>WO<sub>4</sub> in 1.0 *l* of 0.5 *M* NH<sub>4</sub>OH or 1.0 mol of Na<sub>2</sub>WO<sub>4</sub> (each analytical grade) in 1 *l* water. To 20.0 *ml* portions of each solution, one of 4 *M* HCl, 4 *M* HNO<sub>3</sub>, or 2 *M* H<sub>2</sub>SO<sub>4</sub> was added in different quantities. The total volume of each suspension was made 100.0 *ml* with water in a polyethylene bottle (150 *ml*). A number of such suspensions, each containing 0.2 *M* W(VI) ions, were subjected to aging at 25°C for 50 h. The details of the procedure of aging were previously described.<sup>5</sup>

After the pH of suspensions had been determined with a Horiba-Hitachi electrode pH meter, the aging products were separated from the solution by filtration, washed with water and then dried at room temperature on absorbent paper.

The samples thus obtained were examined by means of X-ray powder diffraction using CuK $\alpha$  or FeK $\alpha$  radiation.

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## RESULTS AND DISCUSSION

When an aqueous solution of  $\text{HNO}_3$  was added to a solution of ammonium tungstate containing excess  $\text{NH}_4\text{OH}$ , a whitish precipitate was formed at pH 8, the pH of the suspension being decreased as shown in Fig. 1. The titration curve was obtained by slowly adding 4 M  $\text{HNO}_3$  to 200 ml aqueous solution containing 100.0 ml of the stock solution at 25°C with stirring. The pH decreases suddenly with addition of 65–75 ml of  $\text{HNO}_3$  to a point N of discontinuity. As the pH decreased with addition of  $\text{HNO}_3$ , the dissolution of most precipitate occurred in the  $4 > \text{pH} > 2$  range, and at pH 2 a precipitate again began to be formed.

The point N is considered to be the point of neutralization of  $\text{NH}_4\text{OH}$ , which has been present in excess amount, with 4 M  $\text{HNO}_3$ . The stock solution is estimated from Fig. 1 to contain 1.4 M excess  $\text{NH}_4\text{OH}$ . The pH value of the point N slightly increased with the time palse as a result of the dissolution of a slight amount of the precipitate.

When the suspensions, containing 0.2 M W(VI) ions and different amounts of acids, were subjected to aging, the formation of a precipitate took place in the suspensions with  $4 < \text{pH} < 8$  containing  $\text{NH}_4^+$  ions. As the pH of the suspension was decreased with the increase in the amount of acid, the amount of products increased. However, it began to decrease at pH 6, becoming negligible at pH 4. Optical-microscopic and X-ray diffraction examinations showed that the aging products, obtained in the  $8 > \text{pH} > 4$  range, consist of needle-like particles (5–10  $\mu\text{m}$  in length) with the same crystal structure as that of  $5(\text{NH}_4)_2 \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$ ,<sup>6)</sup> irrespective of the kind of the acid used. In the present experiments, sodium paratungstates were not obtained because of the small W(VI) ion concentration (=0.2 M).

The formation of whitish or yellowish precipitates took place in the suspensions with  $\text{pH} \leq 2$ , containing excess HCl and ammonium or sodium tungstate. Increasing the concentration of excess HCl accelerated the formation of the yellowish precipitate and increased its yield.

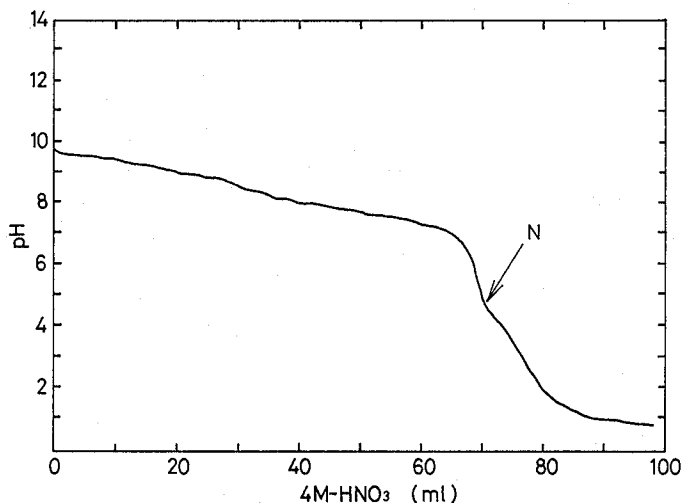


Fig. 1. Titration curve of 0.1 M ammonium tungstate with 4 M  $\text{HNO}_3$  at 25°C.

The aging products were found by X-ray diffraction examination to consist of one of phase B (Fig. 2(b)) or D(e), and mixtures of phases A, B, C, and D. The pH value required for the formation of phases A, B, C, and D decreases in this order as seen in Fig. 2. In the presence of  $\text{NH}_4^+$  ions, an amorphous precipitate was formed besides phases B, C, and D in the pH range for the formation of phase A described above. X-ray diffraction data of phase A in the mixture (Fig. 2(a)) are similar to those of  $\text{Na}_2\text{O} \cdot (\text{WO}_3 \cdot 1/2\text{H}_2\text{O})_{20-40}$ ,<sup>7)</sup> whereas X-ray diffraction data of phases C and D were identical with those of  $\text{H}_2\text{WO}_4$ <sup>8)</sup> and  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ ,<sup>9)</sup> respectively. The product of phase A is estimated to be  $\text{H}_2\text{W}_2\text{O}_7$  (or  $\text{WO}_3 \cdot 1/2\text{H}_2\text{O}$ ) having a cubic crystal structure with  $a_0$  6.41 Å as shown below (Fig. 3) and the product of phase B might be  $\text{WO}_3 \cdot n\text{H}_2\text{O}$  ( $0.5 < n < 1$ ).

When  $\text{H}_2\text{SO}_4$  was used in place of HCl or  $\text{HNO}_3$ , the precipitate of  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  was formed in the strongly acidic suspensions containing  $\text{NH}_4^+$  ions, whereas the precipitates, formed in the pH range for the formation of phases A, B, and C, were amorphous-like.

In order to study the effect of aging temperature on the products, similar experiments were carried out at 50 and 70°C with suspensions containing ammonium tungstate and different amounts of an acid— $\text{HNO}_3$ , HCl, or  $\text{H}_2\text{SO}_4$ . In the  $8 > \text{pH} > 4$  range,  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$  and  $5(\text{NH}_4)_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ <sup>10)</sup> were formed at 50 and 70°C, respectively, irrespective of the kind of the acid used. In the  $\text{pH} < 0.05$  range,  $\text{H}_2\text{WO}_4$  was formed at 50 and 70°C. In the intervening pH range, the products of phase A (Fig. 3) were obtained at 50 and 70°C in the presence of  $\text{SO}_4^{2-}$  ions, whereas

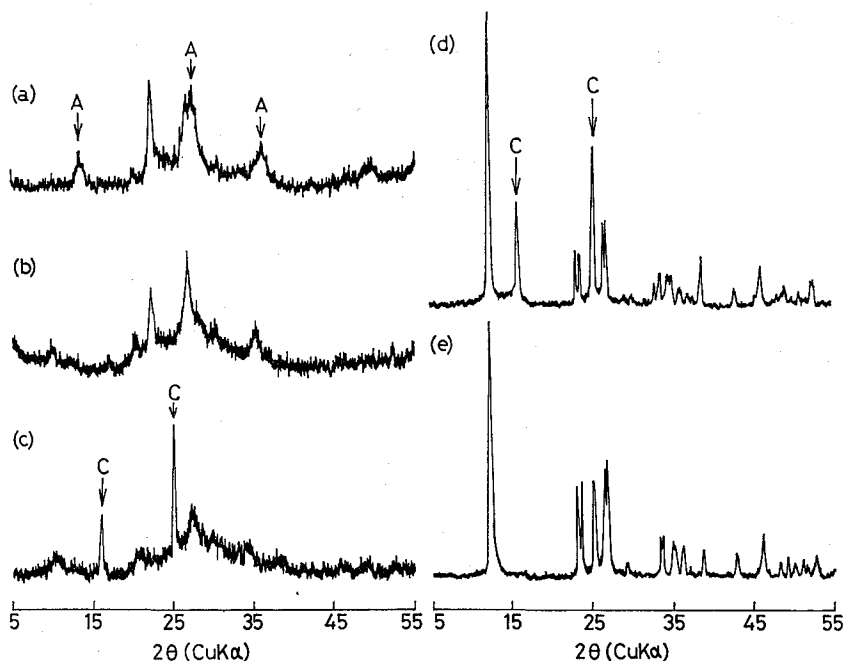


Fig. 2. X-ray diffraction patterns of the aging products obtained at pH 1.43 (a), 1.30 (b), 0.29 (c), 0.16 (d), and 0.05 (e) in the absence of  $\text{NH}_4^+$  ions. Arrows in (a), (c), and (d) indicate the main peaks caused by the presence of each phase.

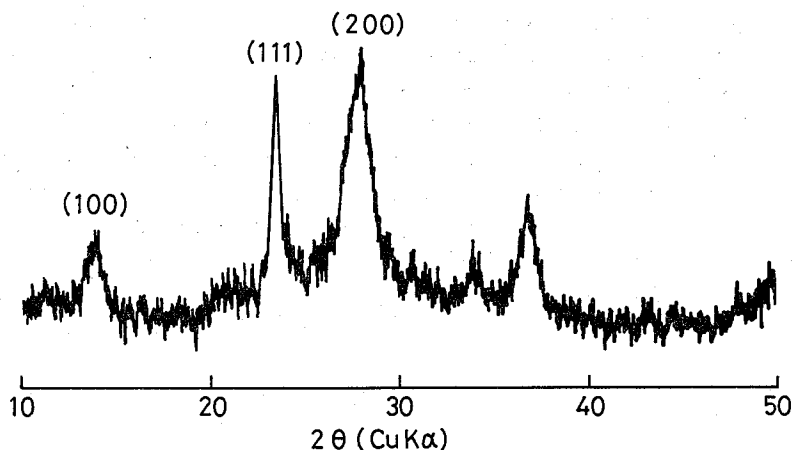


Fig. 3. X-ray diffraction pattern of the product of phase A obtained at 50°C in the suspension with pH 2 containing  $\text{SO}_4^{2-}$  ions.

in the presence of  $\text{Cl}^-$  or  $\text{NO}_3^-$  ions the products of phase B were obtained in spite of the rise of aging temperature.

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