IR, Raman and ^{13}C NMR Spectra of Peroxotungstooxalate

M. HASHIMOTO , T. IWAMOTO*

Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
(Japan)

H. ICHIDA, Y. SASAKI

Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
(Japan)

and T. KUDO**

Central Research Laboratory, Hitachi Ltd., Kokubunji,
Tokyo 185 (Japan)

(Received August 2, 1989)

The present authors have recently reported that tungsten carbide (WC) reacts with dilute hydrogen peroxide to give a yellow glassy peroxotungstate containing carbon (CWHPA) [1–3]. The W/C molar ratio in CWHPA depends on the rate of evaporation of the mother solution [2]. After surveying suitable counter cations, two crystalline compounds have been obtained and their structures have been determined: (18-crown-6 ether K)$_4$CW$_{12}$O$_{40}$ with W/C = 12 [4]; $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$ with W/C = 4 [5]. The latter structure shows that oxalate ion is obtained from WC and it has no C–C bonds [6] as a peroxotungstooxalato complex. As far as the structures of peroxotungstooxalates are concerned, only a mononuclear $K_2[WO(O_2)_2(C_2O_4)]$ has been reported so far [7]. We have investigated the H^+–WO_4^{2-}–$C_2O_4^{2-}$–H_2O_2 systems spectroscopically in order to explain the relationship between the crystal structure and the behavior of CWHPA (W/C = 4) in solution.

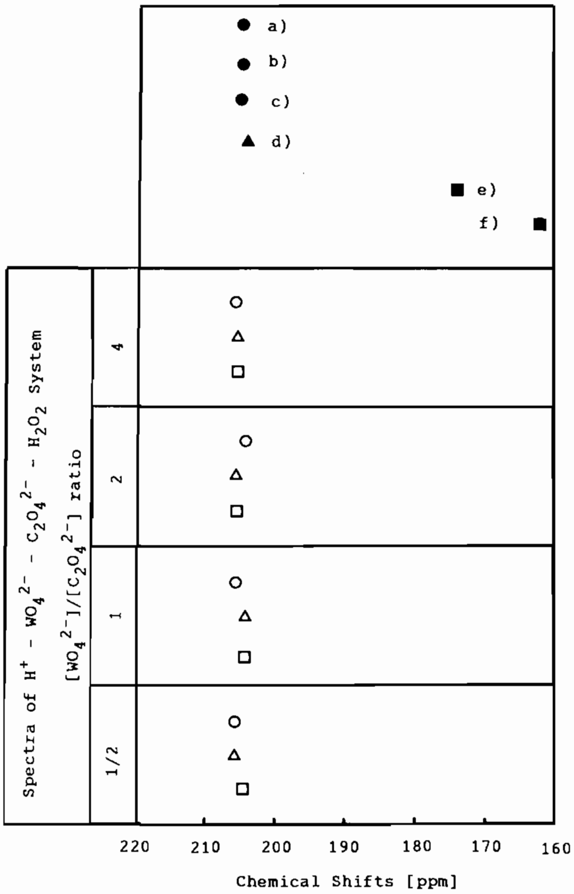

Fig. 1. Results of 22933.30 kHz ^{13}C NMR of oxalic acid, CWHPA, peroxoditungstooxalate and the H^+–WO_4^{2-}–$C_2O_4^{2-}$–H_2O_2 systems: (a) CWHPA (W/C = 4) in H_2O_2; (b) the $[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 solution; (c) "Stomberg's solution", (d) the dinuclear complex salt in CH_2Cl_2; (e) $(COONa)_2$ in H_2O; (f) $(COOH)_2$ in H_2O. In the H^+–WO_4^{2-}–$C_2O_4^{2-}$–H_2O_2 system: (○) pH 5; (△) pH 3; and (□) pH 1.

Experimental

CWHPA (W/C = 4), WIPA (product of dissolving metallic W powder in H_2O_2), $K_2[WO(O_2)_2(C_2O_4)]$ and $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$ were prepared by literature methods [1, 5, 7]. 'Stomberg's solution', standing for the mother liquor of mononuclear peroxotungstooxalate, was prepared as described in the literature [7], but 5 ml 12% H_2O_2 was used instead of 5 ml 30% H_2O_2. Crystals of $K_2[WO(O_2)_2(C_2O_4)]$ can also be obtained from this solution. A solution with $[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 was obtained by dissolving WIPA and oxalic acid in 30% H_2O_2. The concentration of oxalic acid in this sample was 0.7 mol/l. Solutions of the H^+–WO_4^{2-}–$C_2O_4^{2-}$–H_2O_2 system were prepared with sodium tungstate and oxalic acid. The concentration of oxalate ion was 0.6 mol/l and $[WO_4^{2-}]/[H_2O_2]$ = 1/2. The pH was adjusted with concentrated HNO_3 and 6 mol/l NaOH aqueous solution. For this system, spectra were measured at various pH and $[WO_4^{2-}]/[C_2O_4^{2-}]$ values; the molar ratio of $[WO_4^{2-}]/[H_2O_2]$ was fixed at 1/2.

Raman spectra of the following solutions were measured on a JEOL JRS-400: the $[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 solution; Stomberg's solution; CWHPA (W/C = 4) solution (0.1 g amorphous in 0.1 ml water); and oxalic acid saturated aqueous solution.

---

*Author to whom correspondence should be addressed.

**Present address: Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan.

0020-1693/89/$3.50

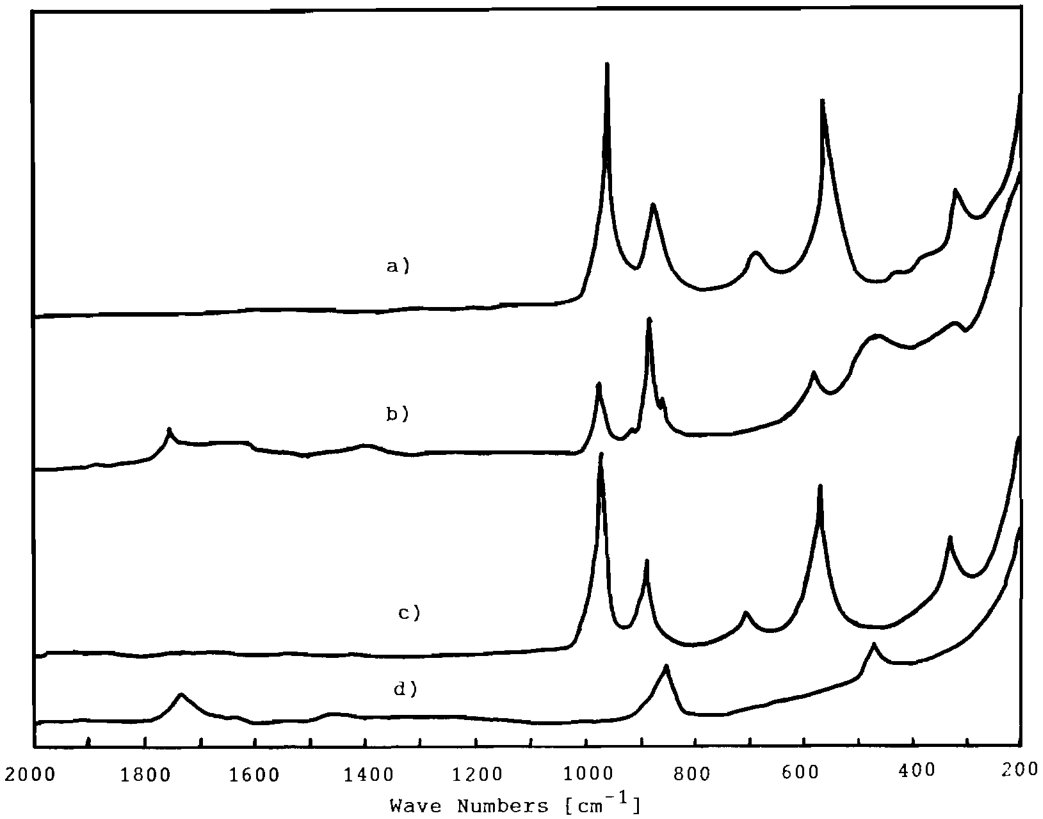

Fig. 2. Raman spectra of (a) the $[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 solution; (b) Stomberg's solution; (c) CWHPA; and (d) oxalic acid.

^{13}C NMR spectra were recorded on a JEOL FX-90Q. Samples were as follows: saturated aqueous solution of oxalic acid and sodium oxalate; CWHPA (W/C = 4, 1.0 g in 1.45 ml 9% H_2O_2); Stomberg's solution; the $[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 solution; $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$ solution (0.5 g crystals in 2.0 ml CH_2Cl_2); and solutions of the tungstate–oxalate–hydrogen peroxide system. Measuring conditions were: single pulse, ^1H non-decoupling, pulse width 13 μs, pulse interval 1 s, pulse delay 1.4 s, data points 16384, spectral width 10000 Hz, acquisition time 0.8190 s, observation frequency 22933.30 kHz, and irradiation frequency 89604.25 kHz.

TABLE 1. Raman peaks of the $[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 solution, Stomberg's solution, CWHPA (W/C = 4) and oxalic acid in aqueous solution

Sample	Wave numbers (cm^{-1})
$[WO_4^{2-}]/[C_2O_4^{2-}]$ = 8 solution	1730, 1630, 1400, 964, 880, 695, 564, 385, 320
Stomberg's solution	1760, 1604, 1400, 975, 878, 578, 460, 320
CWHPA (W/C = 4)	1730, 1630, 1400, 960, 880, 695, 564, 385, 320
Oxalic acid	1745, 1640, 1410, 844, 454

TABLE 2. IR peaks of $(COOK)_2 \cdot H_2O$, $K_2[WO(O_2)_2(C_2O_4)]$ and $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$

Sample	Wave numbers (cm^{-1})	
$(COOK)_2$	1592	1304
$K_2[WO(O_2)_2(C_2O_4)]$	1740, 1720, 1680	1380, 1310, 1290, 1240
$[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$	1708, 1684	1310, 1284, 1380 (ammonium?)

Measurements of IR spectra were made for the CWHPA (W/C = 4), glassy material from a $[WO_4^{2-}]/[C_2O_4^{2-}] = 8$ solution, $[(n\text{-}C_4H_9)_4N][WO(O_2)_2(C_2O_4)WO(O_2)_2]$, tetra-n-butylammonium salt obtained from a $[WO_4^{2-}]/[C_2O_4^{2-}] = 8$ solution (recrystallized from CH_2Cl_2–$(C_2H_5)_2O$ at −20 °C; it was found to be identical to the dinuclear complex from cell constants and elemental analyses of C, H and N), $K_2[WO(O_2)_2(C_2O_4)]$, and potassium oxalate as KBr disks on a Hitachi 260-30 instrument.

Results and Discussion

Chemical shifts of the ^{13}C NMR spectra, externally referenced to tetramethylsilane, are given in Fig. 1. The value of 162.9 ppm for oxalic acid was not affected by the addition of H_2O_2. Assuming $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$ is stable in CH_2Cl_2, resonance at 204.2 ppm can be assigned to the dinuclear peroxotungstooxalato complex. The solution of CWHPA (W/C = 4) gives essentially the same chemical shift (205.4 ppm), being different from another type of CWHPA (W/C = 12, 167.7 ppm) [3]. From these results we presume that the C atoms in CWHPA of different constitutions are also different structurally. Chemical shifts of all other H^+–WO_4^{2-}–$C_2O_4^{2-}$–H_2O_2 systems range only from 204.1 to 205.5 ppm. These facts show that $C_2O_4^{2-}$ coordinates to W in solution, and their structures are similar to one another.

Raman spectra are shown in Fig. 2. The spectra of the $[WO_4^{2-}]/[C_2O_4^{2-}] = 8$ solution and CWHPA agree with each other. Hence these two solutions are identical in terms of ^{13}C NMR and Raman spectra. The spectrum of Stomberg's solution is different from these two, but it resembles that of oxalic acid, with 1700 to 1800, 800 to 900 and 400 to 500 cm^{-1} assigned to remaining free oxalic acid. Other peaks in these three spectra are roughly identical, except for the lack of a band at about 700 cm^{-1} for Stomberg's solution. The results support that there are no substantial differences between the chemical species present in the mother solutions of mononuclear and dinuclear peroxotungstooxalato complexes. Wave numbers of these four spectra are given in Table 1.

Figure 3 shows the IR spectra. The spectra of (a) and (b), and those of (c) and (d) are identical respectively. These ^{13}C NMR, Raman and IR spectra indicate that CWHPA (W/C = 4) is able to be reproduced from WIPA (or $WO_3 \cdot 2H_2O$ and H_2O_2) and oxalic acid, and that oxalate ion coordinates to the W atom in the solution. The IR bands of CO_2 in the antisymmetric (1590–1750 cm^{-1}) and symmetric (1200–1400 cm^{-1}) stretch modes reflect the coordination behavior of the oxalato group, as listed in Table 2. The splittings of the modes are more complex for the bidentate oxalato group in the mononuclear complex than for the quadridentate one in the dinuclear complex.

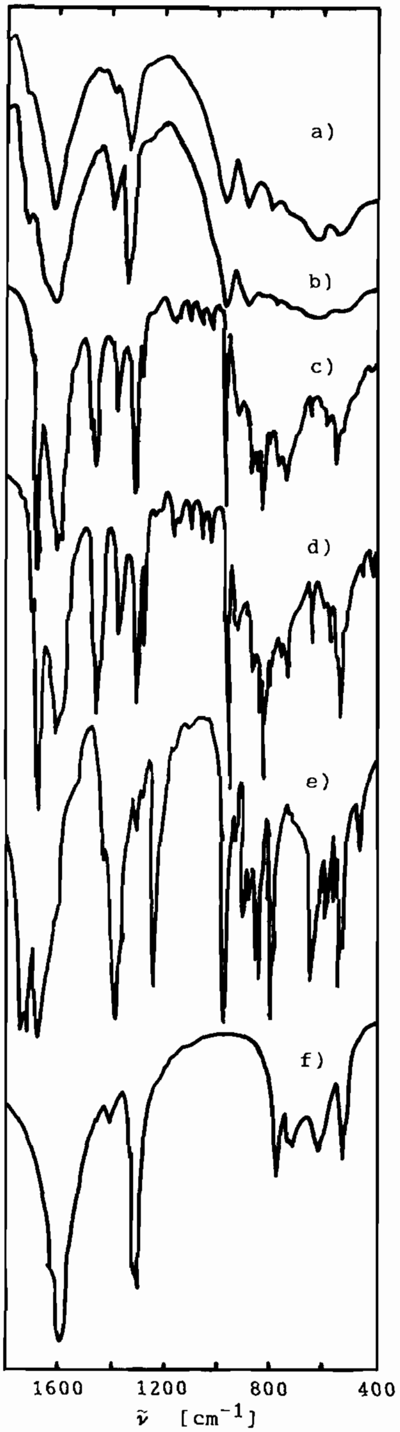

Fig. 3. IR spectra of solids with KBr disks: (a) CWHPA (W/C = 4); (b) glassy material from the $[WO_4^{2-}]/[C_2O_4^{2-}] = 8$ solution; (c) $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$; (d) tetrabutylammonium salt from the $[WO_4^{2-}]/C_2O_4^{2-}] = 8$ solution; (e) $K_2[WO(O_2)_2(C_2O_4)]$; and (f) $(COOK)_2 \cdot H_2O$.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 62470038) from the Ministry of Education, Science and Culture, Japan.

References

1 T. Kudo, *Nature (London), 312* (1984) 537.

2 T. Kudo, H. Okamoto, K. Matsumoto and Y. Sasaki, *J. Solid State Chem., 66* (1987) 283; T. Kudo, Y. Sasaki, M. Hashimoto, H. Ichida and K. Matsumoto, *Inorg. Chim. Acta, 133* (1987) 201.

3 T. Kudo, H. Okamoto, K. Matsumoto and Y. Sasaki, *Inorg. Chim. Acta, 111* (1986) L27.

4 K. Matsumoto, Y. Ozawa, Y. Sasaki, T. Kudo and H. Okamoto, *Inorg. Chim. Acta, 159* (1989) 185.

5 M. Hashimoto, T. Ozeki, H. Ichida, Y. Sasaki, K. Matsumoto and T. Kudo, *Chem. Lett.*, (1987) 1873.

6 K. Becker, *Z. Phys., 51* (1982) 484.

7 R. Stomberg and S. Olson, *Acta Chem. Scand., Ser. A, 39* (1985) 79.