Reaction of Metal, Carbide, and Nitride of Tungsten with Hydrogen Peroxide Characterized by ^{183}W Nuclear Magnetic Resonance and Raman Spectroscopy

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Chemical species formed by reactions of tungsten metal, carbide, and nitride with hydrogen peroxide were characterized by multinuclear nuclear magnetic resonance and Raman spectroscopy and gas chromatography. The results not only showed formation of previously known tetraperoxoditungstate, but also strongly suggested formation of diperoxomonotungstate, its protonated form, monoperoxomonotungstate, and diperoxoditungstate. Carbon in tungsten carbide was only oxidized, and oxalate ion, carbon monoxide, and carbon dioxide were produced. On the other hand, both oxidation and hydrolysis of nitrogen were observed for tungsten nitride. It was suggested that the difference of reactivity was explained by the ionicity of tungsten-heteroatom bond.

Introduction

Carbides or nitrides of group IV to VI transition metals have both metal−metal and metal−carbon or metal−nitrogen bonds and are called interstitial compounds. These interstitial compounds have high thermal and chemical stability and electrical conductivity. Hence, the compounds have been used as hard metallurgical coatings,[1] catalysts,[2] and especially recently, diffusion barriers in semiconductor technology.[3,4] The preparation methods of thin films or ultrafine particles, by chemical vapor deposition (CVD)[5] and ion implanting,[6] and surface states of the materials were also studied.

On the other hand, carbides and nitrides of these transition metals form peroxo complexes by the reaction with hydrogen peroxide, and they can be applied to inorganic precursors to proton conductors,[7] photoresists,[8] electrochromic devices,[9] and metal oxides of tungsten bronzes[10a] and vanadium dioxide.[10b] The investigation of solution chemistry is important for not only the better understanding of the processes but also the peroxo chemistry of group IV to VI transition metals. Recently, we reported that the mononuclear and dinuclear tungsten peroxo complexes were formed by the reaction of tungsten metal with hydrogen peroxide[11] and that peroxotungstates prepared by the reaction of an α-WC with hydrogen peroxide can be precursors to proton conductors.[7] Peroxo complexes of group IV to VI transition metals were extensively studied by Griffith,[12] Stomberg,[13] Thompson,[14] and others,[15] since 1960s. Reviews of tungsten, molybdenum, chromium, and vanadium, were also reported.[16] Recently, the peroxo complexes have also attracted attention as oxidants or catalysts for the oxidation of organic substrates with hydrogen peroxide including biological applications.[17]

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Table 1. Data of Structure, Particle Size, Elemental Analysis, and pH and the Ratio of Amount of Tungsten Reacted

tungsten compound	structure	elemental analysis of tungsten, wt %[a]	pH of reaction solution initial	pH of reaction solution final	amount of tungsten compounds reacted, wt %	solution
metal	cubic W	100 (100)	3.05	0.22	100	(I)
carbide	hexagonal α-WC	93 (94)	3.38	0.18	100	(II)
nitride	amorphous	96 (96[b])	2.46	0.47	99	(III)

[a] Numbers in parentheses were theoretical amounts of tungsten in tungsten compounds. [b] Calculated assuming that the composition of tungsten nitride is W_2N.

However, little is known of the peroxo tungsten complexes formed at low pH and at equilibrium.

The variety of ionicity of the bonds between metal and nonmetal atoms in the interstitial compounds was pointed out by Toth[18] and confirmed by X-ray photoelectron spectroscopy (XPS).[19] The investigation of how the ionicity influences the chemical species of nonmetal elements formed by the reactions with hydrogen peroxide is also interesting.

In this paper, we investigated the species formed by reactions of carbide, nitride, and metal of tungsten with hydrogen peroxide by multinuclear nuclear magnetic resonance (NMR) and Raman spectroscopy and the gas-phase analysis and attempted to clarify the reaction mechanism.[20]

Experimental Section

Reagents and $K_2W(O_2)_4$. Metal (Mitsuwa Chemical Company Ltd., particle size ~1 μm), carbide (Rare Metallic, particle size ~1 μm), and nitride (High Purity Chemicals, particle size ~100 μm) of tungsten and aqueous hydrogen peroxide (30 wt %, Junsei Chemical Company Ltd.) were commercially obtained and used without further purification. The content of W in each sample was determined by inductively coupled plasma (ICP) analysis after the sample was dissolved in an acidic solution of hydrogen peroxide. The data of the structure and elemental analysis for starting materials are summarized in Table 1. The structures of metal and carbide of tungsten consisted of single phases of cubic W and hexagonal α-WC, respectively. Tungsten nitride was amorphous. The atomic ratio of N/W was 0.58 and it was confirmed that the content of hydrogen was <0.04 wt %.

$K_2W(O_2)_4$ was prepared according to Stomberg[13a] as follows: 5 mL of aqueous 30 wt % H_2O_2 (H_2O_2: 50 mmol) was added to a solution of 0.82 g (2.5 mmol) of K_2WO_4 in 10 mL of H_2O ($[WO_4^{2-}] = 0.17$ M; $[H_2O_2] = 3.3$ M). The solution was kept at 0 °C. Light yellow transparent crystals were formed within 1 h.

Reaction with Hydrogen Peroxide. The reaction of tungsten metal and carbide with hydrogen peroxide was carried out as follows: Finely powdered solid tungsten (11 g) or tungsten carbide (11 g) was suspended to 25 mL of water. Then, an aqueous solution (25 mL) of hydrogen peroxide (30 wt %) was added to this solution in a single step without stirring. After 15 min, another 20 mL of 30 wt % hydrogen peroxide was added to dissolve unreacted tungsten metal or carbide and to completely dissolve the metal or carbide of tungsten. Unreacted solids almost disappeared after 1 h, and the solution was kept at room temperature for 24 h. The reaction solutions of metal and carbide of tungsten with hydrogen peroxide were abbreviated as solutions (I) and (II), respectively.

The reaction of tungsten nitride was carried out with a larger amount of hydrogen peroxide because of the larger particle size as follows: Finely powdered solid tungsten nitride (5 g) was suspended in 100 mL of 30 wt % hydrogen peroxide and kept at room temperature for 24 h with stirring (solution (III)).

The reaction of tungstic acid with hydrogen peroxide was carried out as follows: Tungstic acid (16 g) was suspended in hydrogen peroxide (32 mL, 18.75% w/w aqueous solution). After 24 h, the mixture was filtered to remove insoluble residues (≤3%). The pH value was adjusted with an aqueous solution of HNO_3 (60% v/v) or NaOH (2 M).

Measurements. The pH values of solutions were monitored with an HM-30 pH meter (TOA Electrochemical Measuring Instruments). The ^{183}W and ^{14}N NMR spectra were recorded on JEOL GX270 FT spectrometer at frequencies of 11.2 and 19.5 MHz, respectively. The standard conditions used for the ^{183}W NMR measurements were as follows; number of scans, 5000; flip angle, 30°; acquisition time, 0.41 s; interpulse delays, 1.06 s; spectral width, 40 kHz; number of points, 32 768. The changes in integrated intensity ratios were maintained at less than ±10% by increasing numbers of scans and points, and the signal-to-noise ratios were 3.5−22. Na_2WO_4 (2 M) in D_2O ($d = 0$) and liquid ammonia ($d = 0$) were used for ^{183}W and ^{14}N NMR references, respectively. The ^{13}C NMR spectra were recorded on JEOL GX400 FT spectrometer at a frequency of 100.5 MHz using tetramethylsilane as a reference. Raman spectra were measured with a T-64000 (JOBIN YVON) spectrometer. The characterization of the gas phase was carried out by gas chromatography (GC-8A, Shimadzu, TCD detector).

Results and Discussion

Reaction of Metal, Carbide, and Nitride of Tungsten with Hydrogen Peroxide. The reaction of metal, carbide, and nitride of tungsten almost completely proceeded as shown in Table 1. The pH value of the solution (I) after 24 h was 0.22 and close to 0.18 of solution (II), yet different from 0.47 of solution (III). The decreases in pH values show the formation of protons, which are formed, for example, by a reaction, $W + 3H_2O_2 \rightarrow WO_4^{2-} + 2H^+ + 2H_2O$, in the case of reaction of tungsten metal with hydrogen peroxide. A large amount of O_2 was evolved, showing progress of decomposition of hydrogen peroxide to molecular oxygen and water. In all cases, no reaction occurred in the absence of hydrogen peroxide, showing that no hydrolysis of these compounds with water took place.

Investigation of Chemical Species Formed. *(a) Tungsten species. (i) Assignments.* The ^{183}W NMR

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(20) Although using tungsten carbide and nitride with the same structure would be more preferable, the preparation of samples with high purity was unsuccessful and we used commercially available, highly purified samples.

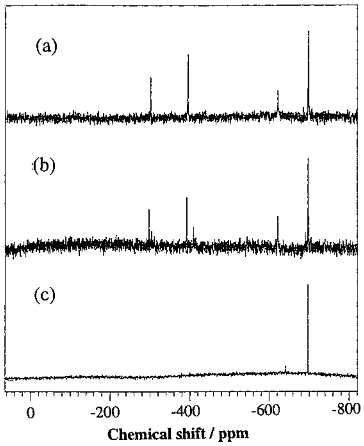

Figure 1. ^{183}W NMR spectra of solutions (I)−(III): (a) solution (I); (b) solution (II); and (c) solution (III).

spectra of solutions (I) − (III) are shown in Figure 1. The ^{183}W NMR spectra changed little after 24 h. This result is consistent with observations that the solid reactants almost disappeared after 1 h and that pH was constant after 1 h, showing that the tungsten speciation reached equilibration after 1 h. Four signals were observed for solution (I) at −698 ($\Delta\nu_{1/2}$, 16 Hz), −622 (25 Hz), −394 (10 Hz), and −300 (8 Hz) ppm. In addition to the four signals, two signals were observed at −306 and −411 ppm for solution (II). For solution (III), one very strong signal and one weak signal were observed at −697 and −643 ppm, respectively.

Next, we assigned the signals. $W_2O_3(O_2)_4^{2-}$ was prepared according to Campbell et al.[12a] and gave the ^{183}W NMR signal around −698 ppm. The signal position is almost in agreement with that for a major tungsten species in solution (III). Therefore, the signal at −698 ppm is assigned to $W_2O_3(O_2)_4^{2-}$. The preparation pH of $W_2O_3(O_2)_4^{2-}$ was in close agreement with that of solution (III), supporting the assignment.

A solution containing $WO_2(O_2)_2^{2-}$ and/or $WO(OH)(O_2)_2^-$ as well as $W_2O_3(O_2)_4^{2-}$ was prepared according to the method reported by Ghiron et al.[14a] The ^{183}W NMR spectrum showed two signals at −699 and −637 ppm. The signal at −699 ppm is assigned to $W_2O_3(O_2)_4^{2-}$ as described, and the position did not change with pH. The signal at −637 ppm is assignable to $WO_2(O_2)_2^{2-}$/$WO(OH)(O_2)_2^-$. The chemical shift was decreased to −657 ppm by increasing pH to 2.1. Effects of protonation on the chemical shift have been explained for vanadium complexes by the variation of the energy of the ligand-to-metal charge-transfer transition, which is the dominant contributor to the paramagnetic part of the chemical shift.[21] Therefore, the decrease in chemical shifts from −637 to −657 ppm with increasing pH is caused by the deprotonation of $WO(OH)(O_2)_2^-$ to form $WO_2(O_2)_2^{2-}$ and H^+. The reason why only one ^{183}W signal was observed for $WO(OH)(O_2)_2^-$ and $WO_2(O_2)_2^{2-}$ is coalescence of the protonated ($WO(OH)(O_2)_2^-$) and deprotonated ($WO_2(O_2)_2^{2-}$) diperoxomonotungstate species. These concentrations depend on that of proton, and therefore, the change of the signal position from −637 to −657 ppm is due to the changes in concentrations.

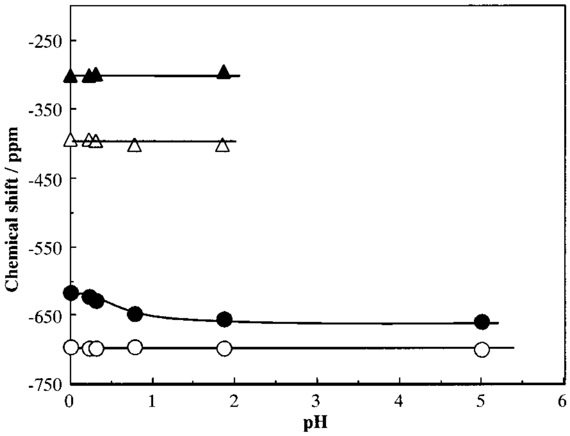

Figure 2. Change in ^{183}W NMR chemical shifts of peroxotungstates with pH. Key: (○) [tetraperoxoditungstate]; (●) [diperoxomonotungstate]; (△) [diperoxoditungstate]; (▲) [monoperoxomonotungstate]. $[WO_4^{2-}]_{total}$ = 0.2−1.6 M, $[H_2O_2]_{total}$ = 0.6−5.0 M. WO_4^{2-} was added as H_2WO_4.

The same changes in ^{183}W NMR spectra with pH as those for Ghiron's solution were observed for a H_2WO_4/H_2O_2/H_2O system (described in the later section) and solutions (I) and (III), and those for a H_2WO_4/H_2O_2/H_2O system were systematically examined. The results are shown in Figure 2. The position of one signal shifted from −658 to −616 ppm by decreasing pH from 5.0 to 0.0, and the change was reversible, whereas positions of the other three signals remained approximately unchanged. The pH values of solutions (I) and (III) were 0.22 and 0.47, respectively. Chemical shifts at pH values of 0.22 and 0.47 in Figure 2 were −622 and −643 ppm, respectively, and in good agreement with those observed for solutions (I) and (III), respectively. The data for Ghiron's solution fitted the curve as well. Therefore, the signals at −622 and −643 ppm, which were observed in Figures 1a and 1c, respectively, result from the coalescence of $WO(OH)(O_2)^{2-}$ and $WO_2(O_2)_2^{2-}$. Salles et al. reported an unidentified ^{183}W signal at −627 ppm, which was formed during epoxidation with hydrogen peroxide catalyzed by 12-tungstophosphoric acid.[17c] The unidentified signal is probably due to the same peroxotungstate species, if one takes into account the low pH of the reaction solution.

Signals around −394 and −300 ppm were observed in the case of a reaction of tungsten metal and carbide with hydrogen peroxide. These signals have never been reported. Figure 3a shows correlation between ^{183}W chemical shifts and O_2^{2-}/W ratios. Here, the ^{183}W chemical shift of $W(O_2)_4^{2-}$ was determined for $K_2W(O_2)_4$ as follows. When 0.57 g of the $K_2W(O_2)_4$ crystal (1.5 mmol) was dissolved in a solution containing 1 mL of 30 wt % H_2O_2 (10 mmol) and 2 mL of D_2O, the pH value was 9.5. The ^{183}W NMR spectrum of the solution showed one signal at −1243 ppm. The mother solution, out of which $K_2W(O_2)_4$ crystallized, also showed one signal at the same position. Therefore, the signal at −1243 ppm is probably due to $W(O_2)_4^{2-}$. The ^{183}W chemical shifts of $W_2O_3(O_2)_4^{2-}$, $WO_2(O_2)_2^{2-}$, and $WO(OH)(O_2)^{2-}$ were determined as described. As shown in Figure 3a, linear correlation was observed. We in part pointed out similar linear correlation for peroxo compounds of Mo as shown in Figure 3b.[11] A similar linear correlation was observed for peroxo compounds of V although the data were

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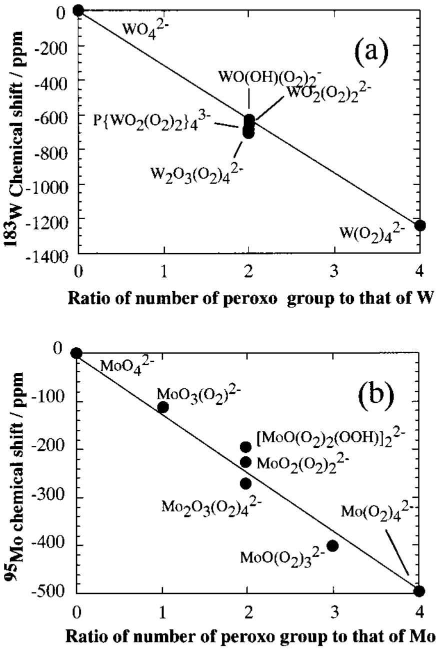

Figure 3. Correlations between ^{183}W and ^{95}Mo chemical shifts and ratios of numbers of peroxo group to those of W and Mo. (a) Correlation between ^{183}W chemical shifts and ratios of numbers of peroxo group to those of W. (b) Correlation between ^{95}Mo chemical shifts and ratios of numbers of peroxo group to those of Mo.

rather scattered.[21] It was reported for molybdenum compounds that the coordination of strong σ donors (i.e., having large ligand field stabilization energy) such as peroxo group caused upfield shifts of ^{95}Mo signals.[12a,21,22] Therefore, the fact that the ^{183}W signals for peroxo compounds lie upfield of that of WO_4^{2-} is due to the coordination of peroxo groups to tungsten atoms. The linear correlation shows that each peroxo group has the same extent of contribution to the ^{183}W chemical shift. The effect of peroxo group is much larger than that of hydroperoxo group because the ^{95}Mo chemical shift of $[MoO(O_2)_2(OOH)]_2^{2-}$ (−200 ppm, MoO_4^{2-} = 0 ppm) was close to that of $MoO_2(O_2)_2^{2-}$ (−215−−230 ppm), showing that hydroperoxo groups do not much contribute to the chemical shift. According to the correlation in Figure 3a, the signals at −394 and −300 ppm are assignable to peroxotungstates with $O_2^{2-}/W = 1$. The chemical shift of dimer species appeared by ∼50−80 ppm higher field than those of monomer species in the case of peroxo complexes with $O_2^{2-}/W = 2$. This fact suggests that the signal at −394 ppm is assigned to a dimer species (e.g., $W_2O_5(O_2)_2^{2-}$) and that at −300 ppm to a monomer species (e.g., $WO_3(O_2)^{2-}$).

Two signals were observed at −306 and −411 ppm only in the case of tungsten carbide. Formation of oxalate ion in solution (II) was confirmed and is described in a later section. Addition of oxalic acid to solution (I) gave signals at −306 and −411 ppm. Therefore, the signals at −306 and −411 ppm are probably assigned to monoperoxomonotungstate and diperoxoditungstate species, respectively, where oxalate ions were coordinated. The assignments of ^{183}W NMR chemical shifts observed in Figures 1a−1c are summarized in Table 2.

A reaction of tungsten trioxide monohydrate (tungstic acid) with hydrogen peroxide gave the same ^{183}W NMR results as those of tungsten metal except the complete dissolution took 24 h.

Raman spectra of solutions (I)−(III) are shown in Figures 4a−4c, respectively. The bands were observed around 560, 610, 850, 870, and 960 cm^{-1} for each solution. The band around 870 cm^{-1} is due to δ(O−O−H) of free H_2O_2.[23] The other bands around 560, 610, 850, and 960 cm^{-1} can be assigned to $\nu_{as}(W(O_2))$, $\nu_s(W(O_2))$, ν(O−O), and ν(W=O), respectively, according to references 12a, 24, and 25, and the peak positions were close to those of $W_2O_3(O_2)_4^{2-}$ and $WO_2(O_2)_2^{2-}$.[12a,24]

(ii) Effects of [WO_4^{2-}], [H_2O_2], and pH and Equilibrium Among Peroxotungstates. Next, effects of [WO_4^{2-}], [H_2O_2], and pH on the tungsten species were investigated. For the precision of concentrations of hydrogen peroxide, a $H_2WO_4/H_2O_2/H_2O$ system in the pH range 0.00−5.04 was examined because the little gas evolution was observed in the system, indicating that the decomposition of H_2O_2 can be ignored for the reaction of tungstic acid with hydrogen peroxide. Here, the concentrations of peroxotungstates were determined by the integrated intensities of ^{183}W NMR signals divided by numbers of W atoms in complexes assigned. It was confirmed that similar results were obtained for an $H_2WO_4/H_2O_2/H_2O$ system as partly described in the previous section.

Figure 5 shows changes in concentrations of peroxotungstate species with the total concentration of WO_4^{2-} ([WO_4^{2-}]$_{total}$). As [WO_4^{2-}]$_{total}$ increased, the concentration of each peroxotungstate increased under these conditions. The solid circles in Figure 6 show the correlation between log[tetraperoxoditungstate] and log[diperoxomonotungstate]. The line slope of 2 reproduced the experimental data, suggesting that eq 1 is valid.

$$2WO(OH)(O_2)_2^{-}\ (\text{or}\ 2WO(O_2)_2O^{2-} + 2H^{+}) \rightleftarrows W_2O_3(O_2)_4^{2-} + H_2O \quad (1)$$

$$K_1 = [WO(OH)(O_2)_2^{-}]^2\ (\text{or}\ [WO(O_2)_2O^{2-}]^2[H^{+}]^2)/[W_2O_3(O_2)_4^{2-}] \quad (2)$$

The same correlation was observed for monoperoxomonotungstate and diperoxoditungstate, as shown by the open circles in Figure 6.

Figure 7 shows changes in concentrations of the peroxotungstate species with the total concentration of hydrogen peroxide ([H_2O_2]$_{total}$). As [H_2O_2]$_{total}$ increased, [tetraperoxoditungstate] increased while [diperoxoditungstate] decreased. Figure 8 shows the correlation between log{[tetraperoxoditungstate]/[diperoxoditungstate]} and log[H_2O_2]$_{free}$, which was calculated by [H_2O_2]$_{total}$ − 4[tetraperoxoditungstate] − 2[diperoxoditungstate] − 2[diperoxomonotungstate] − [monoperoxomonotungstate]. The solid line with a slope of 2 approximately reproduced the experimental data, sug-

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Table 2. ^{183}W Chemical Shifts, Relative Integrated Intensities, and Assignments

^{183}W chemical shift/ppm[a]			
solution			
(I)	(II)	(III)	assignment
−698 (0.48)	−698 (0.44)	−698 (0.85)	tetraperoxoditungstate (($W_2O_3(O_2)_4^{2-}$)
−622 (0.23)	−623 (0.24)	−643 (0.15)	diperoxomonotungstate ($WO_2(O_2)_2^{2-}$/$WO(OH)(O_2)_2^-$)
−394 (0.19)	−394 (0.16)	—	diperoxoditungstate (O_2^{2-}/W = 1 dimer; e.g., $W_2O_5(O_2)_2^{2-}$)
−301 (0.11)	−300 (0.09)	—	monoperoxomonotungstate (O_2^{2-}/W = 1 monomer; e.g., $WO_3(O_2)^{2-}$)
—	−411 (0.05)	—	diperoxoditungstooxalate (O_2^{2-}/W = 1; dimer)
—	−306 (0.03)	—	monoperoxomonotungstooxalate (O_2^{2-}/W = 1; monomer)

[a] Numbers in parentheses were relative integrated intensities.

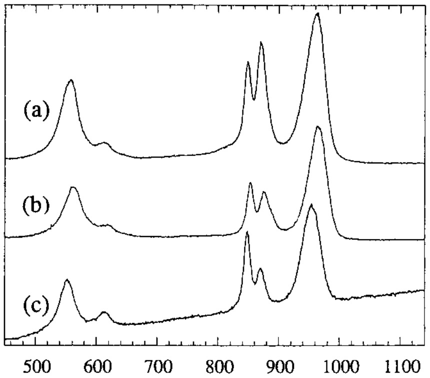

Figure 4. Raman spectra of solutions (I)−(III). (a) Solution (I); (b) solution (II); and (c) solution (III).

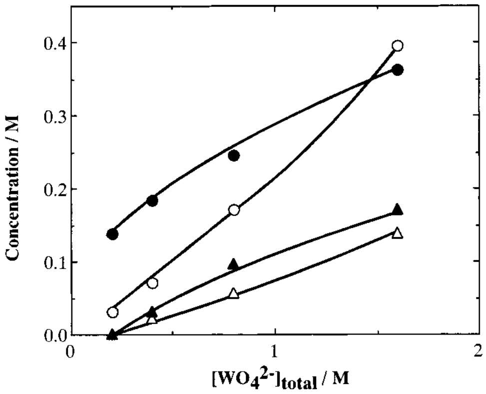

Figure 5. Changes in concentrations of peroxotungstate species with total concentration of WO_4^{2-}. $[H_2O_2]_{total} = 5.0$ M; pH = 0.3. Key as in Figure 2.

gesting that the eq 3 is valid. From the solid line in Figure 8, K_2 is calculated to be 0.38. The

$$W_2O_5(O_2)_2^{2-} + 2H_2O_2 \rightleftarrows W_2O_3(O_2)_4^{2-} + 2H_2O \quad (3)$$

$$K_2 = [W_2O_3(O_2)_4^{2-}]/[W_2O_5(O_2)_2^{2-}][H_2O_2]_{free}^2 \quad (4)$$

correlation of log{[diperoxomonotungstate]/[monoperoxomonotungstate]} and log$[H_2O_2]_{free}$ cannot be obtained because of the few data.

Figure 9 shows the pH dependency of the concentrations of peroxotungstates. Below pH = 1, four species of monoperoxomonotungstate, diperoxomonotungstate, diperoxoditungstate, and tetraperoxoditungstate were formed, whereas at pH = 5, diperoxoditungstate and tetraperoxoditungstate were observed under the experimental conditions. The pH dependency of peroxotungstates formed is consistent with data reported in the literature.[12a,14a] The validity of eqs 1 and 3 also supports

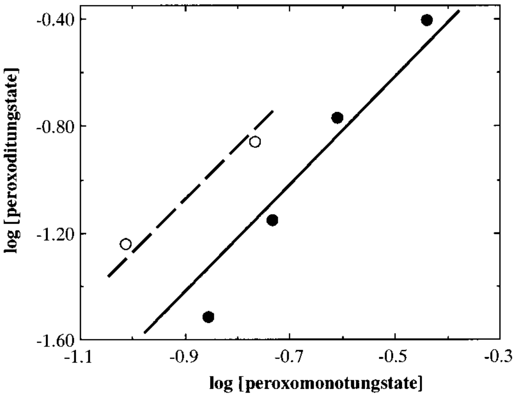

Figure 6. Correlations between log[peroxomonotungstate] and log[peroxoditungstate]. Key: (●) correlation between log[tetraperoxoditungstate] and log[diperoxomonotungstate]; (○) correlation between log[diperoxoditungstate] and log[monoperoxomonotungstate].

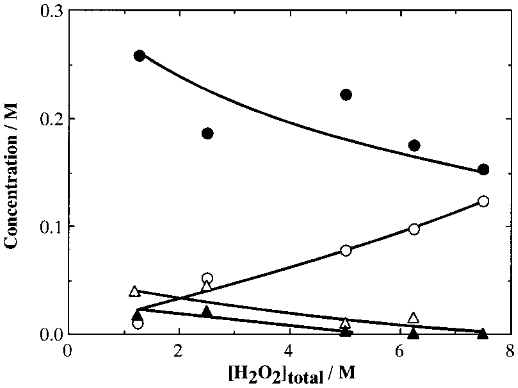

Figure 7. Changes in concentrations of peroxotungstates with total concentration of hydrogen peroxide. $[WO_4^{2-}]_{total} = 0.4$ M, pH = 0.3. Key as in Figure 2.

the assignments of ^{183}W NMR signals discussed in the previous section.

(b) Carbon and Nitrogen Species. (i) Carbon Species. The ^{13}C NMR spectrum of solution (II) showed one broad signal around 166 ppm. This signal is assigned to $C_2O_4^{2-}$ according to Ehde et al.[26] No carbon species other than $C_2O_4^{2-}$ were observed in solution (II). The presence of $C_2O_4^{2-}$ was also quantitatively confirmed by the titration with $Ca(NO_3)_2$, and the amount was almost the same as that in Table 3. The broadening of the signal may be due to the exchange of the coordinated oxalato ligands with free oxalate ions as reported for an aqueous solution of $VO_2(C_2O_4)_2^{3-}$.[26] The Raman spectrum of solution (II) showed strong bands at 1403 and 1727

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(26) Ehde, P. M.; Petterson, L.; Glaser, J. *Acta Chem. Scand.* **1991**, *45*, 998.

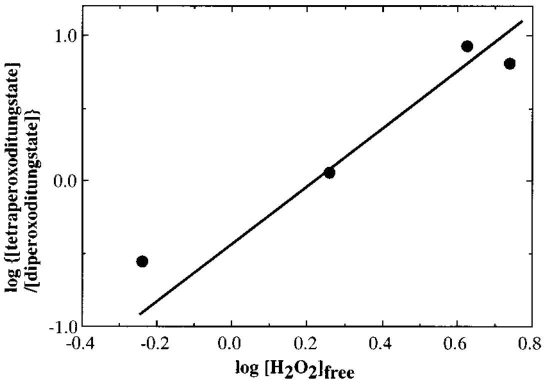

Figure 8. Correlation between log[H_2O_2]$_{free}$ and log{[tetraperoxoditungstate]/[diperoxoditungstate]}.

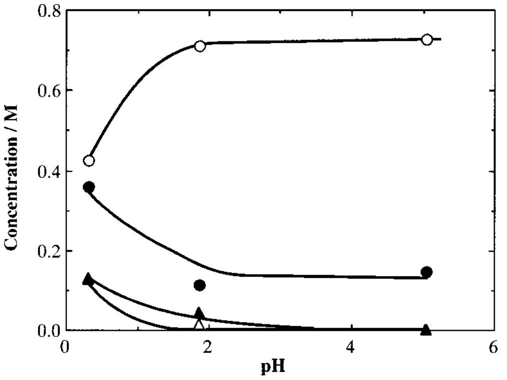

Figure 9. Changes in concentrations of peroxotungstate species with pH. [WO_4^{2-}]$_{total}$ = 1.6 M, [H_2O_2]$_{total}$ = 5.0 M. Key as in Figure 2.

Table 3. Carbon Balance for the Reaction of Tungsten Carbide with Hydrogen Peroxide

species	amount, atom %
$C_2O_4^{2-}$	23 ± 2[a]
CO_2	32 ± 5[b]
CO	44 ± 5[b]
C	0.3± 0.1[c]

[a] Determined by ^{13}C NMR. [b] Determined by gas chromatography. [c] Unreacted carbon in tungsten carbide.

cm^{-1}, with a weaker band at 1240 cm^{-1}, showing that $C_2O_4^{2-}$ is a bidentate ligand.[23]

Next, the carbon species in the gas phase produced by the reaction of tungsten carbide with hydrogen peroxide were investigated by gas chromatography. Only CO and CO_2 were detected, as shown in Table 3. In this reaction, carbon in tungsten carbide was oxidized, in contrast to the oxidation and hydrolysis of nitrogen in tungsten nitride as described next.

Table 4. Nitrogen Balance for the Reaction of Tungsten Nitride with Hydrogen Peroxide[a]

species	amount, atom %
NH_4^+	78 ± 8
NO_3^-	2 ± 1[b]
N_2	20 ± 5[c]

[a] No NO and N_2O were detected. [b] The sum of NH_4^+ and NO_3^- was determined by elemental analysis of the solid obtained from solution (**III**). The NH_4^+/NO_3^- ratio was calculated by ^{14}N NMR. It was confirmed that the amount of NH_4^+ thus determined was in good agreement with that determined by the titration with indophenol reagent. [c] Determined by gas chromatography.

(ii) Nitrogen Species. Elemental analysis and titration of ammonia showed that ~80 at. % of nitrogen in tungsten nitride was retained in solution, as shown in Table 4. The remainings were formed as dinitrogen in the gas phase, as was confirmed by gas chromatography. The ^{14}N NMR spectrum of solution (III) showed two ^{14}N NMR signals at 19.6 and 375.3 ppm, which are assigned to ammonium and nitrate ions, respectively. It was previously reported[27–29] that both ammonium and nitrate ions were formed by the reaction of molybdenum nitride with hydrogen peroxide. In the case of tungsten nitride, nitrogen was also oxidized and hydrolyzed. The other nitrogen species, such as hydrazine and nitrite ions, were not detected in solution (III). Ammonium ions produced caused the increase in pH value of solution (III) and the difference of the pH values caused the formation of different tungsten species from those for tungsten metal and carbide as described in the previous section.

(iii) Comparison of the Reaction of the Interstitial Carbon and Nitrogen. Hydrogen peroxide is a strong oxidizing agent and carbon atoms in tungsten carbide were oxidized. On the other hand, nitrogen atoms in tungsten nitride were little oxidized. This difference is explained by the ionicity of the bond between tungsten and the interstitial atom as follows. Nakajima et al. reported on the basis of XPS data that W–N bonds in tungsten nitride are ionic, whereas W–C bonds in tungsten carbide are quite covalent.[19a] It has been reported that ammonium ions were formed by the reaction of organometallic molybdenum nitride with protons.[30] Hence, protons formed by the oxidation of tungsten metal with hydrogen peroxide could attack anionic nitrogen atoms and ammonium ions were formed. The fact that the reaction of tungsten nitride with hydrogen chloride also produced ammonium ions supports this idea. On the other hand, carbon atoms in tungsten carbide are less anionic and protons cannot attack them. Therefore, only the oxidation of tungsten carbide with hydrogen peroxide took place. The reaction of tungsten carbide with hydrogen chloride did not proceed, supporting this idea.

In conclusion, the present results not only clarify reactions of tungsten metal, carbide, and nitride with hydrogen peroxide but also provide easy preparation methods for the peroxotungstate precursors, which have been used for proton conductors, photoresists, electrochromic devices, etc.[31]

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research in Priority Areas

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[27] Mizuno, N.; Nakajima, H.; Tanaka, H.; Kudo, T. *Chem. Lett.* **1997**, 521.

[28] The concentration of tungsten nitride was five times as high as that previously reported[27] because of the measurement of low-sensitive ^{183}W NMR. The higher concentration resulted in decreasing pH and NH^{4+} was more formed than in ref 26.

[29] Nakajima, H.; Tanaka, H.; Hibino, M.; Kudo, T.; Mizuno, N. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 955.

[30] For example, Hidai. M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.

[31] The crystal structure of tetraperoxoditungstate has been reported.[32] Our attempts to grow crystallographic quality single crystals of K$^+$, Na$^+$, or $(C_4H_9)_4N^+$ salt of peroxotungstates have been unsuccessful to date; attempts with other cations are in progress.

[32] Einstein, F. W. B.; Penfold, B. R. *Acta Crystallogr. (Supplement)* **1963**, *16*, A35.

(No. 260) from The Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: ^{13}C NMR spectrum of solution II and ^{14}N NMR spectrum of solution III. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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