Inorganica Chimica Acta, 133 (1987) 201–203

Formation of Peroxo Oxalato Complex of Tungsten(VI) Directly from Tungsten Carbide and Hydrogen Peroxide – a New Path to the Total Synthesis of the Organic Compound

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(Received March 30, 1987)

One of the present authors reported that tungsten carbide (WC) dissolves in hydrogen peroxide (H_2O_2) solution (normally 15%), to give a heteropolytungstic acid with carbon incorporated as a heteroatom [1]. More recently it was found that this acid (CW-HPA) contains peroxide (O–O) groups and its empirical formula was estimated as $Co_2 \cdot 12WO_3 \cdot 7H_2O_2 \cdot 20H_2O$ [2]. However, the C/W ratio in the compound is not always 1/12 but depends on the synthesis conditions [3].

The single crystal X-ray diffraction of $(C_{12}H_{24}O_6K)_4CW_{12}O_{40}$, derived from CW-HPA with 18-crown-6KCl, showed that its polyanion has a slightly distorted Keggin structure and the carbon atom in the central cavity is bonded with only two oxygen (C–O distance: 1.4–1.5 Å) [4]. However, this polyanion is not identical to that in the original CW-HPA (amorphous matter) because it contains no peroxide groups. At present the structure of the CW-HPA polyanion remains unknown. Recently, we obtained another single crystal salt through the reaction of CW-HPA with $n\text{-}Bu_4NHSO_4$ in a H_2O_2 solution [5]. According to X-ray analysis, its anion contains C_2O_4 as well as O–O groups as shown in Fig. 1. As this anion can be regarded as a fragment of the original polyanion, it is reasonable to think that carbon atoms in the latter are also in the form of C_2O_4. Therefore, we tried to isolate oxalic acid from CW-HPA.

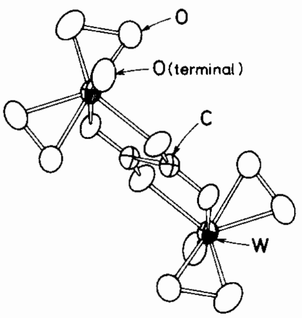

Fig. 1. Structure of anion $[C_2O_4\{WO(O{-}O)_2\}_2]^{2-}$ determined by the single crystal X-ray diffraction of its $(n\text{-}C_4H_9)_4N^+$ salt derived from CW-HPA. Two W atoms are connected by tetradentate C_2O_4.

Experimental

The synthetic procedure of CW-HPA was similar to that previously reported [1, 2]. Hexagonal WC powder (commercial powder, 99.9% pure, free carbon content 0.04%) was dissolved in a 15% H_2O_2 solution. Solid matter, mainly of undissolved WC, was carefully separated using 0.2 μm filter paper, and excess H_2O_2 was removed by catalytic decomposition using a platinized Pt net. The clear acidic solution thus obtained was dried at room temperature, to give a yellow non-crystalline solid (CW-HPA), containing 3.3 mmol W (determined from the ignition residue (WO_3) at 700 °C) and 0.81 mmol C (from the gas chromatographic analysis) per gram, and showing the infrared spectrum in Fig. 2. The Raman spectrum of CW-HPA was basically identical to that of its solution, indicating that its polyanion structure remains unchanged whether in solution or the solid state.

A solution containing 4.75 g of CW-HPA was added to a concentrated NaOH solution (25 mol l^{-1}) and heated on a hot plate until the gas evolution (probably O_2) had completely stopped. After cooling, HCl solution was added until the pH of the solution became 5–6. To the colorless clear solution thus obtained, a solution of $CaCl_2$ was added resulting in a white precipitate which was readily separated from the solution and dried under vacuum to give 0.29 g of white powder (PX).

Results and Discussion

The result of powder X-ray diffraction for PX is shown in Table I together with that for $CaC_2O_4 \cdot 2.5H_2O$ filed in JCPDS (filing number 20-233), showing almost complete accordance between them. Consequently, it is evident that PX contains a significant amount of $CaC_2O_4 \cdot 2.5H_2O$. Elemental analysis revealed that the C and H contents in PX are 11.2 and 2.43% (9.30 and 24.3 mmol/g), respectively. The permanganate titration indicated that all of the carbon was in the form of oxalate. Thus, PX contains 81% (by weight of $CaC_2O_4 \cdot 2.5H_2O$. This was confirmed by thermogravimetric analysis. The remaining

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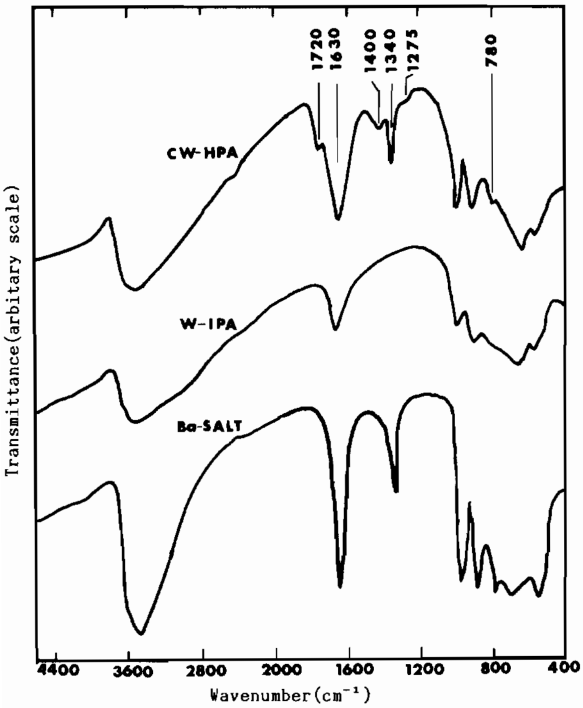


Fig. 2. The infrared spectra of (a) CW-HPA, (b) W-IPA (iso-acid corresponding to CW-HPA, synthesized from metallic W and H_2O_2) and (c) the Ba salt of CW-HPA. Bands at 1720, 1630, 1400, 1340, 1275 and 780 cm^{-1} are due to C_2O_4; 3500 and 1630 cm^{-1} to H_2O; others to the polyanion framework.

19% was estimated to be amorphous $(CaO)_xWO_3$ since the ignition residue of PX (at 850 °C) was identified as a mixture of CaO and Ca_3WO_6. The yield of oxalate was 70% against carbon in CW-HPA.

The infrared spectrum of CW-HPA is shown in Fig. 2, together with the spectra of W-IPA, the carbon-free iso-acid of CW-HPA obtained from metallic W and H_2O_2 [2], and the Ba salt of CW-HPA (amorphous white powder) [3]. Comparison of the spectrum of CW-HPA with that of W-IPA indicates that bands at 1720, 1400, 1340, 1275 and 780 cm^{-1} seen only in the former are due to the vibrations concerning carbon. These can be successfully assigned to the C_2O_4 vibrations as shown in Table II, provided that there are two types of C_2O_4 with different symmetries (C_{2v} and D_{2h}). (Bands at 1630 cm^{-1} are overlapped with H_2O, and 780 cm^{-1} may be assigned to W–O stretching.) The CO stretching vibrations of Co(III) oxalato complexes [6, 7] are shown in Table II for comparison. Therefore, CW-HPA may consist of two similar polyanions that are not identical in relation to the symmetry of C_2O_4. It is noteworthy that the Ba salt is composed purely of the D_{2h} type. The previously reported ^{13}C NMR shift (167–168 ppm from the TMS standard) for CW-HPA [2] is reasonable as the usually reported shift of $H_2C_2O_4$ is 163 ppm (in D_2O).

TABLE I. Powder X-ray Diffraction Result of PX[a] Compared with JPCDS $CaC_2O_4 \cdot 2.5H_2O$

PX		$CaC_2O_4 \cdot 2.5H_2O$ (JPCDS-20-233)		
d (Å)	I	d (Å)	I/I_0	(hkl)
8.84	w	8.74	8	110
6.21	s	6.18	100	020
4.44	m	4.42	30	121
3.92	m	3.91	8	130
3.70	w	3.67	6	002
		3.59	<2	031
3.39	vw	3.39	2	112
3.17	vw	3.16	2	022
		3.11	<2	231
3.10	m	3.09	10	040
		2.913	<2	330
2.81	m	2.812	12	222
2.78	s	2.774	65	141
		2.677	<2	132
2.43	m	2.423	10	150
2.41	m	2.402	10	013
		2.365	2	042
2.34	w	2.343	6	051, 341
		2.282	2	332
2.24	m	2.240	18	123
2.21	w	2.209	6	242
		2.190	2	251
2.12	m	2.119	8	350
		2.105	<2	033
2.03	w	2.023	4	152
2.00	vw	1.993	2	233
1.959	m	1.958	12	161
1.900	m	1.897	12	143
		1.878	<2	442
		1.867	<2	451
1.838	w	1.837	10	004, 352

[a] White powder derived from CW-HPA.

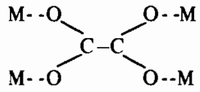
We should comment on the variable C/W ratio in CW-HPA. We found that CW-HPA solidified from a fresh solution takes the C/W of $\frac{1}{4.0} \sim \frac{1}{4.2}$ without exception. However, it was 1/13.8 when solidified from a solution after storage for 21 days at room temperature. Their infrared and Raman spectra were substantially the same except that infrared bands due to C_2O_4 were much weaker in the latter. It is, therefore, evident that 'true' or 'pure' CW-HPA (probably with C/W of 1/4) is slowly changed into W-IPA (iso-acid), releasing its carbons. Thus the compound so far called CW-HPA is really a mixture of CW-HPA (C/W = 1/4) and W-IPA (C/W = 0). Provided C/W = 1/4 in CW-HPA, it contains one C_2O_4 per 8W.

Ionic carbides such as Al_4C_3, CaC_2 or Mg_2C_3 containing carbons as C_n^{m-} yield methane, acetylene or allylene on hydrolysis. The oxidation number of carbon remains unchanged during hydrolysis (+1 in CaC_2 as well as in C_2H_2). In the reaction of WC with

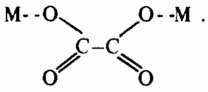
TABLE II. Observed IR Frequencies Concerning Carbons in CW-HPA and its Salts Compared with those of Co(III) Oxalato Complexes [7]

Compound	ν(CO) (cm^{-1})					Symmetry of C_2O_4 [a]
W-IPA						
CW-HPA	1720w	1630s[b]	1400w	1340s	1275vw	$D_{2h} + C_{2v}$
Ba•CW-HPA		1630s[b]		1340s		D_{2h}
Cs•CW-HPA	1720w	1630s[b]	1400w	1340s	1260vw	$D_{2h} + C_{2v}$
$[(Co_2(NH_3)_9(H_2O)(C_2O_4)]^{4+}$	1721m	1629s	1439s		1276m	C_{2v}
$[(Co_4(NH_3)_{12}(OH)_4(C_2O_4)]^{6+}$		1628s		1344s		D_{2h}

[a] D_{2h}:



C_{2v}:



[b] Overlapping with H_2O.

H_2O_2, however, carbon is oxidized from almost 0 to +3. At the same time, the C–C bonding is newly formed. No direct interaction between carbons exists in WC, a kind of interstitial type carbide. Conversely, carbons in CaC_2 are directly bonded with each other.

It is interesting to note that oxalic acid was the first organic compound totally synthesized from dicyan by Woehler in 1824, four years before his historically famous urea synthesis, though it was categorized as an inorganic compound at that time. However, dicyan (NC–CN) is an intermediate molecule between the inorganic and the organic one because it has the C–C bonding in itself. Accordingly, cyanide compounds are useful starting materials for organic synthesis, and the spatial cyans are often regarded as an origin of bio-matters.

The present total synthesis of oxalic acid (abundantly contained in most plants) might provide the chemical evolution theories with alternative possibilities because it proceeds via a non-cyanic path and under oxidizing conditions at a moderate temperature.

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