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Calorimetric Study of Hydrated Potassium Molybdenum Bronze

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Hydrated and dehydrated potassium bronzes, $K_{0.25}H_{0.07}MoO_3\cdot0.54H_2O$ (HyK-H2) with the six-coordination structure and $K_{0.25}H_{0.07}MoO_3$ (DehyK) with the eight-coordination one, were synthesized by a new direct method. The standard enthalpy of formation was determined by solution calorimetry to be -4950 ± 1 kJ mol^{-1} for HyK-H2 and -4817 ± 1 kJ mol^{-1} for DehyK, respectively. According to the thermodynamic data, HyK-H2 is stable.

It is well known that alkali metal molybdenum bronzes have a layer structure, in which alkali metal ions are inserted between the layers of MoO_3 constructed with MoO_6 octahedra. They have been of interest due to their interesting physical properties, such as a low-dimensional property. Therefore, they have some potential for technological applications, such as battery electrodes and electrochromic devices. The synthesis of alkali metal bronzes had required a high temperature of more than 800 K to melt the starting material.[1] However, Sotani et al. obtained alkali metal bronzes ($Na_{0.9}Mo_6O_{17}$,[2] $K_{0.3}MoO_3$,[3] $Rb_{0.3}MoO_3$,[4] and $Cs_{0.3}MoO_3$[5]) by heating the hydrated alkali bronzes in nitrogen at a temperature of lower than that of the usual melt method by about 200 K. We have thus carried out an investigation of the synthesis method and characterization of the hydrated alkali metal bronzes as a starting material for obtaining the alkali metal bronze. We found that hydrated alkali metal bronzes can be classified by two groups of a six-coordination type and a eight-coordination type, as shown in Fig. 1.[6] However, only the hydrated potassium bronzes could have both types.[6]

We recently obtained three kinds of hydrated potassium molybdenum bronzes by an ion-exchange method.[6] HyK-AD with adsorbed water was obtained by filtration just after synthesis, and gave a six-coordination structure. The other two were obtained by drying HyK-AD. One is the six-coordination type (HyK-H2) with two hydrate waters per one K^+ ion; the other is of the eight-coordination type (HyK-H1) with one hydrate water per one K^+ ion. However, it was very difficult to obtain HyK-H1.[6] When HyK-AD was heated in nitrogen or in air, HyK-H1 was fortunately obtained at 573 K, but could not be obtained every time. Therefore, we tried to obtain the HyK-H1 by some other method, and succeeded to synthesize the compound DehyK[7] with no hydrate water, which was the same eight-coordination structure as HyK-H1.

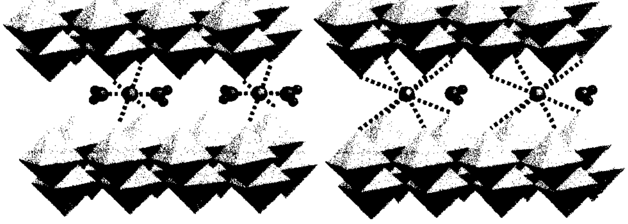

Fig. 1. The crystal structure of hydrated potassium bronzes: (a), six-coordination type; (b), eight-coordination type.

An important factor is to obtain the standard enthalpy of formation, because the stability of the compound is evaluated based on thermodynamic data. We recently reported on the standard enthalpy of formation of alkali decamolybdate, and considered the relation between their enthalpy and stability.[8]

In the present work, because there are no published quantitative thermodynamic data available for hydrated potassium bronzes, we obtained thermodynamic data and tried to clarify why the hydrated potassium bronzes had two coordination types, though the formation of HyK-H1 type was difficult to synthesize.

Experimental

Materials. Usually, hydrated potassium bronzes were prepared only by ion exchange from hydrated sodium bronzes, because of no appropriate reducing reagent to directly obtain the hydrated potassium bronze. However, we newly and directly obtained hydrated potassium bronzes by using a $K_2S_2O_4$ solution as a reducing reagent,[7] which was synthesized by ourselves, because $K_2S_2O_4$ was not on the market. MoO_3 was suspended in distilled water bubbling with nitrogen, and the $K_2S_2O_4$ solution was introduced drop by drop. The hydrated potassium bronze was formed immediately after introducing the $K_2S_2O_4$ solution. The sample was collected by suction filtration and washed well with distilled water. The six-coordination type (HyK-H2) was obtained by an air-dried treatment and the eight-coordination type (DehyK) without hydrate water by a vacuum-dried one. The sample was confirmed to be a single pure phase by X-ray diffraction.

Structure and Chemical Composition. The water contents of the samples were determined using a Mac Science TG-DTA 2010S system and a Cahn 2000 electromicrobalance from room temperature to 773 K at a heating rate of 10 K min^{-1}. The potassium and molybdenum contents in the samples were measured with a

Hitachi 180-80 atomic-absorption spectrometer using the 766.49 nm line for potassium and the 313.26 nm line for molybdenum. X-Ray diffraction (XRD) patterns of the samples were obtained using a Mac Science XMP3 X-ray diffractometer with Cu*Kα* radiation. The contents of Mo^{5+} were determined by using a method of Choain and Marrion.[8]

Calorimetric Procedure. The heat of dissolution of the samples was measured using a Tokyo-Riko MMC-5111 multi-microcalorimeter (conduction type twin calorimeter). The heat flux due to dissolution of the samples was converted to a potential, and recorded by a personal computer at a sampling interval of 1 s. The heat was estimated from the peak area appearing on the heat-flux curve by a comparison with that due to the Joule heat. The internal temperature of this calorimeter was adjusted precisely at (298.15±0.001) K and was monitored using a Beckmann's thermometer calibrated with a ΑΣΛ F25 precision platinum resistance thermometer. More than five measurements were carried out for each sample. The precision of the calorimeter was previously reported.[9] The hydrated and dehydrated potassium bronzes were sealed in a glass ampoule and were put in a calorimeter with 30 ml batches of a calorimetric reaction medium, which was prepared by dissolving 40 g of $K_3Fe(CN)_6$ in 1990 ml of 3.00 M KOH aqueous solution.[9,10] The standard molar enthalpy of formation of hydrated and dehydrated potassium bronzes was estimated from the observed dissolution heats by Hess's law of heat summation.

Results

Figure 2 shows the XRD patterns of the hydrated and dehydrated potassium bronzes. Pattern (a) with d_{020} = 1.057 nm was similar to that of HyK-H2 with the six-coordination type. However, pattern (b) of DehyK with d_{020} = 0.936 nm was identical with that of HyK-H1 with the eight-coordination type. Both samples belonged to the orthorhombic system, and the refined lattice parameters were a = 0.387(3), b = 2.150(3), and c = 0.346(9) nm for HyK-H2, and a = 0.383(1), b = 1.864(2), and c = 0.368(4) nm for DehyK, respectively. The lattice parameter of a and c is almost the same, but b gives a different value. This suggests that the interlayer spacing of HyK-H2 expands along the b-axis by about 0.3 nm. A determination of the atomic coordinates and a full structural discussion have not yet been made.

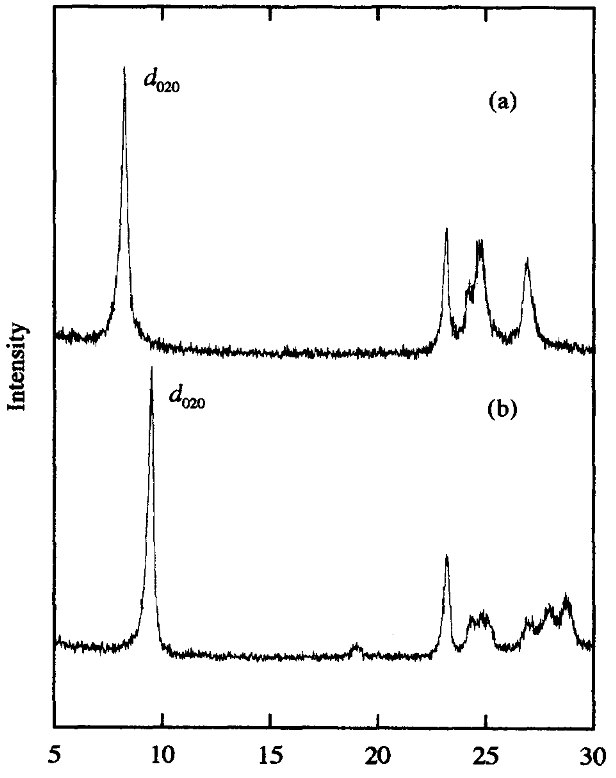

Fig. 2. XRD patterns of hydrated potassium bronze : (a), six-coordination type; (b), eight-coordination type.

The results of chemical and gravimetric analyses are given in Table 1. HyK-H2 possessed 2.32 hydrate waters per one K^+ ion, but DehyK had no hydrate water. The x value of both the hydrated and dehydrated potassium bronzes was 0.32. Because the content of K^+ is 0.25, a small amount of proton (x = 0.07) was inserted, which was confirmed by proton NMR. According to the results, the composition of HyK-H2 and DehyK is $K_{0.25}H_{0.07}MoO_3 \cdot 0.54H_2O$ and $K_{0.25}H_{0.07}MoO_3$, respectively. Both are not exactly the 'ideal formula' of the hydrated potassium bronze ($K_{0.25}MoO_3 \cdot nH_2O$). Although DehyK with the eight-coordination structure has no water, it is reliably and reproducibly produced by a direct reduction method.

The standard enthalpy of formation, $\Delta_f H^\circ$, of $K_xH_yMoO_3 \cdot nH_2O$ is obtained by assuming

$$K_xH_yMoO_3 \cdot nH_2O(s) + xHCl \cdot 55.5H_2O(l) \longrightarrow (x+y)/2MoO_2(s) + (2-x-y)/2MoO_3(s) + xKCl(s) + \{n+(x+y)/2+55.5x\}H_2O(l) \quad \Delta H_0 \tag{0}$$

to be

$$\Delta_f H^\circ(K_xH_yMoO_3 \cdot nH_2O) = (x+y)/2\Delta_f H^\circ(MoO_2) + (2-x-y)\,\Delta_f H^\circ(MoO_3) + x\Delta_f H^\circ(KCl) + \{n+(x+y)/2+55.5x\} \times \Delta_f H^\circ(H_2O) - x\Delta_f H^\circ \times (HCl \cdot 55.5H_2O) - \Delta H_0, \tag{1}$$

where ΔH_0 is the heat of reaction (0). If we could obtain ΔH_0, $\Delta_f H^\circ(K_xH_yMoO_3 \cdot nH_2O)$ could be determined. ΔH_0 can be obtained as

$$\Delta H_0 = \Delta H(a) - (x+y)/2\Delta H(b) - (2-x-y)/2\Delta H(c) - x\Delta H(d) + x\Delta H(e) - \{n+(x+y)/2+55.5x\}\Delta H(f) \tag{2}$$

by using Eqs. (a)—(f) in Table 2. ΔH(a)—ΔH(f) was precisely measured using a calorimeter, as shown in Table 2. By putting these observed data into Eq. 2, ΔH_0 was determined. By combining these data in Table 2 and the data reported for

Table 1. Results of Chemical and Gravimetric Analyses of HyK-H2 and DehyK

	Mo(%)	K(%)	x	H_2O(%)	H_2O / K^+	H^+
HyK-H2	58.42 (1.00)	5.95 (0.25)	0.32	6.36 (0.54)	2.32	0.07
DehyK	62.39 (1.00)	6.36 (0.25)	0.32	0 (0)	0	0.07

Table 2. Calorimetric Reaction Scheme for $K_xH_yMoO_3\cdot nH_2O$

Reaction			ΔH° / kJ[a)]
(a) $K_xH_yMoO_3\cdot nH_2O(s)+(x+y)Fe(CN)_6^{3-}(soln)+(2+y)OH^-(soln)$ $= xK^+(soln)+MoO_4^{2-}(soln)+(x+y)Fe(CN)_6^{4-}(soln)+(1+y+n)H_2O(soln)$	ΔH(a)	K^+(six)	-103.24 ± 0.99
		K^+(eight)	-82.62 ± 0.93
(b) $MoO_2(s)+2Fe(CN)_6^{3-}(soln)+4OH^-(soln)$ $= MoO_4^{2-}(soln)+2Fe(CN)_6^{4-}(soln)+2H_2O(soln)$	ΔH(b)		-293.62 ± 0.58
(c) $MoO_3(s)+2OH^-(soln) = MoO_4^{2-}(soln)+H_2O(soln)$	ΔH(c)		-85.20 ± 0.18
(d) $KCl(s) = K^+(soln)+Cl^-(soln)$	ΔH(d)		15.02 ± 0.18
(e) $HCl\cdot 55.5H_2O(l)+OH^-(soln) = 56.5H_2O(soln)+Cl^-(soln)$	ΔH(e)		-65.85 ± 0.52
(f) $H_2O(l) = H_2O(soln)$	ΔH(f)		-0.061 ± 0.003
$\Delta H_0 = \Delta H(a)-(x+y)/2\Delta H(b)-(2-x-y)/2\Delta H(c)-x\Delta H(d)$ $+x\Delta H(e)-\{n+(x+y)/2+55.5x\}\Delta H(f)$	ΔH_0	K^+(six)	-3.8 ± 1.0
		K^+(eight)	16.83 ± 0.96

a) Uncertainties expressed as twice the standard error of the mean.

Table 3. Standard Molar Enthalpy of Each Standard Compound[a)]

	Δ_fH° / kJ mol^{-1}		Δ_fH° / kJ mol^{-1}
MoO_2 (*s*)	−587.9	H_2O (*l*)	−285.830
MoO_3 (*s*)	−745.2	$HCl\cdot 55.5H_2O$ (*l*)	−165.47
KCl (*s*)	−436.7		

a) "Kagaku Binran," Maruzen, Tokyo (1975) Chap. 8, p. 953.

the standard enthalpy of each standard compound in Table 3, Δ_fH° of hydrated and dehydrated potassium molybdenum bronzes were determined according to Eq. (1), as listed in Table 4.

Discussion

As previously mentioned, it is difficult to obtain HyK-H1 with the eight-coordination structure. Possible reasons may depend on the strength of the hydration energy, the stereochemistry of the hydrated ion, and/or the interaction between the hydrated ion and terminal oxygens of MoO_6 octahedra. We thus tried to clarify this problem thermodynamically.

The enthalpy of the reaction, ΔH_3, of HyK-H2 from DehyK can be estimated according to

$$0.54H_2O(g) + K_{0.25}H_{0.07}MoO_3(s) = K_{0.25}H_{0.07}MoO_3\cdot 0.54H_2O(s), \tag{3}$$

where ΔH_3 corresponds to the enthalpy of a solution of gaseous water into $K_{0.25}H_{0.07}MoO_3$. The value of ΔH_3 is calculated to be $\Delta_fH^\circ(\text{HyK-H2}) - \Delta_fH^\circ(\text{DehyK}) - 0.54\Delta_fH^\circ[H_2O(g)]$ ($= -3.0\pm1.0$ kJ), which shows an exothermic process. The molar enthalpy corresponding to 1 mol water inserted into $K_{0.25}H_{0.07}MoO_3$ is obtained from ΔH_3 to be $\Delta H_3/0.54 = -5.5$ kJ mol^{-1}. This may be a measure of the binding energy of water with the K^+ ion and the terminal oxygen of the MoO_6 octahedra. According to the literature,[11] the entropy of H_2O (*g*) is 188.72 J K^{-1} mol^{-1}. Because $K_{0.25}H_{0.07}MoO_3(s)$ and $K_{0.25}H_{0.07}MoO_3\cdot 0.54H_2O(s)$ have the same crystal system, the entropy change of Eq. 3 approximates that for the loss of gaseous water. Consequently, we assume, roughly, that ΔG° at 298 K is −33 kJ for 0.54 H_2O. Therefore, Eq. 3 proceeds spontaneously.

Table 4. The Enthalpies of Formation for Hydrated and Dehydrated Potassium Molybdenum Bronzes

Phase	Δ_fH° / kJ mol^{-1}
HyK-H2	-4950 ± 1
DehyK	-4816 ± 1

Because we could not yet determine the atomic coordinate and the full structure, we could not precisely understand the structure. However, it is roughly considered that the lattice parameter "*a*" corresponds to the oxygen–oxygen distance of the terminal oxygen along the *a*-axis, and "*c*" to that along the *c*-axis. The oxygen–oxygen distance between the interlayers was estimated to be Δd $\{= d_{020}-d_{020}(MoO_3)\}$, obtained from the difference in the interlayer spacing. Based on the above assumption, the distance, $r_{K\text{–}O}$, between potassium ion and terminal oxygens was calculated to be 0.259 nm for the six-coordination type and 0.287 nm for the eight-coordination type. Because the strength of the Coulomb interaction is inversely proportional to the square of the distance, the interaction between the K^+ ion and the terminal oxygen in the six-coordination structure is slightly stronger than that in the eight-coordination one. This may be one possible reason that the hydrated potassium bronze prefers to take the six-coordination type rather than the eight-coordination type.

The hydrated lithium and sodium bronzes have the six-coordination structure with two hydrate waters per one alkali ion, and the hydration energy is 519 kJ mol^{-1} for Li^+ and 406 kJ mol^{-1} for Na^+, respectively.[12] On the other hand, the hydrated rubidium and cesium bronzes have the eight-coordination structure with one hydrate water per one alkali ion and the hydration energy is 293 kJ mol^{-1} for Rb^+ and 264 kJ mol^{-1} for Cs^+, respectively.[12] The hydration energy of K^+ is 322 kJ mol^{-1}, which falls between the value of the six and eight-coordination structures. This suggests that the

K^+ ion has a possibility to take two positions, depending on the condition. Assuming that the interaction energy of K^+–O (terminal) is equal to K^+–O (hydrated water) in the six-coordination type, we can simply estimate the interaction energies per one K^+–O bond; the value is 40.3 kJ mol^{-1} for the eight-coordination type and 53.7 kJ mol^{-1} for the six-coordination type, respectively. This means that the strength of the interaction between the K^+ ion and O (terminal) of the six-coordination type is larger than that of the eight-coordination one. This fact predicts that the six-coordination structure is rather preferable to the eight-coordination structure. Indeed, DehyK changed spontaneously to HyK-H2 upon standing in an air atmosphere. Therefore, we are reasonable to consider that ΔH_3 becomes a negative value. It is clear that the hydrate water plays an important role in a change from DehyK to HyK-H2. It is understandable that the enthalpy of formation provides us a good information about the stability of HyK-H2 and DehyK.

The thermochemical data determined here for the two kinds of hydrated potassium bronzes can be used as a basis for further discussing the stabilities of water coordination formed in the same component system.

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