Gmelin Handbook of Inorganic Chemistry

8th Edition

Mo
Molybdénum

Supplement Volume B 3a

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With 45 illustrations

Molybdenum Oxide Hydrates.
Oxomolybdenum Species in Aqueous Solutions

AUTHORS

Karl-Heinz Tytko, Universität Göttingen

Ursula Trobisch, Gmelin-Institut, Frankfurt am Main

EDITORS

Hartmut Katscher, Friedrich Schröder

CHIEF EDITOR

Hartmut Katscher

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Preface

In the first part of this volume the oxide hydrates including the hydroxides and hydroxide oxides of Mo^{III} to Mo^{VI} are described. (The anhydrous molybdenum oxides can be found in the volume "Molybdän" Erg.-Bd. B 1, 1975.) The compounds $MoO_3 \cdot nH_2O$ with $n=1$ and 2 are investigated in detail. They are true oxide hydrates and not "molybdic acids". For completeness the hydrogen insertion compounds H_xMoO_3 with $0<x<2$ are also included in this part. These "bronzes" are obtained by the introduction of hydrogen into MoO_3.

The second part, which covers most of the volume, deals with the oxomolybdenum species in aqueous solutions. Molybdenum is able to form cationic species with oxidation states II to V in aqueous solutions. Mixed-valence species are also known, e.g., with Mo^{V} and Mo^{VI}, which are characteristic for the aqueous molybdenum blues.

The monomeric and polymeric oxomolybdenum(VI) species in aqueous solutions have been investigated the most. Before treating the individual anionic, cationic, and uncharged species, the conditions under which the species can be investigated and characterized, i.e., the quantities characterizing oxomolybdenum(VI) solutions and equilibria, the ionic media, the methods of investigation, etc. are clarified. For the individual species (and their protonated forms) the conditions for their occurrence and their formula, structure, and properties are described. The unprotonated monomolybdate ion occurs at high pH values. The protonated monomeric species occur especially at low molybdenum(VI) concentrations, the polymeric species at higher molybdenum(VI) concentrations in overlapping equilibria. The exact formulas of the mono- to tetraprotonated monomers are so far unproven. The only anionic polymeric species proven to exist with certainty in solutions as well as in solids are the two ions $Mo_7O_{24}^{6-}$ and $Mo_{36}O_{112}(H_2O)_{16}^{8-}$. However, there is strong evidence for additional species, namely $Mo_8O_{26}^{4-}$, $Mo_{12}O_{40}(OH)_2^{10-}$, and $Mo_{18}O_{56}(H_2O)_{10}^{4-}$, and for protonated forms of $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$, and $Mo_{12}O_{40}(OH)_2^{10-}$. The exact formulas of the cationic polymeric species, a series of the protonated forms of a dimer, are so far unproven. The last section deals with theoretical investigations and considerations on the polymolybdate system and the polymolybdate ions in aqueous media.

The chemical reactions in aqueous solutions and the species in nonaqueous solutions and melts are described in the "Molybdenum" Suppl. Vol. B 3b.

Frankfurt am Main, October 1986 — Hartmut Katscher

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Molybdenum and Oxygen (continued)

The Mo–O system and the anhydrous molybdenum oxides can be found in the volume "Molybdän" Erg.-Bd. B 1, 1975, pp. 21/144. The anhydrous molybdates with Sb to Cs (System Nos. 18 to 25) are described in "Molybdän" Erg.-Bd. B 1, 1975, pp. 145/241, those with Be to Cr (System Nos. 26 to 52) in "Molybdän" Erg.-Bd. B 2, 1976. The hydrous molybdates with Sb to Cr (System Nos. 18 to 52) can be found in "Molybdenum" Suppl. Vol. B 4, 1985.

1 Molybdenum Oxide Hydrates

Older data are given in "Molybdän", 1935, pp. 102/13.

Overview

Solid compounds of molybdenum containing hydrogen and oxygen exist with Mo in each of the oxidation states 3 through 6. In addition, mixed-valence compounds containing Mo in the formal oxidation state 4.8 and 5.5 to 5.86 have been described. These compounds are generalizing designated as oxide hydrates but in some cases may also be formulated as hydroxides or hydroxide oxides. "Molybdic acids" do not exist in the solid state. The compounds $MoO_3 \cdot nH_2O$ with $n = 1$ and 2 have clearly been identified as oxide hydrates although the term "molybdic acid" is used even in recent papers.

A gaseous hydroxide oxide of Mo^{VI} was detected at high temperatures.

For Mo^{VI} the formation of a crystalline peroxo compound has been reported.

For formal reasons the hydrogen insertion compounds, H_xMoO_3 ($0 < x < 2$), are also described in this section. These compounds, which are obtained by the introduction of hydrogen into MoO_3, are termed "bronzes" in the literature. There is still little knowledge about the exact equilibrium location of the hydrogen in the MoO_3 host structure, the amount of charge transfer, the mobility, and the bonding properties. Recent papers (up to 1985) dealing with these subjects have been considered. Details of the formation and properties of the hydrogen tungsten oxide bronzes can be found in "Wolfram" Erg.-Bd. B 3, 1979, pp. 31/9.

1.1 $Mo(OH)_3$

In the literature this compound is usually designated as $Mo(OH)_3$ but the formulation $Mo_2O_3 \cdot 3H_2O$ can also be found.

$Mo(OH)_3$ is precipitated during the electrolytic reduction of Na_2MoO_4 (0.025 M) in weakly acidic solutions (e.g., 0.01 to 0.03 N HCl or H_2SO_4) [1] or of ammonium molybdate solution [2]. From brown Mo^{III} solutions, produced by electrolytic reduction of molybdate(VI) in 0.5 to 3 N HCl, the $Mo(OH)_3$ was precipitated by dilution [3]. A dense deposit of $Mo_2O_3 \cdot nH_2O$ was obtained on a Ni-plated dull electrode in an ammonia electrolyte at 4.5 V and 40 to 50°C. After 5 min drying at 160°C the number of H_2O molecules, n, is 3. Optimum conditions for the electrogravimetric determination of Mo as $Mo_2O_3 \cdot 3H_2O$ are given in the paper [4]. Anhydrous molybdenum(III) oxide, prepared by the reduction of MoO_3 with K in liquid NH_3 at −33.5°C, was converted to $Mo_2O_3 \cdot 3H_2O$ by agitation with H_2O at 23°C for 15 min. The insoluble black solid was dried in vacuum over concentrated sulfuric acid [2].

A black precipitate, assumed to be $Mo(OH)_3$, was obtained by the reduction of Mo^{VI} with Zn in weakly acidic solution in N_2 atmosphere and in neutral solution containing an ammonium salt (NH_4F, NH_4Cl, or $(NH_4)_2SO_4$) [5]. Small amounts of $Mo(OH)_3$ form during the disproportionation of pentavalent molybdenum in alkaline solution [6].

Using the SCF-Xα-scattered wave method the ground state electronic structure of the hypothetical molecule $Mo_2(OH)_6$ has been calculated [7].

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1.2 $MoO_{2-n}(OH)_{2n}$, n = 0 to 2; $MoO_2 \cdot xH_2O$, x = 1, 2, or 2.5

A brown precipitate of analytical composition $MoO_2 \cdot xH_2O$ with $x \approx 2$ (however, designated as "$MoO(OH)_2$") was obtained by adding aqueous NaOH to a 0.3 M solution of Mo^{IV}. This solution was prepared by heating at 80°C for several hours a 2 N HCl solution containing Mo^{VI} and Mo^{III} in the molar ratio 1:2 [1].

The polarographic reduction of a molybdate solution of concentration 0.125 g-atom Mo/L in 3 M NaCl with pH > 2 produces a dark brown $MoO_2 \cdot 2H_2O$ film on the surface of the Hg cathode [2]. The deposit formed on a Pt cathode during the electrolysis of a Mo^{VI} solution at pH 3.8 was found to be $MoO_2 \cdot 2.5H_2O$ [3] and $MoO_{2-n}(OH)_{2n}$ (n = 0 to 2) at pH 10.5 [4]. The formation of thin black films, the composition of which is given as $MoO_2 \cdot H_2O$ [5], $MoO(OH)_2$, or $Mo(OH)_4$ [6], was observed on Mo anodes using acetic acid based electrolytes.

The $MoO_2 \cdot 2H_2O$ film formed on an Hg cathode shows semiconductor properties [2].

Freshly precipitated $MoO(OH)_2$ is easily soluble in excess 2 N HCl whereas a dried sample (130°C) does not dissolve. With excess aqueous MOH (M = Li, Na, or K) insoluble brownish green compounds of composition $MHMoO_3$ form [1].

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1.3 $MoO_{1.6}(OH)_{1.6}$

This brown crystalline compound which has also been formulated as $Mo_5O_8(OH)_8$ [1] or $Mo_5O_7(OH)_{10}$ [2] was obtained from the green H_2MoO_3 (see p. 17) by treating with boiling KOH solution (1 h). The product was washed and dried upon exclusion of oxygen. The d values are listed in [1]. On heating, H_2O was lost at 165 to 175°C and $MoO_2 + MoO_3$ formed. Oxidation in air or in aqueous suspension yields the blue $HMoO_3$ (see p. 7) in 1 to 2 d. $MoO_{1.6}(OH)_{1.6}$ dissolves in hot concentrated sulfuric acid to give a dark green solution [1], see also [2, 3].

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1.4 $MoO_2(OH)$

The gaseous $MoO_2(OH)$ species was mass-spectrometrically detected in high-temperature vapors produced by the interaction between gaseous H_2O and Mo wire at 1400°C. The importance of the $MoO_2(OH)$ formation in the high-temperature corrosion of steel has been discussed.

Sin-Shong Lin (J. Electrochem. Soc. **127** [1980] 1108/11).

1.5 $MoO(OH)_3$ and $MoO(OH)_3 \cdot 2H_2O$

The brown amorphous $MoO(OH)_3$ is usually prepared by the reduction of ammonium molybdate(VI) to Mo^V in acid solution, followed by precipitation with aqueous NH_3 [1 to 4] or ammonium carbonate solution [5]. Reducing agents are hydrazine [1], hydrogen liberated from strips of Al in HCl solution [2], mercury [5], or HI [3]. The molybdate(VI) was also electrochemically reduced [4]. An easily filterable product was obtained by reducing a molybdate(VI) solution or an aqueous suspension of MoO_3 with a pH value between 4 and 7 at room temperature with $NaBH_4$ in 1.5- to 2-fold excess and heating the precipitate in the mother liquor at 60 to 70°C. Yield >98% [6], see also [7]. Also a hydrate of composition $MoO(OH)_3 \cdot 2H_2O$ has been obtained by reducing a molybdate(VI) solution with $NaBH_4$ [6]. $MoO(OH)_3$ was precipitated by adding alkali solutions to a hydrochloric acid solution containing Mo^{VI} and Mo^{III} at a ratio 2:1 [8], to aqueous $(NH_4)_2[MoOCl_5]$ [9], or to a solution of $MoCl_5$ in dilute sulfuric acid [10]. For the formation of $MoO(OH)_3$ by decomposition of amorphous molybdenum blue hydrates with aqueous alkali hydroxide or NH_3 solution, see p. 6.

IR absorption bands were measured at 960 [ν(Mo-O)], 740 [ν(Mo-O-Mo)], and 450 to 500 cm^{-1} [ν(Mo-OH)]. Additional bands at 3500, 3400, 1650, and 1620 cm^{-1} were assigned to stretching and deformation frequencies of H_2O [11]. IR wave numbers were also reported in [12]. The IR spectrum of the solid compound was identical to that recorded in [13] for solutions with pH 8 to 10 [6].

The ^1H NMR spectrum at room temperature exhibits a single line, 0.7×10^{-4}T broad. The broadening of the line on cooling and the appearance of two feeble lines at −165°C was found to be typical for the ^1H NMR spectra for solitary protons from OH groups and water molecules, respectively [6]. $MoO(OH)_3$ gives a very strong asymmetric EPR signal with a g value of 1.9 [12].

In the dry state, the compound is stable against air but is slowly oxidized when it is moist [5]. On heating in flowing He, dehydration occurs in three steps at 115, 250, and 350°C with the loss of 1 mol H_2O each time to give "Mo_2O_5" [11]. $MoO(OH)_3 \cdot 2H_2O$, dried over $CaCl_2$, showed endothermic effects at 95, 165, and 340°C resulting from the loss of 0.5, 1.0, and 1.5 mol H_2O, respectively. At 370°C oxidation to Mo^{VI} occurred [6].

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1.6 $[Mo_2O_4(OH)_2(H_2O)_4] \cdot 6H_2O$

The hydrolysis of $(NH_4)_2[MoOCl_5]$ in aqueous HCl (<4 N) with $NaHCO_3$ solution or in methanol with stoichiometric amounts of H_2O yields a brown precipitate which was formulated as the dinuclear complex of Mo^V, $[Mo_2O_4(OH)_2(H_2O)_4] \cdot 6H_2O$ (in the author's abstract: $[Mo_2O_4(OH)_2(H_2O)_4] \cdot 4.5H_2O$). The compound is diamagnetic which can be explained by the strength of its Mo-Mo bond resulting from electron pairing in the A_g molecular orbitals. An energy-level scheme obtained from LCAO calculations is given. No EPR signal was detected.

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1.7 $MoO_{2.88} \cdot xH_2O$, x = 0.7 to 1.03

Blue crystalline products of composition $MoO_{2.88} \cdot xH_2O$ (x = 0.95 to 1.03) were produced on reacting $MoO_3 \cdot 2H_2O$ with molybdenum powder. Mixtures corresponding to overall compositions $MoO_{2.80}$ to $MoO_{2.95}$ were heated in vacuum at 110°C for several weeks. The X-ray line diagram (see the paper) suggests the existence of a definite compound which was formulated as $Mo_8O_{15}(OH)_{16}$ ($\triangleq MoO_{2.88} \cdot H_2O$) [1, 2]. Using the same procedure, a product of composition $MoO_{2.88} \cdot 0.7H_2O$ was later isolated, for which the X-ray line diagram is given [3].