reactions at or adjacent to a metal–oxygen bond, have nearly identical rates under the separately specified conditions in the Rh(III) case, but differ by a factor of 4.5 for Cr(III) under similarly specified conditions. Finally, the contrast in rates between the M–O and M–Cl types of complexes is somewhat more clear-cut for the Rh(III) series than for the Cr(III) series. These facts are quite understandable in terms of the contrasting mechanism assumption made earlier. Thus, the Cr(III) reactions, being largely associative with participation of a seven-coordinate activated state, require that bond-making to the entering water molecule be very significant and M–Cl or M–O bond stretching of less importance. One therefore would expect the mono- and dichloro complexes to differ in rate at least by the statistical factor of two as observed. Similarly, since the reactive intermediate for the oxalato complex is the proton-pre-equilibrated form[10] $Cr(C_2O_4)_2OC_2O_3H\cdot OH_2^{-2}$, with aquation taking place at the $Cr\text{–}OC_2O_3H$ bond, one would expect a statistical factor between this and the $Cr(H_2O)_6^{+3}$ species of not less than 2 and not more than 6, again as observed. The Rh(III) complexes, on the other hand, reacting largely in a dissociative fashion with formation of a distorted octahedral activated state by stretching of the M–O or M–Cl bond to be broken, should show a distinct contrast in rate for the two types of bond stretch, as observed.

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Preparation and Properties of Sodium and Potassium Molybdenum Bronze Crystals

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Pure MoO_2 crystals were grown by electrolytic reduction of MoO_3–Na_2MoO_4 mixtures at 675°. In addition both sodium molybdenum bronze and potassium molybdenum bronze crystals were grown from molybdenum(VI) oxide–alkali molybdate melts under carefully controlled conditions.

Introduction

There have been conflicting reports in the literature concerning the existence of alkali metal molybdenum bronzes. Stavenhagen and Engels[2] prepared sodium molybdenum bronze by electrolytic reduction of fused sodium molybdate and Cannert[3] prepared the lithium, sodium, and potassium molybdenum bronzes by electrolytic reduction. Burgers and Van Liempt[4] as well as Hägg[5] obtained only molybdenum oxides in similar experiments. Straumanis and Irani[6] have reported that molybdenum(VI) oxide could not be dissolved by a tungsten bronze and that solid solutions of the type $NaW^{V}O_3(Mo^{VI}O_3)_x$ were impossible to prepare. In addition, they attempted to prepare alkali metal molybdenum bronzes by heating dry sodium molybdate, molybdenum(VI) oxide, and molybdenum powder under vacuum at 510 and 450°, respectively The insoluble product that remained was identified as MoO_2.

The purpose of this paper is to describe the preparation, by electrolytic reduction, of sodium and potassium molybdenum bronze single crystals in addition to molybdenum(IV) oxide single crystals. The successful preparation of alkali metal molybdenum bronzes is dependent upon both the reduction temperature and the molar ratio of alkali metal molybdate to molybdenum(VI) oxide.

Experimental

Electrolytic Reduction Apparatus.—Molybdenum bronze crystals were grown by electrolytic reduction of alkali metal molybdate–molybdenum(VI) oxide mixtures. A detailed drawing of the apparatus used in the growth of these crystals is shown in Fig. 1, with an insert showing its position in a vertically mounted split tube furnace. It can be seen that the crucible support assembly centers the crucible in the hot zone of the furnace. In addition the support assembly positions the temperature control thermocouple and provides external electrical connections between the cell and its power supply. The bottom of the ceramic (Lava) support column is mounted in a brass plate and the crucible support plate (Lava) is fitted to the upper end of the column. The cell power leads and the thermocouple leads are brought up through the hollow center of the column and out through the support plate. The furnace control thermocouple is inserted through the support plate to a fixed position midway between the radiation shield and the cell wall. The external anode lead wire is connected to a platinum washer seated on the recessed edge of the crucible support plate, and the external cathode lead wire is connected to a platinum disk seated in the center of the support

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(1) Operated with support from the U. S. Army, Navy, and Air Force.

(2) A. Stavenhagen and E. Engels, *Ber.*, **28**, 2281 (1895).

(3) C. Cannert, *Gazz. chim. ital.*, **60**, 113 (1930).

(4) W. G. Burgers and J. A. M. Van Liempt, *Z. anorg. allgem. Chem.*, **202**, 325 (1931).

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TABLE I

Initial flux compn.	Temp., °C.	Product by X-ray ident.	M^+, wt. %	Mo^{+4}, wt. %	Total Mo, wt. %	Density, g./cc.	Habit	Crystal quality
$1MoO_3:2Na_2MoO_4$	675	MoO_2	0.029	73.28			Plate	Good
$1MoO_3:1Na_2MoO_4$	675	MoO_2	0	74.37			Rod	Excellent
$17MoO_3:Na_2MoO_4$	675	MoO_2 powder	0.002	74.37			Polycrystalline	
$3MoO_3:Na_2MoO_4$	550	Bronze	2.48	16.98	66.1		Plate	Good
$4MoO_3:Na_2MoO_4$	550	Bronze	2.33	14.83	66.16	4.17	Plate	Good
$3.35MoO_3:K_2MoO_4$	550	Bronze	6.94	8.98	62.34		Plate	Good
$3MoO_3:K_2MoO_4$	560	Bronze	6.48	10.50	62.62		Plate	Fair

plate. A removable Inconel radiation shield ensuring a minimum temperature gradient across the cell is seated upon the anode washer. This shield also provides electrical contact to the cell anode through an internally mounted sliding contact.

The main body of the electrolytic cell consists of an alumina crucible (Morganite No. N3149) set into a close-fitting platinum cup approximately one-half the height of the crucible. A heavy-walled small-bore alumina tube is placed in the crucible in such a manner that it extends a few millimeters from the bottom of the crucible to approximately 10 mm. above the top edge of the crucible. A platinum wire, welded to the platinum cup, is brought up the outside of the crucible and down the alumina tube. It is attached to the edge of the cathode (either a seed crystal or a 4.5-cm.^{2} platinum disk) which is allowed to rest on the bottom of the crucible. The cell anode consists of a U-shaped platinum strip, approximately 0.5 cm. in width, suspended from the top edge of the crucible down into the melt. The platinum crucible cover rests on the edge of the anode strip and makes contact with the sliding contact from the Inconel radiation shield.

Preparation of Crystals.—Baker's reagent grade sodium molybdate, potassium molybdate, and molybdic anhydride were dried for 12 hr. at 500° before use. The desired molar proportions of these materials were mixed and fused for approximately 1 hr. at 650° in a platinum crucible. The melt was removed and ground until it had the consistency of a coarse powder. The electrolytic cell was filled with this material and mounted as shown in Fig. 1. The furnace was brought up slowly to the desired temperature and electrolysis begun after waiting a sufficient interval of time for the flux material to melt completely. Initially, a platinum disk (4.5 cm.^{2}) was used as the cathode; later a seed crystal was substituted to obtain large crystals. All the electrolytic reduction reactions were carried out for a period of 7–8 days at a current density of 10 ma./cm.^{2} in air.

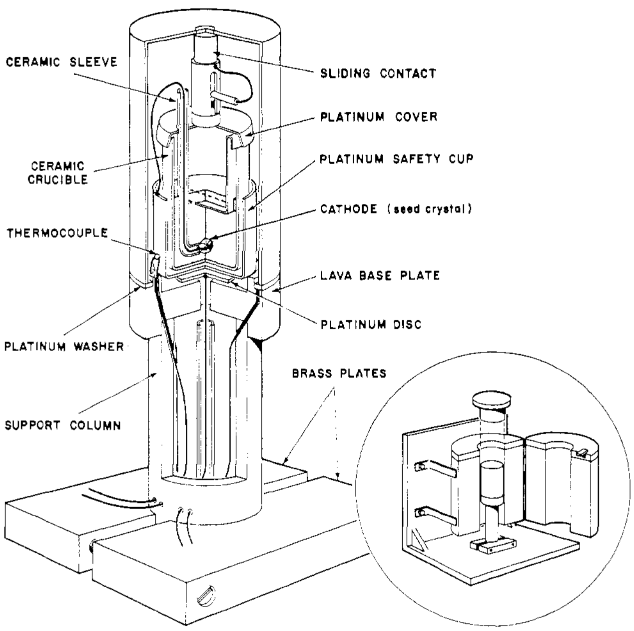

Fig. 1.—Furnace arrangement for electrolytic crystal growth.

The sodium molybdenum and potassium molybdenum bronze crystals were analyzed by standard procedures. The alkali metal content was determined by means of a Beckman flame photometer analysis on samples dissolved in hydrochloric acid. The amount of reduced molybdenum in the sample was obtained by the procedure of Wickham and Whipple[7] for determination of total reducing power. The total molybdenum was obtained by reduction with a silver reductor and titration of the resulting solution with ceric sulfate in the presence of ferroin indicator.

The resistivity was determined by a four-probe method using a Keithley 610A electrometer for the measurements of samples with high resistivities and a Keithley Model 502 milliohmeter for the lower resistivities. Thermal e.m.f. was generated by placing the crystals between copper contacts, one of which was heated by a coil heater and the other kept at constant ice bath temperature; the Seebeck coefficient was measured with a Rubicon potentiometer.

Results and Discussion

Table I summarizes the various electrolytic products obtained as a function of composition and other experimental conditions. The electrolytic reduction of various molar mixtures of $xMoO_3$ and $(1 - x)Na_2MoO_4$, where $0.15 \leq x \leq 0.75$, at temperatures above 600° resulted in the formation of MoO_2. However, the best crystals of MoO_2 were formed by reduction of equimolar mixtures of MoO_3 and Na_2MoO_4 at 675°. As the ratio of MoO_3 to Na_2MoO_4 increased, the crystals appeared to be more poorly formed and finally only polycrystalline powders resulted. Sodium molybdenum bronze crystals were obtained by the electrolytic reduction of mixtures containing $3MoO_3$ or $4MoO_3$ to $1Na_2MoO_4$ at 550°. When the reduction of similar compositions is carried out above 600°, MoO_2 is formed. From the phase diagram MoO_3–Na_2MoO_4,[8] it can be noted that at the molar ratio $3MoO_3:1Na_2MoO_4$ the melting point is below 575°. Bronze crystals were grown at 550° and MoO_2 appeared in the products when the reduction was carried out above 575°. A low melting eutectic is also formed at a high sodium molybdate concentration but the electrolytic product is MoO_2 regardless of the reduction temperature.

The formulas obtained from chemical analyses of the bronzes formed by electrolytic reduction of $3MoO_3:1Na_2MoO_4$ and $4MoO_3:1Na_2MoO_4$ indicate a composition range from $Na_{0.93}Mo_{5.9}O_{17}$ to $Na_{0.87}Mo_{5.95}O_{17}$. It appears that the bronze $Na_{0.93}Mo_{5.9}O_{17}$ is approaching the composition $NaMo_6O_{17}$. From preliminary examination of Weissenberg photographs, this bronze

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(7) D. G. Wickham and E. R. Whipple, *Talanta*, **10**, 314 (1963).

(8) A. N. Zelikman and N. N. Gorovits, *Zh. Obshch. Khim.*, **24**, 1920 (1954).

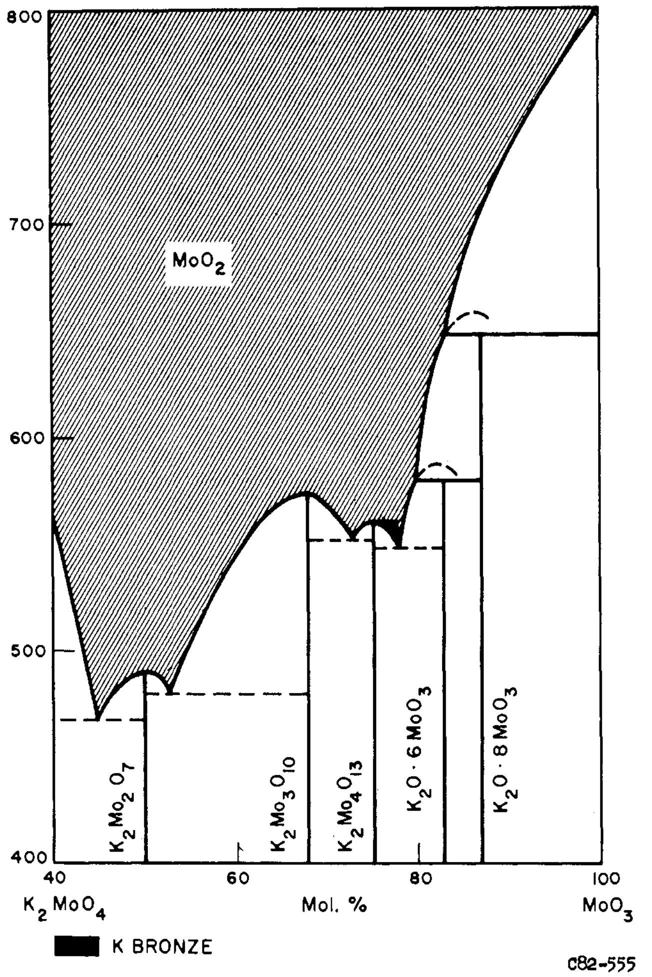

Fig. 2.—Phase diagram of the system K_2MoO_4–MoO_3 indicating the electrolytic products.

is apparently hexagonal with $a = 5.52$ and $c = 12.97$ Å. However, on examination of the powder pattern, it was found that, whereas all of the 00*l* lines are sharp, the others are broad or split, indicating that the lattice is probably only psuedo-hexagonal. The molecular weight of the compound $Na_{0.93}Mo_{5.9}O_{17}$ is 859.4 and the molecular weight obtained from the hexagonal unit cell volume (342 Å.^{3}) and density (4.17 g./cc.) is 858.9.

TABLE II

RESISTIVITY VALUES OF MOLYBDENUM BRONZES

Compound	Resistivity, ohm cm.	Temp., °C.
MoO_2	3.7×10^{-4}	−90
MoO_2	1.27×10^{-3}	60
$Na_{0.93}Mo_{5.9}O_{17}$	5.6×10^{-1}	−90
$Na_{0.93}Mo_{5.9}O_{17}$	2.6×10^{-1}	60
$K_{0.26}Mo_{1.01}O_3$	5.01×10^{5}	−90
$K_{0.26}Mo_{1.01}O_3$	1.97×10^{4}	60
$K_{0.28}Mo_{1.02}O_3$	$\sim 2.3 \times 10^{-3}$	−90
$K_{0.28}Mo_{1.02}O_3$[a]	$\sim 1.4 \times 10^{-3}$	18

[a] Conductivity measurements were not made above room temperature for this sample.

The phase diagram[9] for the system MoO_3–K_2MoO_4 is shown in Fig. 2. It is apparent that there are only a limited number of K_2MoO_4–MoO_3 compositions that melt below 600°. The electrolytic reduction of mixtures of $xMoO_3$ and $(1 - x)K_2MoO_4$, where $0.5 \leq x \leq 0.9$, above 575°, resulted in the formation of MoO_2. Electrolysis of mixtures containing a higher K_2MoO_4 concentration than that needed to form $K_2Mo_4O_{13}$ resulted in poor products that contained MoO_2, regardless of the temperature at which the reduction was carried out. In addition, the higher K_2MoO_4 mixtures were extremely reactive and presented a container problem. There is only one other very narrow composition range at approximately $3MoO_3{:}1K_2MoO_4$ were the melting point occurs below 575°. It is in this range that two potassium molybdenum bronzes were formed. A blue-black bronze was formed at 550° and a red bronze was the product at 560°. From analytical data their formulas appear to be $K_{0.28}Mo_{1.02}O_3$ and $K_{0.26}Mo_{1.01}O_3$, respectively.

The resistivities of MoO_2 and several alkali metal molybdenum bronzes are listed in Table II. The resistivity of MoO_2 was less than 10^{-5} ohm cm. at liquid nitrogen temperature and exhibited a positive temperature dependency. The sign of the Seebeck voltage for MoO_2 is negative in reference to copper and the Seebeck coefficient rose from a value of 23.6 μv./deg. at 31° to 39.3 μv./deg. at 90°. The molybdenum bronzes were of a plate-like habit and cleaved readily. This made it difficult to obtain good electrical measurements. However, the relative values listed in Table II are correct and a striking difference is observed for the two potassium bronzes with almost identical composition. The red potassium bronze $K_{0.26}Mo_{1.01}O_3$ showed typical semiconduction behavior with a positive temperature dependency. The blue-black bronze $K_{0.28}Mo_{1.02}O_3$ has a much lower resistivity with an apparent transition from semiconductor to metallic behavior above −100°. This transition takes place over a broad temperature region. A preliminary crystallographic investigation of the potassium molybdenum bronzes by Dr. A. D. Wadsley has shown them both to be monoclinic, space groups C2, Cm, or C2/m but with different unit cell dimensions. The red bronze, $K_{0.26}Mo_{1.01}O_3$, has $a = 14.24$, $b = 7.70$, $c = 6.37$ Å., and $\beta = 92.0°$, and the blue bronze, $K_{0.28}Mo_{1.02}O_3$, has $a = 18.28$, $b = 7.56$, $c = 9.88$ Å., and $\beta = 117° 43'$.

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(9) V. Spitzyn and I. M. Kuleshov, *ibid.*, **21**, 1367 (1951).