

Studies on Peroxidomolybdates

II. Potassium Peroxidomolybdates Crystallizing from Aqueous Solution. A Preliminary Report

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The crystalline products formed during the isothermal evaporation of aqueous solutions containing molybdates and hydrogen peroxide have been studied in the pH range 4–8. At high hydrogen peroxide concentrations the product is always $K_2Mo_2O_{11} \cdot 4H_2O$. At low hydrogen peroxide concentrations the nature of the substance which separates from the solution is determined, within rather narrow limits, by the $H_2O_2:Mo$ ratio. During the evaporation the $H_2O_2:Mo$ ratio and the pH change, and, if this is not compensated for, mixtures of different crystals will eventually be obtained.

The structure of the molybdates and the degree of polymerization in aqueous solution has been studied extensively during the last twenty years by Lindqvist¹⁻³ and Sillén.³ Lindqvist¹ has established the existence of hepta- and octamolybdates, whereas Sasaki and Sillén^{3,4} have, by means of emf measurements, detected the presence of the following complexes in solutions of molybdates of varying acidity: MoO_4^{2-} , $HMoO_4^-$, H_2MoO_4 , $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $H_3Mo_7O_{24}^{3-}$, and possibly even $Mo_{19}O_{53}^{4-}$.

The formation and structure of the peroxidomolybdates is less well understood, though a large number of papers have appeared on the subject since the first publication by Baerwald⁵ in 1885 (see the review by Connor and Ebsworth;⁶ the contradictory nature of most investigations is not, however, fully brought out in their summary).

The most well-established peroxidomolybdates are the tetraperoxidomolybdates, $M_2[Mo(O_2)_4]$, and the tetraperoxidodimolybdates, $M_2[(H_2O)(O_2)_2OMoOMoO(O_2)_2(H_2O)](H_2O)_2$. (The crystal structures of $[Zn(NH_3)_4][Mo(O_2)_4]$ and $K_2Mo_2O_{11} \cdot 4H_2O$ have recently been determined by Stomberg^{7,8}). They are both obtained from solutions with high H_2O_2 concentrations, the tetraperoxidomolybdate ion being formed in moderately alkaline solutions and the tetraperoxidodimolybdate ion in neutral

or moderately acidic solutions. That the information concerning the other existing peroxidomolybdates is so controversial may be due to the fact that the analyses have been performed on mixtures of different crystalline species. Hardly any of the preparations are described in such a manner that it is possible to reproduce them. The starting material is often an unknown quantity of "di-", "tri-", meta or paramolybdate to which an unspecified amount of hydrogen peroxide (3 or 30 %) is added. These solutions are then evaporated to dryness or nearly to dryness, or the peroxidomolybdate is precipitated by addition of ethanol. Since the number of crystalline products formed in solutions with low H_2O_2 concentrations is large, and because the products are sometimes difficult to distinguish with the naked eye or under the microscope, the prevailing uncertainty is understandable.

The investigations performed at this Department concerning the formation and structure of the peroxidomolybdates have shown that the nature of the crystals formed by the isothermal evaporation of solutions obtained by adding hydrogen peroxide and a strong acid (HNO_3 , HCl) to solutions of normal potassium molybdate depend on the $H_2O_2:Mo$ ratio and on the acidity of the solution. Since most of the crystalline phases were obtained in the pH range 4–8 this investigation was limited to that interval.

Molybdates, like most other transition metal compounds, homogeneously catalyze the decomposition of hydrogen peroxide. During the slow evaporation of the solvent the composition of the solution will, therefore, undergo a considerable change. (The rate of the decomposition of hydrogen peroxide is pH-dependent, it is rapid in neutral medium and even more rapid in alkaline medium). A suitable concentration of molybdenum was found to be about 1 M. With this concentration well-crystallized phases were obtained within 1–20 h. This made it possible to follow the composition of the solution and to pick out the first crystallization product. X-Ray single crystal and powder methods were then used to identify the phases.

When a crystal phase is allowed to crystallize extensively the composition of the solution with respect to the acidity and the $H_2O_2:Mo$ ratio is altered because the composition of the crystals differs from that of the solution. The consequence of this is that new crystalline phases will be formed. If the crystallization is allowed to proceed for a long time, up to at least four different crystalline phases may be obtained simultaneously.

By keeping the $H_2O_2:Mo$ ratio constant and varying the acidity of the solution in each series it has been possible to establish composition intervals of the solution within which the different crystalline products can be obtained. As a result of this rather comprehensive investigation it is at present possible to state that the following crystalline potassium peroxidomolybdates can be obtained within the pH-range 4–8.

1. When the $H_2O_2:Mo$ ratio in the solution is greater than 1.5, $K_2Mo_2O_{11} \cdot 4H_2O$ is obtained as the first crystallization product within the whole pH-range.

2. With an $H_2O_2:Mo$ ratio between 0.9 and 1.3 one obtains

- a) at pH 6.8–8 a compound with rather large peroxide content.
- b) at pH 5–6.5 a product consisting of very thin needle-shaped crystals with a peroxide content of about 9 %.

3. When the $\text{H}_2\text{O}_2:\text{Mo}$ ratio is 0.1–0.8 one obtains

a) at pH 7–8 a tetragonal product with the empirical formula KMoO_4 . (Crystal data for this compound have been determined by Trysberg and Stomberg⁹ and the structure is under consideration).

b) at pH 5.8–6.8 two heptamolybdates, one with orthorhombic symmetry and the other with monoclinic symmetry. The precise conditions governing the formation of one or the other are still somewhat uncertain. The orthorhombic form is obtained from an equilibrated molybdate solution by adding acid and then H_2O_2 in amounts consistent with the above conditions. The empirical formula is $\text{K}_6\text{Mo}_7\text{O}_{22}(\text{O}_2)_2 \cdot 9\text{H}_2\text{O}$. The monoclinic form is obtained by rapidly adding acid and hydrogen peroxide to a freshly prepared potassium molybdate solution. (It may also be obtained by boiling a neutral solution of a peroxido molybdate rich in H_2O_2 in order to reduce the H_2O_2 content and allowing the solution to evaporate at room temperature. Rapid cooling and crystallization at 0°C often gives the orthorhombic form). The empirical composition of the monoclinic form is $\text{K}_6\text{Mo}_7\text{O}_{24-x}(\text{O}_2)_x \cdot 9\text{H}_2\text{O}$ where $0.5 < x < 3$. The exact limits for x have not yet been settled.

The formulae given are consistent with the replacement of an oxygen ion in the molybdenum complex by a peroxide group. It is, however, impossible to say at the present stage of the investigation whether or not this is so. The peroxide could equally well partly or completely be hydrogen peroxide of crystallization. For the monoclinic compound there is a slight indication that the latter possibility is the most probable one. The density and unit cell dimensions have been determined by Stomberg.¹⁰ These observations strongly support the formulation of these compounds as heptamolybdates.

c) at pH 4.0–5.5 a monoclinic product with rather large cell dimensions and with the empirical formula $\text{K}_5\text{HMo}_7\text{O}_{22}(\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$.

4. When the $\text{H}_2\text{O}_2:\text{Mo}$ ratio in the solution is less than 0.05 one obtains

a) at pH 7–8 a solid solution of peroxide in normal potassium heptamolybdate with the composition $\text{K}_6\text{Mo}_7\text{O}_{24-x}(\text{O}_2)_x \cdot 4\text{H}_2\text{O}$ ($0 < x < 0.1$). The peroxide may, of course, be hydrogen peroxide of crystallization. The upper limit for x has not yet been settled. The crystals are yellow in contrast to those of $\text{K}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. A similar ammonium compound has been described by Hansson and Lindqvist.¹¹

b) at pH 4–6 a yellow powder of varying composition.

Though the investigation has not yet been completed it is possible to draw some general conclusions:

Addition of hydrogen peroxide to an acidified or unacidified molybdate solution produces a colouring of the solution and a change in the pH to an extent which depends on the amount of hydrogen peroxide added. For a large $\text{H}_2\text{O}_2:\text{Mo}$ ratio (>2) the dinuclear ion $[(\text{H}_2\text{O})(\text{O}_2)_2\text{OMoOMo}(\text{O}_2)_2(\text{H}_2\text{O})]^{2-}$ dominates in the acid and neutral range, while the mononuclear ion, $[\text{Mo}(\text{O}_2)_4]^{2-}$, dominates in the alkaline range. When the $\text{H}_2\text{O}_2:\text{Mo}$ ratio is decreased other ions appear to a greater extent. At low $\text{H}_2\text{O}_2:\text{Mo}$ ratios peroxidoheptamolybdate ions seem to exist in weakly acidic solutions, judging by the compounds which crystallize. It is interesting to note that a crystalline protonated peroxidoheptamolybdate can be obtained, since no similar oxido molybdate has been identified. The peroxido molybdates and the oxido molyb-

dates differ in yet another respect. Whilst the dinuclear peroxidomolybdate is easily formed, the corresponding oxidomolybdate has not been obtained from aqueous solution.

Further work on this system is in progress and a complete report will be published in a forthcoming paper.

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