Amorphous and Crystalline Peroxopolytungstic Acids Formed from Tungsten and Hydrogen Peroxide

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Synopsis. Peroxopolytungstic acids, $WO_3\cdot xH_2O_2\cdot yH_2O$ $(0\leqq x\leqq 1)$, formed directly from tungsten and hydrogen peroxide are found to be crystalline or amorphous depending on x.

A tungsten powder dissolves vigorously in a hydrogen peroxide (H_2O_2) aqueous solution.[1,2] A systematic study on the products obtained from the aqueous solution with various peroxide ion (O_2^{2-}) to W molar ratio showed that an amorphous or crystalline solid of peroxopolytungstic acids could be obtained depending on the molar ratio. This note presents the synthesis for and some characteristics of various peroxopolytungstic acids formed directly from W and H_2O_2.

After W was dissolved in an H_2O_2 solution, the H_2O_2 in the solution was catalytically decomposed stepwise with a platinized platinum net, then the solution was dried under blown air at room temperature to leave solids. The peroxo content in the solids obtained by this way was related to the H_2O_2 concentration in the solution just before drying, as shown in Fig. 1. Here, the H_2O_2 and W concentrations in the original solutions were varied as shown in the figure legend. The H_2O_2 concentration in solutions and peroxo content in solids were determined by a titration using a $KMnO_4$ solution.

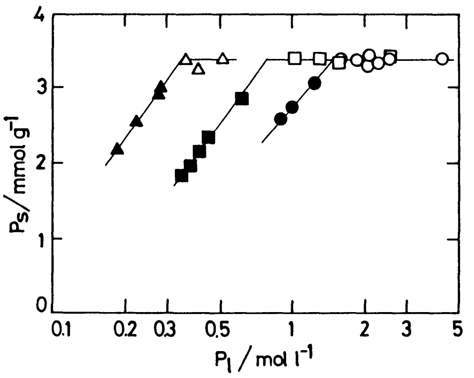

Fig. 1. Formation conditions for IPA and XW.
P_l: H_2O_2 concentration in the solution just before drying, P_s: Peroxo content in the obtained solids. Open symbols stand for XW and closed symbols for IPA. H_2O_2 and W concentrations in the starting solutions are 10 and 1.45 mol l^{-1} for circles, 5 and 0.79 mol l^{-1} for rectangles, and 1.7 and 0.35 mol l^{-1} for triangles.

Despite decrease in the H_2O_2 concentration in the solution down to some value, the peroxo content for the solids remained constant at 3.39±0.07 mmol g^{-1}. The solids were crystalline, which was confirmed by XRD. Some *d*-values are shown in Table 1. The crystal, XW, was insoluble in water or in an H_2O_2 solution. As H_2O_2 decomposition proceeded to pass through the point where a peroxide ion to tungsten molar ratio in the solution was approximately 1, an amorphous substance, IPA, was given instead of XW. A further decrease in H_2O_2 concentration in the solution allowed precipitation to take place, which is not shown in Fig. 1. The precipitate was amorphous. When the peroxo content in solid was decreased to 0, crystalline H_4WO_5 ($WO_3\cdot 2H_2O$) was obtained.

To determine the composition for the solids, a thermal weight change was measured using TGA. The XW exhibited two discrete weight loss steps and finally changed to WO_3 at 398 °C. The first weight loss at approximately 110 °C caused XW to turn into another crystal, which we call XW′. Some *d*-values are shown in Table 1. The second weight loss at approximately 200 °C changed XW′ to an amorphous substance. On the the other hand, IPA showed indistinct weight loss steps and changed to WO_3 at 428 °C.

The peroxo content and the thermal weight change between rt and 500 °C gave the experimental formula as $WO_3\cdot xH_2O_2\cdot yH_2O$. It was found that XW had a maximum value of x, 0.97±0.03, and a minimum value of y, 1.1±0.1. Therefore, the formula for XW is thought to be basically $WO_3\cdot H_2O_2\cdot H_2O$. When $1>x>0$, $1.5<y<3.0$ and the peroxopolytungstic acids were amorphous IPA. The IPA with $1>x\gtrsim 0.53$ was water-soluble, while the IPA with $0.53\gtrsim x>0$ was insoluble. For the extreme case of $x=0$, the substance was $WO_3\cdot 2H_2O$, as previously mentioned. Therefore, it follows that the substances formed directly from W and H_2O_2 are crystalline only for $x=1$ or 0, while for $1>x>0$ they are amorphous, and phase sepa-

Table 1. Some XRD Lines for XW and XW′

XW		XW′	
d/pm	I/I_0	*d*/pm	I/I_0
902	27	682	16
610	82	588	46
548	18	559	100
472	27	381	13
448	3	467	18
393	8	340	50
365	41	315	28
359	28	309	31
322	100	294	4
307	55	279	10

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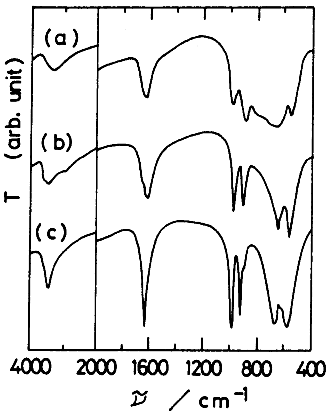

Fig. 2. Infrared spectra for IPA, XW, and XW′. (a) IPA, (b) XW, and (c) XW′.

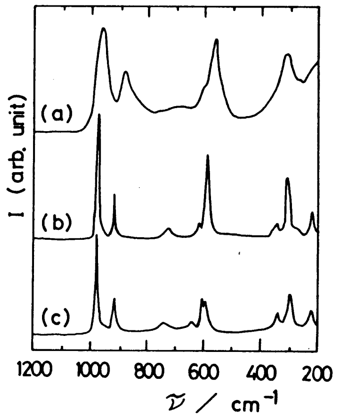

Fig. 3. Raman spectra for IPA, XW, and XW′. (a) IPA, (b) XW, and (c) XW′.

ration does not occur. The only water-soluble peroxopolytungstic acids are the IPA with $1>x\gtrsim 0.53$.

A similar compositional analysis for XW′, led to the formula for XW′ being $WO_3\cdot 0.94H_2O_2\cdot 0.14H_2O$. However, the thermal changes from XW to XW′ and from XW′ to the amorphous substance were found to be time-dependent. Actually, the peroxo content for XW′ decreased gradually with heating time and/or temperature increases. Therefore, an intermediate phase of XW′ might have been mixed with some amorphous substance and XW fragments. Accordingly, the formula for XW′ is supposed to be basically $WO_3\cdot H_2O_2$.

Infrared and Raman spectra for IPA, XW, and XW′ were very similar, as shown in Figs. 2 and 3, except for band sharpening and a small wavenumber shifting in the latter two. Although these small differences reflect differences in fine structures, the basic structure of IPA, XW, and XW′ is concluded to be quite similar. Until now, all known coordination structures around W in peroxo containing polytungstic acid salts with a peroxo to W molar ratio=1, are octahedral with one corner of the octahedron at the center of the peroxo bond.[3,4] Therefore, IPA, XW, and XW′ are supposed to have the same WO_7 pseudo-octahedral structure. By reference to the vibrational analyses[5,6] for $[Mo_6O_{19}]^{2-}$ and the Keggin structure such as $[SiW_{12}O_{40}]^{2-}$, IPA, XW, and XW′ are considered to have both edge-shared and corner-shared pseudo-octahedral structures.

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