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Hydrothermal Synthesis and Calorimetric Study of Blue Molybdenum Bronze, $K_{0.28}MoO_3$

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The hydrothermal heating of $H_{0.28}MoO_3$ in a KCl solution at 431 K led to the formation of a single phase of $K_{0.28}MoO_3$. Hydrated molybdenum bronze was formed as a mid-product during conversion from hydrogen molybdenum bronze to blue bronze. The formation enthalpy of $K_{0.28}MoO_3$ was determined by solution calorimetry to be $\Delta_f H^\circ$ ($K_{0.28}MoO_3$, s) $= -840.2$ kJ mol^{-1} at 298.15 K. The enthalpies of the transformation reaction from hydrogen bronze to hydrated bronze and of the formation reaction of blue $K_{0.28}MoO_3$ from hydrated bronze were calculated to be $+33$ kJ mol^{-1} and -48 kJ mol^{-1} at 298.15 K, respectively. The calculated enthalpies of the reactions were concordant with the suggested reaction mechanism for a transformation from hydrogen molybdenum bronze to potassium bronze.

Blue molybdenum bronzes, A_xMoO_3 ($0.28 \leq x \leq 0.30$, A = K, Rb, Cs, and Tl), attracted the attention of scientists during past decades. They display a wide variety of crystal structures and interesting physical properties, such as a low-dimensional metallic behavior,[1–3] metal-to-semiconductor transitions driven by a charge-density wave and superconductivity.[4–7]

Blue K_xMoO_3 ($0.28 \leq x \leq 0.30$) is a monoclinic (space group *C2/m*) structure (Fig. 1c), built of infinite sheets of distorted octahedra of MoO_6 held together by potassium cations. Potassium molybdenum bronzes have been prepared mainly

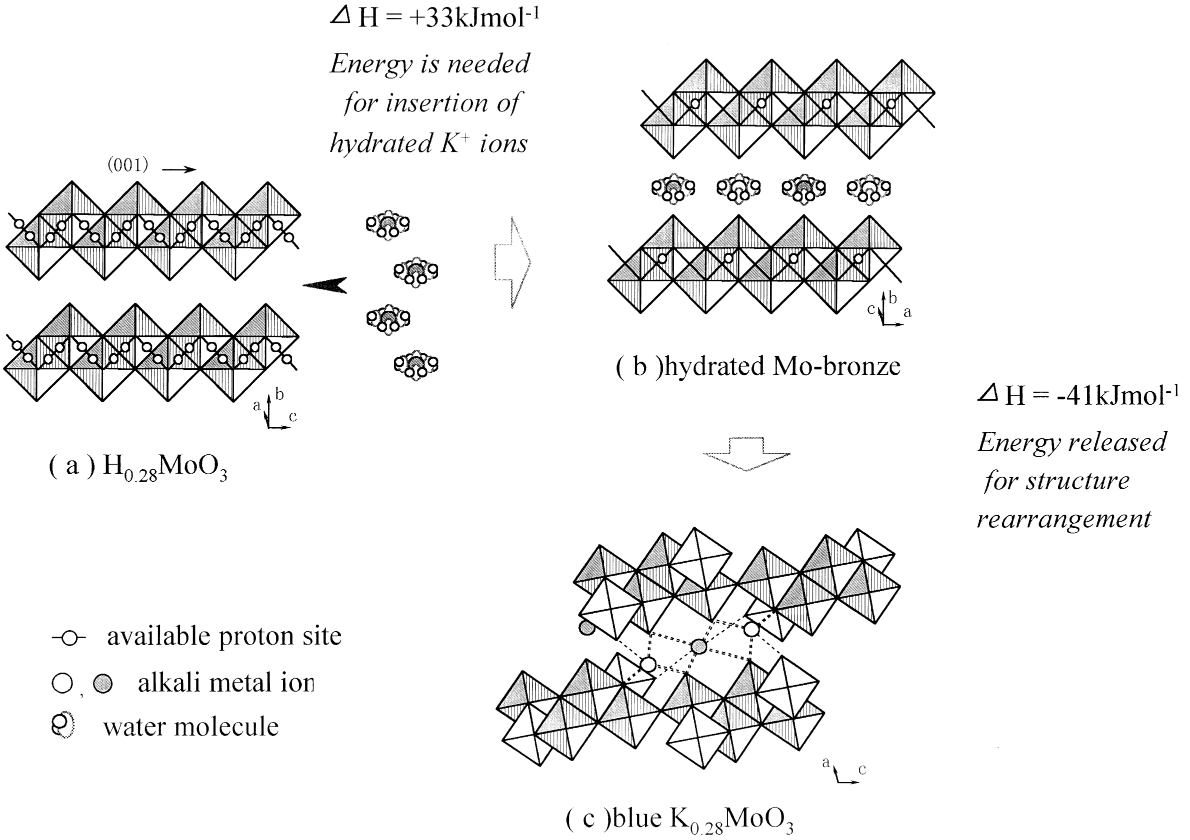

Fig. 1. Structure projections of (a) hydrogen molybdenum bronze, H_xMoO_3 ($0.23 < x < 0.4$), along (100); (b) hydrated molybdenum bronze, $(K{\cdot}nH_2O)_yMoO_3$, along (001); (c) blue molybdenum bronze along (010).

by molten salt methods[8] at temperatures exceeding 800 K: (1) electrolytic reduction of molten mixtures of MoO_3 and K_2MoO_4, and (2) reaction between stoichiometrically mixed K_2MoO_4, MoO_3 and MoO_2. A temperature-gradient flux technique was reported by Greenblatt et al. in 1984 for the preparing of single-crystal blue molybdenum bronzes.[9,10]

Recently, we successfully prepared single phase blue $K_{0.28}MoO_3$ at a temperature of 431 K by a hydrothermal synthesis route.[11] Compared with the traditional methods, the formation temperature of blue potassium molybdenum bronzes was lowered dramatically. It was observed in our work that the formation of blue potassium molybdenum bronzes was completed by a multi-step pathway at low temperature, and several kinds of molybdenum oxides acted as intermediates. The reaction mechanism was found to be as follows by our previous work:[11]

$$\begin{aligned}&H_{0.28}MoO_3(s) + xK^+(aq) + nxH_2O(l)\\ &\rightarrow [K(H_2O)_n]_xH_{0.28-x}MoO_3(s) + xH^+(aq),\end{aligned} \tag{i}$$

$$\begin{aligned}&[K(H_2O)_n]_xH_{0.28-x}MoO_3(s) + (0.28-x)K^+(aq)\\ &\rightarrow K_{0.28}MoO_3(s) + (0.28-x)H^+(aq) + nxH_2O(l).\end{aligned} \tag{ii}$$

The overall reaction is

$$\begin{aligned}&H_{0.28}MoO_3(s) + 0.28K^+(aq)\\ &\rightarrow K_{0.28}MoO_3(s) + 0.28H^+(aq).\end{aligned} \tag{iii}$$

In order to evaluate and gain insight into the above-described formation mechanism of potassium molybdenum bronze, we determined the formation enthalpies of $K_{0.28}MoO_3$ in the present work by means of solution calorimetry and tried to find out the thermodynamic reasons for the evolution of molybdenum oxides during a hydrothermal heating process.

Experimental

Preparation of Blue Potassium Molybdenum Bronze. First, 0.432 g of $H_{0.28}MoO_3$ (0.003 mol) was suspended in 30 mL of a 0.9 M deaerated KCl aqueous solution in a teflon-lined autoclave, and stirred well by a magnetic stirrer. All of the loading operations were done in a nitrogen-filled glove-box. The loaded autoclave was heated in an oven for 30 hours at 431 K, and then cooled by electrical fan. The resulting products were separated by filtration and washed several times by distilled water.

Phase identification was accomplished by X-ray powder diffraction (XRD) using a Mac Science MXP3VZ X-ray diffractometer with Cu$K\alpha$ radiation. The products were analyzed for the potassium/molybdenum ratios by a HITACHI 180–80 atomic absorption spectrometer using the 313.3 nm line for Mo, 766.5 nm for potassium, and for the molybdenum mean oxidation state by a method of Choain & Marrion.[12]

Calorimetric Procedure. The heats of dissolution of the samples were measured by a Tokyo-Riko MMC-5111 multi-microcalorimeter (conduction-type twin calorimeter). The heat flux due to dissolution was converted to a potential and recorded by a computer at a sampling interval of 1s. The heat was estimated from the peak area appearing on the heat flux curve by a comparison with that due to Joule heat. The internal temperature of this calorimeter was adjusted precisely at (298.15 ± 0.0001) K and was monitored using a Beckmann's thermometer calibrated with a ΑΣΛ F 25 precision platinum resistance thermometer. The precision of the calorimeter was tested by measuring the dissolution heat of 0.1 g of tris(hydroxymethyl)aminomethane (NIST, SRM 724a) in 20 mL of 0.10 M HCl. The result was (−245.81 ± 0.26) K, which agreed well with that reported in the literature.[13,14]

The molar ratios of solute to reactant species were arranged to be very small in order to justify carrying out reactions independently in the same starting medium; as far as possible, stoichiometric amounts of the reactants were used according to the chosen thermodynamic cycle.

Ten to 15 mg charges of molybdenum bronze were dissolved in 30 mL batches of the calorimetric reagent, which were prepared by dissolving 40 g of $K_3Fe(CN)_6$ in 1990 mL of a 3.00 M KOH solution. Three measurements were made on each sample. The standard molar enthalpies of formation of potassium molybdenum bronzes were calculated from the measured dissolution heats by Hess's law of heat summation.

Results and Discussion

Determination of the Enthalpies of Formation of Blue $K_{0.28}MoO_3$. The solid phase collected after hydrothermal heating showed the XRD pattern of a single phase blue potassium molybdenum bronze. All of the observed peaks coincided well with the reflection data of single-phase blue potassium molybdenum bronze recorded by JCPDS cards. The chemical analysis confirms the composition of blue bronze as being $K_{0.28}MoO_3$.

The calorimetric reaction scheme used to calculate the enthalpies of formation of $K_{0.28}MoO_3$ is listed in Table 1. The symbols (s) and (l) designate solid and liquid substances respectively. The symbol (sol) indicates that the designated substance was dissolved in the reaction medium.

The enthalpies for reactions (2)–(6) in Table 1 were determined using an identical calorimetric reagent at 298.15 K and with similar solute/solvent ratios. Reaction (7) is the overall calorimetric reaction determined. The standard enthalpy of formation of blue $K_{0.28}MoO_3$ is given by the following equation:

$$\begin{aligned}\Delta_f H^\circ\,(K_{0.28}MoO_3, s) = {}&\Delta H_7 - 0.28\Delta_f H^\circ\,\{[HCl, 55.5H_2O], l\}\\ &+ 0.14\Delta_f H^\circ\,(MoO_2, s)\\ &+ 0.86\Delta_f H^\circ\,(MoO_3, s)\\ &+ 0.28\Delta_f H^\circ\,(KCl, s)\\ &+ 0.14\Delta_f H^\circ\,(H_2O, sol).\end{aligned}$$

Combining the measured data of ΔH_7 with the standard enthalpies of formation (298.15 K, kJ mol^{-1}) listed in Table 2 gives the following standard enthalpy of formation of blue bronze (298.15 K, kJ mol^{-1}): $\Delta_f H^\circ\,(K_{0.28}MoO_3, s) = -840.2$ kJ mol^{-1}. The integral molar enthalpy of a solution of K into MoO_3 ($\Delta H'$) is $\Delta H'\,(K_{0.28}MoO_3, s) = -339.4$ kJ mol^{-1} according to

$$K(s) + 1/xMoO_3(s) \rightarrow 1/xK_xMoO_3(s). \tag{8}$$

Dickens et al.[15] have prepared blue $K_{0.30}MoO_3$ by the electrolytic reduction of molten mixtures of MoO_3 and potassium molybdate, K_2MoO_4, and determined the enthalpy of formation of $K_{0.30}MoO_3$ by different thermochemical reaction

Table 1. Calorimetric Reaction Scheme for $K_{0.28}MoO_3$

Reaction		ΔH_{298K}/kJ mol^{-1}
(1) $K_{0.28}MoO_3(s) + 0.28[Fe(CN)_6]^{3-}(sol) + 2OH^-(sol)$ $= 0.28K^+(sol) + [MoO_4]^{2-}(sol) + 0.28[Fe(CN)_6]^{4-}(sol) + H_2O(sol)$	ΔH_1	-90.7 ± 0.5[a)]
(2) $MoO_2(s) + 2[Fe(CN)_6]^{3-}(sol) + 4OH^-(sol)$ $= [MoO_4]^{2-}(sol) + 2[Fe(CN)_6]^{4-}(sol) + 2H_2O(sol)$	ΔH_2	-293.6 ± 0.6[a)]
(3) $MoO_3(s) + 2OH^-(sol) = [MoO_4]^{2-}(sol) + H_2O(sol)$	ΔH_3	-85.2 ± 0.2[a)]
(4) $KCl(s) = K^+(sol) + Cl^-(sol)$	ΔH_4	$+15.0 \pm 0.2$[a)]
(5) $[HCl, 55.5H_2O](l) + OH^-(sol) = Cl^-(sol) + 56.5H_2O(sol)$	ΔH_5	-65.9 ± 0.5[a)]
(6) $H_2O(l) = H_2O(sol)$	ΔH_6	-0.1 ± 0.0[a)]
(7) $K_{0.28}MoO_3(s) + 0.28HCl(sol)$ $=0.14MoO_2(s) + 0.86MoO_3(s) + 0.28KCl(s) + 0.14\ H_2O(sol)$	ΔH_7	$+ 1.1 \pm 1.0$[b)]
$\Delta H_7 = \Delta H_1 - 0.14\Delta H_2 - 0.86\Delta H_3 - 0.28\Delta H_4 + 0.28\Delta H_5 - 15.68\Delta H_6$		

a) Uncertainties expressed as twice the standard deviation of the mean. b) Uncertainty is the square root of the sum of the square of the uncertainties in the individual terms.

Table 2.

$\Delta_f H°$ (MoO_3, s) = −745.2[a)]	$\Delta_f H°$ (MoO_2, s) = −587.9[a)]	$\Delta_f H°$ (KCl, s) = −436.7[a)]
$\Delta_f H°$ (H_2O, l) = −285.8[a)]	$\Delta_f H°$ {[HCl, $55.5H_2O$], l} = −165.5[b)]	

a) Kagaku Binran, Maruzen, Tokyo (1975), Ch.8, p. 953.
b) U.S. National Bureau of Standards, Circular 500, Washington (1952)

scheme. The integral molar enthalpy of solution of K into MoO_3, $\Delta H'$ ($K_{0.30}MoO_3$, s), is −336.7 kJ mol^{-1}, quite close to the value of blue $K_{0.28}MoO_3$ obtained by our work. The small discrepancy between the two sets of values obtained by the two different thermochemical reaction schemes may be due to the different compositions of the calorimetric solvents and the solute/solvent ratios used.

Dickens[15] had also measured the enthalpies of formation of the β-phase $Na_xV_2O_5$ ($0.20 \leq x \leq 0.33$) with various values of x, and found over the range of composition that the standard enthalpy of formation of $Na_xV_2O_5$ varied linearly with x; namely, the integral molar enthalpy of solution of Na into V_2O_5 ($\Delta H'$) is a constant. The good agreement between our data [$\Delta H'$ ($K_{0.28}MoO_3$, s) = −339.4 kJ mol^{-1}] and that of Dickens [$\Delta H'$ ($K_{0.30}MoO_3$, s) = −336.7 kJ mol^{-1}] was parallel with the result found for $Na_xV_2O_5$.

Enthalpy Change for the Formation Reactions of Blue $K_{0.28}MoO_3$. In this work, for the convenience of calculation, the following three assumptions were made:

(1) The formula of the intermediate hydrated molybdenum bronze in reaction (i) and (ii) was $[K(H_2O)_6]_{0.25}H_{0.03}MoO_3(s)$ ($n = 6$, $x = 0.25$). This is supported by two facts: (a) The theoretical maximum amount of the inserted potassium cation in a hydrated molybdenum bronze[16] is 0.25; (b) In aqueous solution, it was estimated that one K^+ ion of hydrated sodium molybdenum bronze is surrounded by $6H_2O$ molecules.[17]

(2) Our previous systematic study[18] clarified the relationship between the standard enthalpy of formation of hydrated sodium molybdenum bronze, $Na_{0.25}H_yMoO_3 \cdot nH_2O$ ($0 \leq y \leq 0.12$), and the coordinated amount of hydrogen ions. The insertion of hydrogen led to lower $\Delta_f H°$ of hydrated molybdenum bronze. However, the maximum negative drops did not exceed 8 kJ mol^{-1} in the range of $0 \leq y \leq 0.12$. Therefore, because the hydrated potassium bronze showed a similar behavior to that of the hydrated sodium bronze, we assume that the variations in $\Delta_f H°$ of the hydrated potassium molybdenum bronze caused by the small changes (≤ 0.04) in the amount of hydrogen ions were very small and negligible, i.e., $\Delta_f H°\{[K(H_2O)_6]_{0.25}H_{0.03}MoO_3 \cdot 0.54H_2O, s\} \approx \Delta_f H°\ \{[K(H_2O)_6]_{0.25}H_{0.07}MoO_3 \cdot 0.54H_2O, s\}$. The value of $\Delta_f H°\{[K(H_2O)_6]_{0.25}H_{0.07}MoO_3 \cdot 0.54H_2O, s\}$was previously measured, giving −983.1 kJ mol^{-1} at 298.15 K.[19]

(3) Former studies[18] also found that the $\Delta_f H°$ of hydrated alkaline earth metal molybdenum bronze changed linearly with the amount of water molecules in the range of $0.41 \leq n \leq 1.25$. This provided the grounds to presume that a linear relation also exits between the standard enthalpy of formation of hydrated potassium molybdenum bronze and the H_2O content. Thus, the following equation was assumed:

$$\begin{aligned}&\Delta_f H°\ \{[K(H_2O)_n]_{0.25}H_yMoO_3, s\}\\ &\approx \Delta_f H°\ (K_{0.25}H_{0.07}MoO_3, s) - 0.25n \cdot Q,\end{aligned}$$

where Q is a constant which equals to +247.8 kJ mol^{-1} calculated by [$\Delta_f H°$ ($K_{0.25}H_{0.07}MoO_3$, s) − $\Delta_f H°$ ($K_{0.25}H_{0.07}MoO_3 \cdot 0.54H_2O$, s)]/0.54. The standard enthalpy of formation of the de-hydrated type of $K_{0.25}H_{0.07}MoO_3(s)$ was already measured at 298.15 K to be −849.3 kJ mol^{-1} in our former work.[19]

Based on the above-described suppositions, the enthalpies of reactions (i), (ii), and (iii) at 298.15 K, were calculated, giving:

$$\begin{aligned}\Delta H_{(i)} &= \Delta_f H°\ \{[K(H_2O)_n]_xH_{0.28-x}MoO_3, s\}\\ &\quad + x\Delta_f H°\ (H^+, aq) - \Delta_f H°\ (H_{0.28}MoO_3, s)\\ &\quad - x\Delta_f H°\ (K^+, aq) + nx\Delta_f H°\ (H_2O, l)\\ &\approx \Delta_f H°\ \{[K(H_2O)_6]_{0.25}H_{0.03}MoO_3, s\}\\ &\quad + 0.25\Delta_f H°\ (H^+, aq)^{20} - \Delta_f H°\ (H_{0.28}MoO_3, s)\\ &\quad - 0.25\Delta_f H°\ (K^+, aq)^{20} + 6 \times 0.25 \times \Delta_f H°\ (H_2O, l)\\ &\approx \Delta_f H°\ (K_{0.25}H_{0.07}MoO_3, s) - 247.8 \times 1.5\\ &\quad + 0.25 \times 440 - (-763.3) - 0.25 \times 193\end{aligned}$$

$$- 6 \times 0.25 \times (-285.8)$$
$$\approx +33 \text{ kJ mol}^{-1},$$
$$\Delta H_{\text{(ii)}} \approx -41 \text{ kJ mol}^{-1}, \text{ and}$$
$$\Delta H_{\text{(iii)}} \approx -8 \text{ kJ mol}^{-1}.$$

In our previous work, we proposed a mechanism model of formation of blue potassium molybdenum bronze (Fig. 1).[11] Hydrogen molybdenum bronze and hydrated bronze have the same layer structure of MoO_3, which are held together only by van der Waals forces (Figs. 1a and 1b). During reaction (i), energy is needed for the topotactical insertion of hydrated K^+ ions into the empty interlayers of hydrogen molybdenum bronze, which was proved by the positive value of $\Delta H_{\text{(i)}}$. Because the entropy of solids is very small, if we neglect the difference in the entropy between the solid hydrogen bronze and hydrated bronze, the change in the free energy for reaction (i) and (ii) can be estimated. Since the entropy of H^+ in aqueous solution is smaller than that of K^+ [21] and H_2O is on the left side of the equation (i), the change in the free energy of reaction (i) is positive. Therefore, a higher temperature seems to be requested to promote the reaction proceeding to the right side. Low temperature hydrothermal heating provided just the necessary energy to initiate the reaction, which was not so much as to destroy the layer structure of the hydrogen bronze. In reaction (ii), the formation of blue molybdenum bronze is a process involving structure rearrangement from hydrated bronze. The negative value of enthalpy shows a transformation to more stable phases along with releasing energy. Since the coefficient of the enthalpy of K^+ and H^+ in equation (ii), i.e., $(0.28 - x)$, was quite small (about 0.03, since the maximum amount of inserted K^+ in hydrated molybdenum is 0.25 per formula),[16] and H_2O was formed, the entropy change was presumed to be negative. Hence, the change in the free energy of reaction (ii) was also negative; namely, the hydrated molybdenum bronze was metastable upon the dehydration reaction. Though hydrated molybdenum bronze with a high content of hydrated water molecules usually lost part of its hydrated waters when dried in air, reaction (ii) under ambient conditions was never observed, presumably because of the low cation mobility. The overall reaction (iii) is marginally exothermic.

Conclusion

The standard enthalpy of formation of blue $K_{0.28}MoO_3$ was determined to be -840.2 kJ mol^{-1} at 298.15 K by solution calorimetry. The enthalpies of the transformation reaction from hydrogen bronze to hydrated bronze, and the formation reaction of blue $K_{0.28}MoO_3$ from hydrated bronze were calculated as $+33$ kJ mol^{-1} and -41 kJ mol^{-1} at 298.15 K, respectively. The obtained enthalpies of the formation reactions provided useful information to understand the formation mechanism of the blue molybdenum bronze.

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