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Peroxopolytungstic Acids Synthesized by Direct Reaction of Tungsten or Tungsten Carbide with Hydrogen Peroxide

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Recently one of the present authors reported a novel heteropolytungstic acid with carbon as a heteroatom (CW-HPA) [1]. Based on thermogravimetric, gas-chromatographic and IR analyses of the compound, it was concluded that the carbon atom exists as a triangular CO_3 group in the tungsten–oxygen framework of the polytungstic acid. In a subsequent attempt to clarify the structure and chemical properties of CW-HPA, we have found that a similar polytungstic acid without carbon (W-IPA, the corresponding 'iso' acid) can be synthesized through the reaction of metallic W with H_2O_2, while CW-HPA is produced by the reaction of WC with H_2O_2. Both acids are isostructural in terms of their anion frameworks and elemental compositions, except that W-IPA contains no carbon atom. What is more interesting is that both acids contain almost the same molar amount of peroxo (O–O) groups per W atom. In this paper we report synthesis and some preliminary characterizations of these two acids.

Experimental

Synthetic procedure of W-IPA is similar to that previously reported for CW-HPA [1]. A H_2O_2 solution (15%, 25 ml) was added to 4 g of W powder (1 μm in diameter). After a 3 to 10 min induction period, a vigorous reaction took place and the W was almost instantaneously dissolved. The solution thus formed was almost colorless and strongly acidic. After removing a small amount of undissolved impurities, and decomposing excess H_2O_2 catalytically with platinized Pt nets, the solution was dried under blown air at room temperature. Pale yellow amorphous glassy matter (W-IPA) was obtained.

The content of W in the compounds was determined from the weight of WO_3 given by heating them at 700 °C in air. The C/W molar ratio was determined gas-chromatographically using a CHN analyzer (Hitachi 026-type). The number of peroxo (O–O) groups was measured by the conventional iodometric titration of I_2 produced by the reaction of the present acids with KI aqueous solution. The IR spectra were recorded with KBr pellet samples using a Nicolet MX-S Fourier transform spectrometer. The Raman spectra were recorded using a JEOL JRS-400 spectrometer equipped with an Ar laser (514.5 nm). The 100 MHz ^{13}C and 16.5 MHz ^{183}W NMR spectra of the samples dissolved in D_2O were recorded using a JEOL GX-400 Fourier transform spectrometer at 15–17 °C. The thermal decomposition process of the compounds was monitored either with a ULVAC TA-1500 TG/DTA thermal analyzer or a ANELVA TE-600 QMS spectrometer.

Results and Discussion

The Raman spectra of CW-HPA and W-IPA solutions shown in Fig. 1, a and b are practically identical, indicating that these two compounds are substantially isostructural. Their IR spectra recorded between 400–4600 cm^{-1} were identical except that the absorption band(s) at 1340 cm^{-1} (accompanied by a weak band at 1400 cm^{-1}) due to $\nu_3(CO_3)$ [1] is completely absent in W-IPA. In the ^{13}C NMR spectrum of CW-HPA (Fig. 2, a), only one weak but reproducible resonance line was observed at 167.7 ppm (from the TMS standard), suggesting that the carbon atom is in a planar CO_3 group, since all the reported ^{13}C shifts for the CO_3 species including CO_3^{2-}, $C(OH)_3^+$, $CO_2(OH)^-$ etc. lie in the range of 160–170 ppm [2]. The chemical shifts of other species such as CO, CO_2 and CO_4 (in $C(OC_2H_5)_4$) are in the vicinity of 181, 124 [2] and 139 ppm [3], respectively.

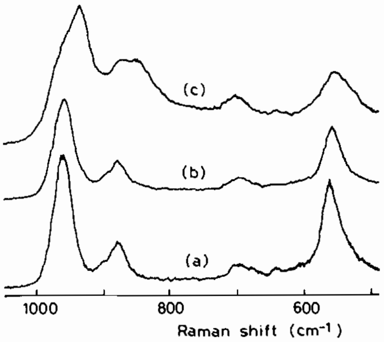

Fig. 1. Raman spectra of peroxopolytungstic acids and a Ba salt of W-IPA: (a) CW-HPA (solution), (b) W-IPA (solution), (c) Ba·W-IPA (solid).

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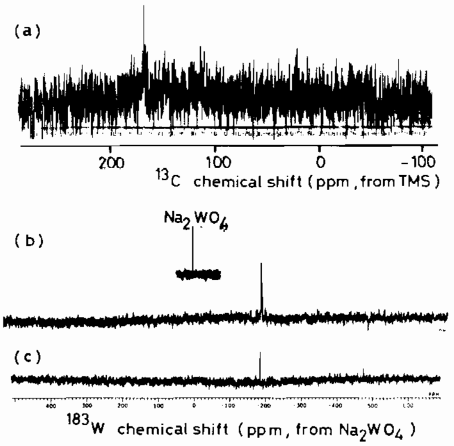

Fig. 2. 100 MHz ^{13}C and 16.5 MHz ^{183}W NMR spectra for peroxopolytungstic acid(s) in D_2O (^{1}H nondecoupled): (a) ^{13}C spectrum of CW-HPA, (b) ^{183}W spectrum of CW-HPA, (c) ^{183}W spectrum of W-IPA.

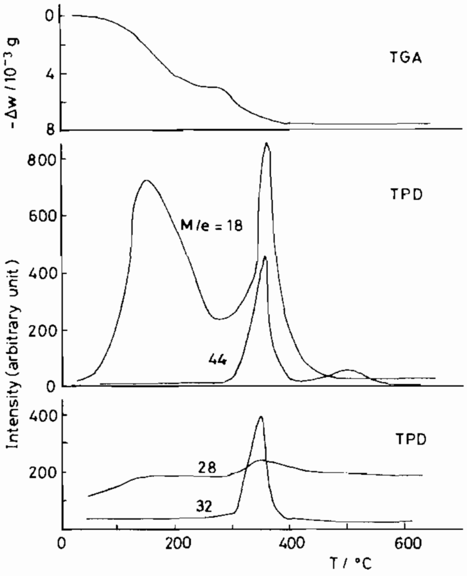

Fig. 3. TG and TPD spectra of CW-HPA solidified at 100 °C. TG: Heating rate, 10 °C/min; initial weight, 72.1 mg; atmosphere, dry air. TPD: M/e = 18, 28, 32 and 44 are due to H_2O, N_2 (contamination), O_2 and CO_2. Heating rate, 10 °C/min, MS scan rate, M/e (4 to 50)/30s; MS carrier gas, He; MS ionization pressure and energy, 10^{-4} torr and 70 eV.

The ^{183}W NMR spectra of CW-HPA and W-IPA are shown in Fig. 2, b and c. There is one resonance line in each spectrum with almost the same chemical shift (185.5 ppm from Na_2WO_4 for CW-HPA and 186.6 ppm for W-IPA). This result again indicates the structural similarity between the two compounds.

In Fig. 3, TG and TPD (temperature programmed decomposition) spectra recorded for a CW-HPA sample solidified at 100 °C are shown. The compound undergoes two step-decomposition up to 700 °C. The material left after the measurement was confirmed to be pure WO_3 by X-ray diffraction. In the first decomposition step, only water is released. The second step beginning at 280 °C is accompanied by evolution of H_2O, CO_2 and O_2 as well. It is, therefore, obvious that peroxo groups and carbon (as CO_3) remain in the polytungsten framework of CW-HPA anion up to its decomposition temperature (280 °C). Similar TG and TPD spectra were obtained for W-IPA except for CO_2 evolution. The Raman band at 880 cm^{-1} seen in each spectrum of Fig. 1 is likely to arise from O–O groups [4].

Iodometric determination of peroxo groups showed that the O–O/W molar ratio is 0.58 for CW-HPA and 0.57 ($\approx 7/12$) for W-IPA (at room temperature). The C/W ratio in CW-HPA was found to be 0.083 (1/12). Then, the empirical formulae of CW-HPA and W-IPA can be expressed as

$$CO_2 \cdot 12WO_3 \cdot 7H_2O_2 \cdot nH_2O$$

and

$$12WO_3 \cdot 7H_2O_2 \cdot mH_2O$$

where n and m are in the range of 20–25 for samples solidified at room temperature.

These acids precipitated white amorphous barium salts from a $Ba(NO_3)_2$ solution. Both IR and Raman spectra of the salts were much the same as those of the starting acids. The Raman spectrum of the Ba salt of W-IPA is shown in Fig. 1, c.

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