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Calorimetric study of alkali-metal decamolybdates

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The enthalpies of formation of the alkali-metal decamolybdates $(A_2O)_{x/2}\cdot10MoO_3\cdot nH_2O$ (A = Li, Na, K, Rb, and Cs) have been determined by solution calorimetry; relations between the thermodynamic quantities obtained, chemical composition and crystal structures are discussed.

Introduction

The alkali-metal decamolybdates of ideal formula, $A_2O\cdot10MoO_3\cdot nH_2O$, form a structurally related family.[1] The complete crystal structures of two members of which, A = K, Na, have been determined.[2,3] For both, the framework structure consists of double chains of edge-sharing MoO_6 octahedra linked by common corners which form wide (0.29 nm diameter) tunnels occupied by the alkali metal ion (Fig. 1). In the case of $K_2O\cdot10MoO_3\cdot5H_2O$,[2] space group $P6_3/m$, only 5/6 of the 6(h) sites are randomly occupied by Mo and it is suggested that 5 H atoms are attached to the oxygens surrounding the vacant Mo site as two OH_2 and one OH group leading to its structural formulation as $KMo_5O_{15}(OH)\cdot2H_2O$. The analogous Na compound[3] differs only in detail from the K-decamolybdate and, as shown below, the lattice parameters of the whole family of the alkali-metal decamolybdate are closely related. For all these compounds the presence of wide one-dimensional tunnels suggest that there should be a rich intercalation chemistry and related properties to investigate. There are no published quantitative thermodynamic data available for these compounds and we present the determination of their enthalpies of formation here.

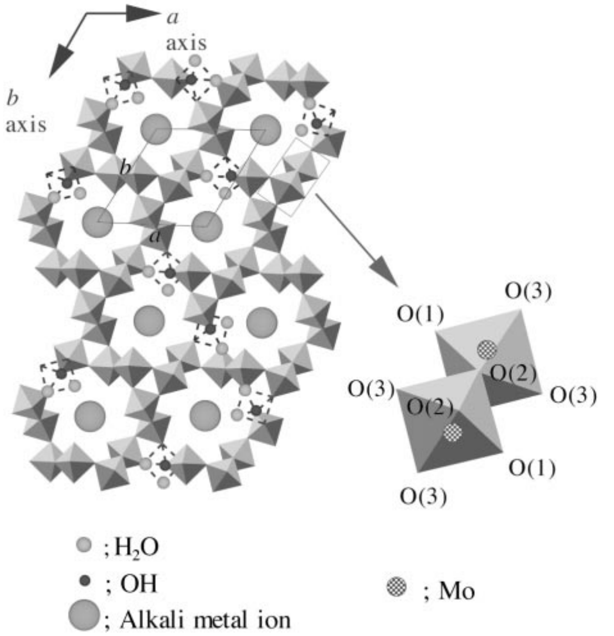

Fig. 1 The crystal structure of alkali-metal decamolybdate (after B. Krebs and I. Paulat-Böchen, reference 2 in the text).

Experimental

Materials

Alkali-metal decamolybdates were prepared by heating acidified A_2MoO_4 solutions.[1,4] A_2MoO_4 solutions were obtained by dissolving the stoichiometric mixture of A_2CO_3 and MoO_3 with water ($2A^+ + CO_3^{2-} + MoO_3 \rightarrow 2A^+ + MoO_4^{2-} + CO_2\uparrow$).† In the typical preparation of A-deca samples, 20 ml of 0.30 M A_2MoO_4 solution and 30 ml of 0.4 M HNO_3 solution were mixed [degree of acidification of solution $HNO_3/Mo = 2$, (molar ratio)], and then heated at 343 K for 2 h with constant stirring. The A-deca samples were formed as precipitates after such treatment. The samples were collected by suction filtration, washed well with distilled water, and air-dried for a few days. It was confirmed by X-ray diffraction that the samples were single pure phases. A-deca samples gradually changed from milky white to light blue in the light. Thus, they were stored in the dark to avoid discoloration.

Structure and chemical composition

The water contents of the samples were determined by TG–DTA with measurements performed on a Mac Science TG-DTA 2010S system from room temperature to 773 K at a heating rate of 10 K min^{-1} in air. The alkali-metal and molybdenum contents in the samples were measured with a Hitachi 180–80 automatic absorption spectrometer using the 670.78 nm line for lithium, the 589.00 nm line for sodium, the 766.49 nm line for potassium, the 780.02 nm line for rubidium, the 852.11 nm line for caesium, and the 313.26 nm line for molybdenum. X-Ray diffraction (XRD) patterns of the samples were obtained using a Rigaku RINT 1200M X-ray diffractometer with Cu-Kα radiation.

Calorimetric procedure

The heats of dissolution of the samples were measured using a Tokyo-Riko MMC-5111 multi-microcalorimeter (conduction type twin calorimeter). The heat flux due to the dissolution was converted to a potential and was recorded by computer at a sampling interval of 1 s. The heat was estimated from the peak area appearing on the heat flux curve by comparison with that due to 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 AΣΛ F 25 precision platinum resistance thermometer. More than five measurements were carried out for each sample. The precision of the calorimeter was tested by measuring the dissolution heat of tris(hydroxymethyl)aminomethane (NIST,

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† Na_2MoO_4 solution was prepared by dissolving $Na_2MoO_4\cdot2H_2O$ in water.

Table 1 Chemical compositions of $(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O$

	Composition[a]	$[n-(x/2)]/x$
Li-deca	$Li_{1.6}Mo_{10}O_{30.8}\cdot 5.27H_2O$	2.7
Na-deca	$Na_{2.0}Mo_{10}O_{31.0}\cdot 6.16H_2O$	2.6
K-deca	$K_{1.8}Mo_{10}O_{30.9}\cdot 4.14H_2O$	1.8
Rb-deca	$Rb_{1.7}Mo_{10}O_{30.9}\cdot 3.50H_2O$	1.5
Cs-deca	$Cs_{1.8}Mo_{10}O_{30.9}\cdot 3.23H_2O$	1.3

[a] The errors of alkali-metal and water contents are within 5 and 0.5% respectively.

SRM 724a) and was confirmed to be adequate for calorimetric estimation.‡

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 and, as far as was possible, stoichiometric amounts of reactants were used according to the thermodynamic cycle chosen.§

The samples were sealed in glass ampoules and used in the calorimeter with 25 ml batches of 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.§ Hygroscopic materials, such as ACl, were dried at 473 K in vacuum (10^{-3} Pa), for 2 h and then sealed in a glass ampoule together with dried air.¶ The mixing heat of water with the calorimetric medium was measured using water, purified by ion exchange, distillation, and degassing just before usage. The standard molar enthalpies of formation of alkali-metal decamolybdates were estimated from the observed dissolution heats by Hess's law of heat summation.

Results

Table 1 lists the chemical compositions of the A-deca samples prepared. None have exactly the 'ideal' decamolybdate formula for which $x=2$ and $n=5$. Other authors[3,7] have reported similar deficiencies in alkali-metal and water contents with retention of the basic structural type. The H_2O/alkali-metal ratio is clearly related to the size of the metal ion, higher ratios being associated with the smaller Li and Na ions.

The XRD patterns of the A-decamolybdates are shown in Fig. 2 and all the patterns could be satisfactorily indexed. The Na, K and Rb decamolybdates belong to the hexagonal system with $a=b>c$, $\gamma=120°$; for the corresponding Li and Cs compounds there are small monoclinic distortions causing $a\neq b$ $(\neq c)$, $\gamma\neq 120°$. The refined lattice parameters are listed in Table 2. Parameters a and b vary in a complex fashion but c is almost constant over the whole range. The determination of atomic coordinates is now in progress and a full structural discussion will be given in a future publication.

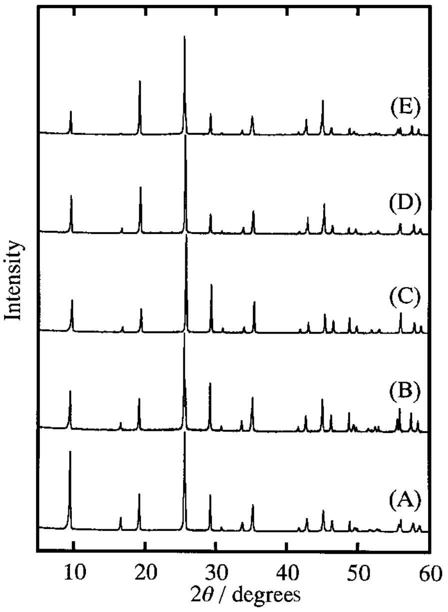

Fig. 2 XRD patterns of alkali-metal decamolybdates: (A) Li-deca; (B) Na-deca; (C) K-deca; (D) Rb-deca; (E) Cs-deca.

Table 2 Lattice constants of alkali-metal decamolybdates

	Crystal system	Space group	Lattice constants[a]
Li-deca	Monoclinic	$P2_1/m$	$a=1.0613(5)$, $b=1.0572(5)$, $c=0.3716(1)$, $\gamma=120.14(2)$
Na-deca	Hexagonal	$P6_3/m$	$a=1.0644(3)$, $c=0.3726(1)$
K-deca	Hexagonal	$P6_3/m$	$a=1.0578(3)$, $c=0.3731(1)$
Rb-deca	Hexagonal	$P6_3$	$a=1.0579(3)$, $c=0.3729(1)$
Cs-deca	Monoclinic	$P2_1$	$a=1.0655(6)$, $b=1.0622(6)$, $c=0.3721(1)$, $\gamma=120.08(3)$

[a] a–c are in nm and γ is in degrees.

The calorimetric reactions used for the determination of the enthalpies of formation of $(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O$ are given in Table 3 together with the average measured heats of reaction and their uncertainties. From these data the enthalpy change, $\Delta H°$, for the overall reaction,

$$A_xO_{x/2}\cdot 10MoO_3\cdot nH_2O(s)+xHCl\cdot 55.5H_2O(l)$$
$$=xACl(s)+10MoO_3(s)+[n+(x/2)+55.5xH_2O](l)$$

was obtained. Combination of the standard enthalpies of formation for the compounds listed in Table 4 with the corresponding values of $\Delta H°$ so obtained enabled the standard enthalpies of formation (at 298.15 K) listed in Table 5 to be determined. The values of $\Delta_f H°$ given there refer to formation of the decamolybdates from the elements in standard states,

$$xA(s)+10Mo(s)+1/2[30+n+(x/2)]O_2(g)+nH_2(g)$$
$$=A_xO_{x/2}\cdot 10MoO_3\cdot nH_2O(s)$$

Also given in Table 5 are the corresponding enthalpies of formation of the decamolybdates from the constituent oxides,

$$(x/2)A_2O(s)+10MoO_3(s)+nH_2O(l)$$
$$=A_xO_{x/2}\cdot 10MoO_3\cdot nH_2O(s) \qquad (1)$$

For ease of a later comparison, the enthalpies of formation of the alkali-metal molybdates, $A_2MoO_4(s)$ from the constituent oxides[1] are included in Table 5,

$$A_2O(s)+MoO_3(s)=A_2MoO_4(s) \qquad (2)$$

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‡About 0.1 g of tris(hydroxymethyl)aminomethane was dissolved in 20 ml of 0.10 M HCl solution. The enthalpy of reaction was (-245.81 ± 0.26) J g^{-1}. This value agreed well with that in the literature.[5,6]

§The molar ratios of solute to reactant species must be very small in order to justify carrying out each reaction independently, rather than consecutively, in the same starting medium. Strictly the maintenance of stoichiometry in the weights of solute used for calorimetric measurements as per the reaction scheme was necessary on both sides of overall reaction equation. Although we attempted to realize these conditions in our work some solutes gave very small heats of solution and very large errors in measured values and thus for such solutes, we used slightly larger masses than those desirable from stoichiometry considerations. The masses used were as follows: A-deca (A: Li, Na, K, Rb and Cs) (0.03 g), MoO_3 (0.03 g), ACl (0.1–0.5 g), 1.0 M HCl (aq) (0.4 g), and H_2O (0.5 g).

¶When the ampoule, which was sealed in vacuum, was broken for the measurement, a significant step due to vaporization of solution appears in the heat flow curve. The step could not be compensated for even by using the empty ampoule, sealed in vacuum, as the reference. So dried air, which was prepared by passing through a cold trap soaked in liquid N_2, was used to fill the ampoule after the vacuum drying treatment.

Table 3 Calorimetric reaction scheme for $(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O$

Reaction	Alkali-metal ion	$\Delta H^{\circ a}$/kJ mol^{-1}
(a) $A_xO_{x/2}\cdot 10MoO_3\cdot nH_2O(s)+(20-x)OH^-(aq)=xA^+(aq)+10MoO_4^{2-}(aq)+\{[20-x)/2]+n\}H_2O(aq)$: ΔH_1	Li^+	-766.4 ± 2.2
	Na^+	-696.3 ± 2.3
	K^+	-710.4 ± 4.3
	Rb^+	-670.7 ± 4.8
	Cs^+	-688.4 ± 2.7
(b) $MoO_3(s)+2OH^-(aq)=MoO_4^{2-}(aq)+H_2O(aq)$: ΔH_2		-85.20 ± 0.18
(c) $ACl(s)=A^+(aq)+Cl^-(aq)$: ΔH_3	Li^+	-38.75 ± 0.16
	Na^+	-0.419 ± 0.040
	K^+	15.02 ± 0.18
	Rb^+	14.97 ± 0.07
	Cs^+	14.66 ± 0.10
(d) $HCl\cdot 55.5H_2O(1)+OH^-(aq)=56.5H_2O(aq)+Cl^-(aq)$: ΔH_4		-65.85 ± 0.52
(e) $H_2O(1)=H_2O(aq)$: ΔH_5		-0.061 ± 0.003
(f) $A_xO_{x/2}\cdot 10MoO_3\cdot nH_2O(s)+xHCl\cdot 55.5H_2O(1)=xACl(s)+10MoO_3(s)+[n+(x/2)+55.5x]H_2O(1)$: ΔH_0 $\Delta H_0=\Delta H_1-10\Delta H_2-x\Delta H_3+x$: $\Delta H_4-[(n+(x/2)+55.5x])$: ΔH_5	Li^+	48.0 ± 3.0
	Na^+	32.0 ± 3.1
	K^+	2.4 ± 4.8
	Rb^+	49.9 ± 5.2
	Cs^+	25.0 ± 3.4

[a] Uncertainties expressed as twice the standard error of the mean.

Table 4 Standard molar enthalpies used to determine the standard molar enthalpies of formation of alkali-metal decamolybdates[a]

	Δ_fH°/kJ mol^{-1}		Δ_fH°/kJ mol^{-1}
MoO_3	-745.2	NaCl	-411.1
$HCl\cdot 55.5H_2O$	-165.47	KCl	-436.7
H_2O	-285.830	RbCl	-430.6
LiCl	-408.3	CsCl	-442.8

[a] *Kagaku binran*, Maruzen, Tokyo, 1975, ch. 8, p. 953.

Table 5 Standard molar enthalpies of formation

Li	Na	K	Rb	Cs
Standard enthalpies of formation (kJ mol^{-1}) for A-deca				
-9623 ± 3	-10022 ± 3	-9383 ± 5	-9196 ± 5	-9157 ± 3
Enthalpies of formation of $(2/x)(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O(s)$ from the oxides, $\Delta H_I/(x/2)$ (kJ mol^{-1})				
-235	-391	-469	-544	-551
Enthalpies of reaction of oxides to form $A_2MoO_4(s)$, ΔH_{II}				
-176	-307	-390	-402	-423

Table 6 The site binding energy of the various alkali-metal ions in the decamolybdate framework

A	ΔH_{III}/kJ mol^{-1}
Li	-1091
Na	-1012
K	-931
Rb	-925
Cs	-882

Discussion

The enthalpy of formation data provided in Table 5 show relatively small and irregular variations in the absolute values of $\Delta_fH[(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O(s)]$. Of more direct chemical significance is the nearly monotonic variation shown for the enthalpies of their formation, from the constituent oxides,

$$A_2O(s)+(2/x)(10MoO_3)(s)+(2/x)nH_2O(1)$$
$$=2/x\{(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O\}(s)$$

given by $(2/x)\ \Delta H_I$. These changes parallel changes in the enthalpy of formation of the simple molybdates, $A_2MoO_4(s)$,[8] from their constituent oxides, as measured by ΔH_{II}. In both cases the increasing exothermicity of the formation of the alkali-metal molybdates and decamolybdates from the alkali-metal oxides, which follows increasing atomic number of the alkali-metal, is a direct consequence of the decreasing stabilities of the alkali-metal oxides, as measured by $\Delta_fH[A_2O(s)]$.[8]

The decamolybdate phases are thermodynamically stable (in so far as the entropy changes between solid phases may be presumed to be small) towards decomposition into $A_2MoO_4(s)$, $MoO_3(s)$ and $H_2O(1)$ at room temperature, as comparison between corresponding values of ΔH_I and ΔH_{II} reveals. A measure of the site binding energy of the various alkali metal ions in the decamolybdate framework is given in Table 6 by the enthalpy changes, ΔH_{III}, for the reaction,

$$A^+(g)+(1/4)O_2(g)+(10/x)MoO_3(s)+(n/x)H_2O(1)+e^-(g)$$
$$=(1/x)\{(A_2O)_{x/2}\cdot 10MoO_3\cdot nH_2O\}(s)$$

The sequence of ionic binding energies again follows that of ionic size monotonically. A similar trend is found for enthalpies of hydration of the gaseous ions; Li, -519, Na, -406, K, -322, Rb, -301, Cs, -286 kJ mol^{-1}.[9]

The thermochemical data determined here for the decamolybdate phases can be used as a basis for further discussion of the stabilities of species formed in the three-component system MoO_3–A_2O–H_2O.

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