ture determinations of $Hg_2NCl \cdot H_2O$,[5] $HgNH_2Cl$[6] and $Hg(NH_3)_2Cl_2$[7] provide conclusive evidence that these are really mercury(II) compounds. Thus the investigations of Gleditsch and Egidius do not prove the existence of mercury(I) intermediates in these reactions.

In addition, we have found no mercury(I) intermediates in investigations over the full ranges of concentrations of aqueous solutions, whether diffraction patterns are taken of wet or dry precipitates.

An interesting change occurs in the precipitates at the early stages of the reaction. When wet or immediately after drying, Hg_2Cl_2 may not be observed, but gradually appears on standing, sometimes rapidly, and sometimes after a day or so. We believe that this phenomenon is due to the presence of Hg and other reaction products formed at the surface of Hg_2Cl_2 crystals, which are therefore obscured from the relatively non-penetrating CuKα radiation. Subsequent agglomeration and evaporation of the Hg thus makes these crystals of Hg_2Cl_2 available for diffraction.

The chloride of Millon's base appears to show also a crystalline modification which is a very slight distortion of the cubic form previously reported.[6] The (222) reflection shows splitting into two nearly equal components 0.6° apart on the diffraction pattern. This split reflection becomes single on conversion to the base by treatment with 20% aqueous KOH, and becomes split again when the base is reconverted to the chloride in 20% aqueous KCl. The nature of this distortion has not been ascertained, partly because the particle size broadening of the reflections makes the details of the pattern obscure, especially at higher scattering angles. The variations of this small distortion may be related to the degree of hydration of this compound, or to the degree of substitution of OH^- for Cl^-.

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[6] W. N. Lipscomb, *ibid.*, **4**, 266 (1951).

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The Reaction of Sodium Tungsten Bronze with Molybdenum(VI) Oxide. The Sodium Molybdenum Bronze[1]

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Sodium tungsten bronze easily dissolves tungsten(VI) oxide at elevated temperatures, forming solid solutions.[2] It was expected that molybdenum (VI) oxide, which is very similar in its properties to tungsten(VI) oxide, would also form solid solutions with the sodium tungsten bronze. The purpose of this paper is to describe the reactions that occurred during the heating of a mixture of the two compounds just mentioned.

Closely related to the reactivity of molybdenum (VI) oxide with sodium tungsten bronze is the preparation and existence of alkali molybdenum bronzes. Sodium molybdenum bronze was first mentioned by Stavenhagen and Engels,[3] who obtained the bronze, by the electrolytic decomposition of fused sodium molybdate in the form of a dark bluish-grayish, or reddish-violet powder, having the properties of the bronzes. Later the lithium, sodium and potassium molybdenum bronzes were prepared by Canneri,[4] using the same method and with a small yield. However, the next year Burgers and van Liempt[5] showed that the bronzes mentioned by Canneri were mixtures consisting of molybdenum(IV) oxide and molybdenum blue. Finally, according to Magnéli, only molybdenum oxides were obtained by Hägg in similar experiments.[6]

An attempt was made to prepare sodium molybdenum bronze by a method described previously.[2]

Experimental

The materials for the experiments were sodium tungsten bronzes containing 10 and 22% by weight tungsten(VI) oxide,[2] dry molybdenum(VI) oxide and sodium molybdate. The molybdenum metal used was an electrolytically produced powder.

Calculated amounts of these reagents were weighed, intimately mixed, and ground. Then the mixtures were put in porcelain crucibles with a copper lid and heated in a furnace which could be evacuated. Or else the mixtures were put into quartz glass bulbs, evacuated, sealed off, and heated at different temperatures between 450 and 1000°.

The reaction products were well washed with water.[2] The composition of all water soluble and insoluble compounds were identified by their X-ray diffraction patterns. The corresponding compounds for the identification were synthesized (*e.g.*, $Na_2WO_4(MoO_3)_x$, $x < 1$). All reagents used were of the highest purity obtainable.

Results and Discussion

Sodium Tungsten Bronze and Molybdenum(VI) Oxide.—Qualitative tests showed that a reaction proceeds between these two substances, because the mixture turns deep blue when heated. Samples of sodium bronze (with 10% tungsten(VI) oxide) containing 5, 10, 15, 20 and 30% by weight of molybdenum(VI) oxide were prepared and heated for two hours at 800°. This resulted in there still being a bronze in the first four cases, but with a lattice parameter which rapidly decreased from 3.8436 kX. to 3.8310 kX. as the molybdenum(VI) oxide content was increased. However, the appearance of strange lines in the patterns of samples even with 5% molybdenum(VI) oxide testified that no equilibrium was reached during the heating and that a chemical reaction occurred. The strange lines belonged to the powder pattern of molybdenum(IV) oxide. Hence, the following reactions occur during heating in a vacuum, assuming that reaction (1) represents the equilibrium of the sodium bronze at elevated temperatures as shown previously[2]

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[1] Excerpt from a thesis submitted by K. K. Irani to the Graduate School of the University of Missouri, School of Mines and Metallurgy, in partial fulfillment of the requirements for a Master's Degree.

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[3] A. Stavenhagen and E. Engels, *Ber.*, **28**, 2281 (1895).

[4] C. Canneri, *Gazz. chim. ital.*, **60**, 113 (1930).

[5] W. G. Burgers and J. A. M. van Liempt, *Z. anorg. Chem.*, **202**, 325 (1931).

[6] A. Magnéli, *N. Acta Reg. Sc. Upsaliensis*, **14**, No. 8, 16 (1949).

$$2NaWO_3 \rightleftarrows 2Na + 2WO_3 \quad (1)$$

$$2Na + MoO_3 \longrightarrow Na_2O + MoO_2 \quad (2)$$

$$Na_2O + xWO_3 \longrightarrow Na_2WO_4(WO_3)_{x-1}\ x > 1 \quad (3)$$

The excess $(2 - x)$ of WO_3 dissolved in the unreacted bronze, forming bronzes with a deeper (red or blue) color showing a smaller lattice constant

$$NaWO_3 + yWO_3 \longrightarrow NaW^{V}O_3(W^{VI}O_3)_y,\ y = 2 - x \quad (4)$$

If the molybdenum(VI) oxide content was increased $Na_2W_2O_7$ as an added product, according to reaction (3), was formed.

Thus, as a final product, a mixture of a deeper colored bronze and molybdenum(IV) oxide resulted, while the sodium bitungstate was removed by the washing operation. Qualitative tests showed that there was only a trace of molybdenum in the sodium bronze. Therefore, molybdenum (VI) oxide was not dissolved by the bronze and acted only as an oxidizer, making solid solutions of the type $NaW^{V}O_3(Mo^{VI}O_3)_x$ impossible. Even the copper lid of the crucible (with larger amounts of molybdenum(VI) oxide present) was attacked: $Cu + MoO_3 \rightarrow MoO_2 + CuO$. This strong oxidizing property of molybdenum(VI) oxide at elevated temperatures was also observed by others.[7]

In the case of 30% molybdenum(VI) oxide, the reactions (2) and (4) proceeded far enough to leave very little of the original bronze which, in addition, was transferred into the tetragonal bronze because of the large amount of tungsten(VI) oxide dissolved according to (4). The formation of $Na_2Mo_2O_7$, and of a water-soluble compound $Na_2WO_4(MoO_3)_x$ $(x < 1)$ instead of (3) is also possible. The powder patterns of these three substances including $Na_2W_2O_7$ are identical except that the sodium tungstate containing molybdenum(VI) oxide has a contracted lattice.

The experiments performed with a sodium bronze containing 22% tungsten(VI) oxide at 1000° for two hours led to the same final products.

No molybdenum(VI) oxide containing sodium bronze was obtained when molybdenum was chosen instead of tungsten as a reducer

$$2Na_2WO_4 + 2WO_3 + Mo \longrightarrow 4NaWO_3 + MoO_2 \quad (5)$$

Of course, the bronze $NaWO_3$ always contained a dissolved excess of tungsten(VI) oxide.

All other combinations of the 3 substances, as shown on the left side of equation (5), being partly replaced by the corresponding molybdenum (or tungsten) compounds after the reaction at 800–900° in a vacuum gave only molybdenum(IV) oxide. The products such as Na_2WO_4, $Na_2W_2O_7$, $Na_2WO_4(MoO_3)$ and $Na_2Mo_2O_7$ were washed away in the subsequent treatment with water.

The Alkali Molybdenum Bronzes.—Completely replaced the initial products of reaction (5) by the corresponding molybdenum compounds, in no case gave any molybdenum bronzes. The chemical reason of the failure to prepare these bronzes might be as follows: For the formation of the bronzes it is necessary that the heavy metal should have the property to coexist in two valency stages at the elevated temperatures of formation. In the alkali tungsten bronzes tungsten is hexa- and pentavalent.[8] This, evidently, is impossible in the case of molybdenum bronzes because of the high oxidizing power of molybdenum(VI) oxide. Glemser and Lutz[9] showed that all lower molybdenum oxides above 700° were decomposed into molybdenum-(VI) and -(IV) oxides.[9] But four-valent molybdenum, similar to four-valent tungsten, does not enter the lattice of the bronzes.

The only possibility of obtaining molybdenum bronzes seemed to be by synthesis below 700°. Dry sodium molybdate, molybdenum(VI) oxide and molybdenum powder were heated in a vacuum in two separate experiments at 510 and 450° for 24 and 50 hours, respectively. After the soluble compounds were washed away, only molybdenum (IV) oxide remained.

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Adsorption and Reaction of Carbon Monoxide on Promoted Iron Catalysts

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Adsorption of carbon monoxide on iron catalysts has been the subject of many investigations,[1] and it has been inferred[1e,f,h] that it is possible to make such studies up to 150° without interfering chemical reactions. However, during the course of studies at 0–108° on the adsorption of carbon monoxide on potassium carbonate promoted iron catalysts, it has been found that chemical reactions occur that produce iron pentacarbonyl and carbon dioxide.

The experiments were carried out in an adsorption apparatus of conventional design[2] and operating at constant pressure.[3] The iron catalyst was of a type used for the synthesis of hydrocarbons from carbon monoxide and hydrogen. It consisted of mill scale in the form of a powder finer than 100 mesh, promoted with 0.5 wt. % K_2O.[4] After reduction with hydrogen at 340° under 250 p.s.i., the promoted catalyst was degassed at 450° until a pressure of 1.5×10^{-6} mm.

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