

Redox Chemistry of Aqueous Molybdenum

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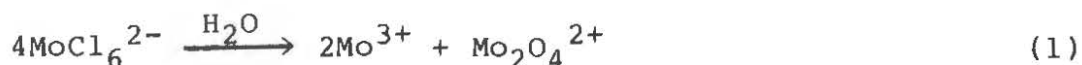
Final Seminar

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The redox chemistry of aqueous molybdenum ions is fairly complicated and has required over 30 years of work to reach the present state of knowledge.[1] Among the many reasons for this complexity are the existence of several different structural forms for some of the oxidation states,[2] the great tendency for molybdenum to disproportionate and conproportionate to produce secondary products,[3] and the lack of experimental techniques for characterizing the resulting products. Although the redox reactions of molybdenum in the oxidation states of +6 to +2 are now considered "known", a review of these redox studies reveals the widespread use of large excesses of the oxidizing/reducing agent with respect to the molybdenum species being studied.[4] In these cases, it is usually not possible to determine whether the observed product was the initial product or the result of secondary reactions with the excess oxidant/reductant.

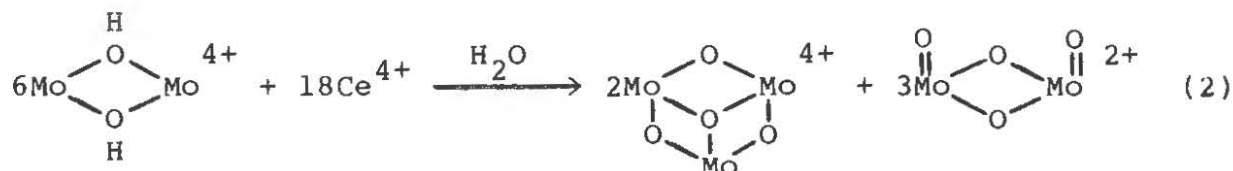
In an attempt to reinvestigate these systems, potentiometric titrations of the various molybdenum species by the appropriate oxidant/reductant were performed. In this way, not only were excesses of the redox agent avoided, but also the progress of any reaction could be monitored by the observed potential at a gold or platinum electrode.

In initial studies, the oxidation of Mo^{3+} by all oxidants (Ce^{4+} , Mo(VI) , $\text{Cr}_2\text{O}_7^{2-}$, etc.) resulted in the sole production of $\text{Mo}_2\text{O}_4^{2+}$, the only known stable form of Mo(V) and the expected product as suggested by the literature.[5] No indication of Mo(IV) was found, despite the use of Ce^{4+} as a one electron oxidant. Subsequent studies with Mo(IV) halides (MoCl_4 , $(\text{Et}_4\text{N})_2\text{MoCl}_6$, etc.) demonstrated that rapid disproportionations occurred upon their contact with water,



thus showing the instability of monomeric $\text{Mo(IV)}_{\text{aq}}$ and explaining its absence as a product during the oxidation of Mo^{3+} .

Contrary to the literature,[6] the oxidation of $\text{Mo}_2(\text{OH})_2^{4+}$ yields equal amounts of Mo(IV) and Mo(V) .

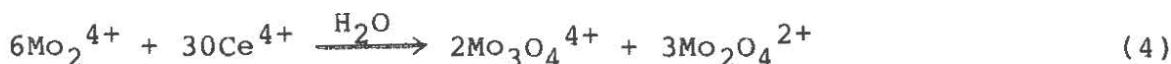


Reaction 2 occurs under all conditions and is oxidant independent. Although the use of Mo(VI) as oxidant introduces another source of molybdenum, the resulting products remain the same.

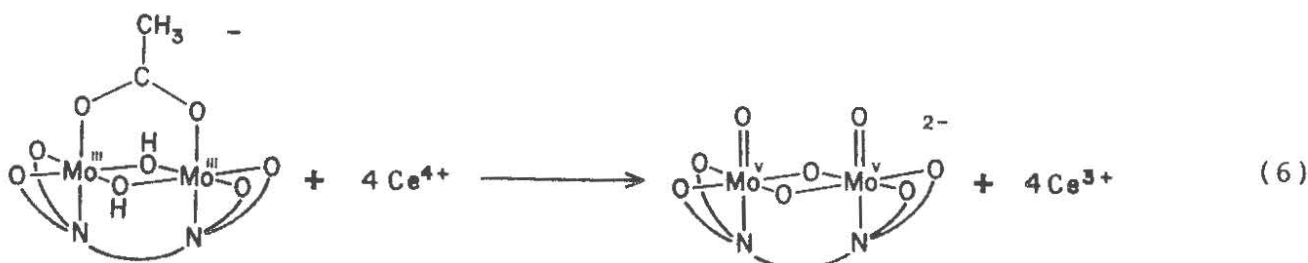
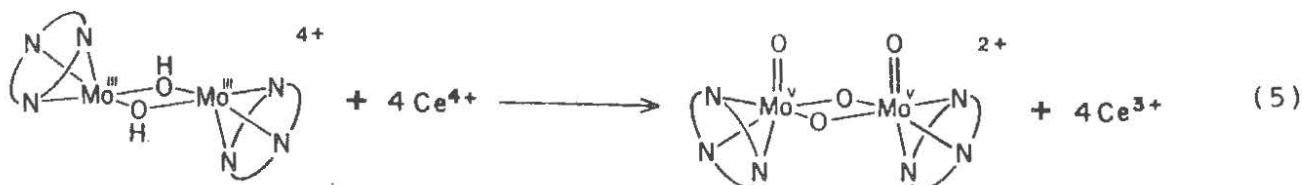


^{95}Mo labeling studies show that molybdenum from both reactants are found in both products in approximately a 1:1 ratio.

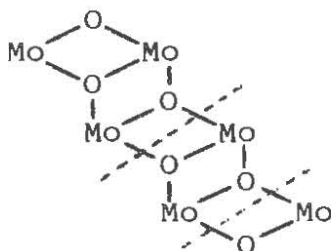
A similar reaction occurs with dimeric Mo_2^{4+} .



A common intermediate (or activated state) is suspected for these reactions. The intermediate is probably a large (4 or more molybdenum atoms) molybdenum-oxygen oligomer produced by the combination of two or more molybdenum dimers resulting from the initial oxidation of $\text{Mo}_2(\text{OH})_2^{4+}$ or Mo_2^{4+} . Removal of coordination sites from the original molybdenum starting materials with chelating agents changes the product stoichiometries, probably by inhibiting the formation of large oligomeric intermediates.



Large oligomeric intermediates would allow the necessary trimeric and dimeric structures found in the products to be preformed with very few rearrangements. For example:



Oxidation of $\text{Mo}_4\text{O}_4(\text{OH})_2^{4+}$ and $\text{Mo}_4\text{O}_6^{4+}$ give the same $2\text{Mo}_3\text{O}_4^{4+}/3\text{Mo}_2\text{O}_4^{2+}$ ratio suggesting their close similarity to the proposed intermediate.

References

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