# Reactions involving Oxidation of Hexa-aquamolybdenum(III): Kinetic and Mechanistic Studies

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Rate laws for the oxidation of $[Mo(H_2O)_6]^{3+}$ with $[IrCl_6]^{2-}$, $[Co(C_2O_4)_3]^{3-}$, and aqua VO^{2+} show variations on patterns previously established for hexa-aqua ions.

There have been no previous detailed kinetic studies of reactions involving the oxidation of hexa-aquamolybdenum-(III). Here we consider rate laws for the reactions with three oxidants $[IrCl_6]^{2-}$ (0.89 V),[1] $[Co(C_2O_4)_3]^{3-}$ (0.58 V),[2] and aqua VO^{2+} (0.36 V)[3] which indicate an unusual versatility in reactivity. All three oxidants give the Mo^V aqua dimer, $Mo_2O_4^{2+}$, as final product, and all observations (including a well-defined isosbestic at 598 nm in the case of the VO^{2+} oxidation) indicate that Mo^{IV} is a transient intermediate only. Indeed it is now known that the only stable aqua ion of Mo^{IV} is a trimer.[4,5] The reaction sequence can accordingly be represented as in equation (1). Use of perchlorate was avoided because of its potential redox involvement, and instead toluene-*p*-sulphonate (PTS$^-$) and trifluoromethanesulphonate (TFMS$^-$) were used.

$$2Mo^{III} \xrightarrow{-2e^-} 2Mo^{IV} \xrightarrow[\text{fast}]{-2e^-} Mo^V{}_2 \qquad (1)$$
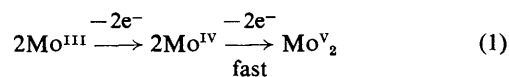
The reaction with $[IrCl_6]^{2-}$ was studied by the stopped-flow method by monitoring the disappearance of $[IrCl_6]^{2-}$ at the 489 nm peak ($\epsilon = 4075$ M^{-1} cm^{-1}), with $[Mo(H_2O)_6]^{3+}$ present in >10-fold excess. The rate law (2) was found to apply.

$$\text{Rate} = (k_1 + k_2[H^+]^{-1})[Mo^{III}][IrCl_6{}^{2-}] \qquad (2)$$

At 25 °C, $I = 0.20$ M (LiPTS), $k_1 = (3.4 \pm 1.1) \times 10^4$ M^{-1} s^{-1} and $k_2 = (2.9 \pm 0.2) \times 10^4$ s^{-1} with k_2 dominant at $[H^+] \leqslant$ 0.10 M. Since rate constants for substitution reactions of $[Mo(H_2O)_6]^{3+}$ with Cl^- and NCS^- (both of which are independent of $[H^+]$) are much smaller, 4.6×10^{-3} M^{-1} s^{-1} and

0.27 M^{-1} s^{-1} respectively at 25 °C and $I = 1.0$ M (LiPTS),[6] it can be concluded that k_1 and k_2 are outer-sphere electron-transfer processes. The k_2 path, involving the conjugate-base form $MoOH^{2+}$ is favoured presumably because the higher Mo oxidation states are more extensively hydrolysed than $[Mo(H_2O)_6]^{3+}$.[4]

The initial slopes method has been used to define the rate law for the conventional time range study with $[Co(C_2O_4)_3]^{3-}$ as oxidant, monitored at $\lambda = 420$ nm ($\epsilon = 218$ M^{-1} cm^{-1}), with $[Mo(H_2O)_6]^{3+}$ in excess. This method was adapted to avoid effects due to the reaction of free oxalate with $[Mo(H_2O)_6]^{3+}$, as well as aquation of $[Co(C_2O_4)_3]^{3-}$. The rate law (3) has a dominant k_3 term, which is first order in each reactant and independent of $[H^+]$, alongside two oxidant independent terms k_4 and k_5. At 25 °C, $I = 2.00$ M (LiPTS), $k_3 = 0.67$ M^{-1} s^{-1}, $k_4 = (9.0 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1}, and $k_5 = (9.4 \pm 0.1) \times 10^{-5}$ s^{-1}. The observation that k_3 is independent of $[H^+]$ is

$$\text{Rate} = k_3[Mo^{III}][Co(C_2O_4)_3^{3-}] + k_4[Mo^{III}]^2 + k_5[Mo^{III}] \quad (3)$$

consistent with a substitution-controlled process, where k_3 is of similar magnitude to the rate constant for the reaction of NCS^- with $[Mo(H_2O)_6]^{3+}$.[6] The conjugate-base pathway for substitution (normally I_d) does not make a significant contribution for the hexa-aquamolybdenum(III) ion, presumably because of the strong associative character of the main pathway involving $[Mo(H_2O)_6]^{3+}$, which remains the most facile route. Since the reactions of for example $[Co(C_2O_4)_3]^{3-}$ and O_2 with the green aqua Mo^{III} dimer are ca. 10^2-times faster than those for $[Mo(H_2O)_6]^{3+}$, it would appear that for the slower redox processes, the sequence (4) in which the dimerisation process is rate determining, makes a significant contribution.

$$2\,Mo^{III} \rightarrow Mo^{III}_2 \xrightarrow[\text{fast}]{-4e^-} Mo^V_2 \quad (4)$$
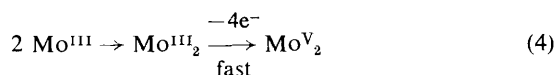
The reaction with VO^{2+} as oxidant, Mo^{III} in large excess, is also slow with k_4 and k_5 now dominant in the rate law (5).

$$\text{Rate} = k_4[Mo^{III}]^2 + k_5[Mo^{III}] + k_6[Mo^{III}][V^{IV}] \quad (5)$$

When the reaction is monitored at the VO^{2+} peak at 760 nm ($\epsilon = 17.2$ M^{-1} cm^{-1}), the kinetics approximate to zero order in oxidant with $[VO^{2+}] \leqslant 1 \times 10^{-3}$ M. From studies at 25 °C, $I = 2.00$ M (LiPTS), k_4 and k_5 are the same as in the $[Co(C_2O_4)_3]^{3-}$ study. Both these paths give $[H^+]^{-1}$ dependencies, with no detectable contributions from other terms. We are uncertain

as to the full implications of k_5. Contributions from k_6 are small, and the precise concentration dependences are difficult to establish with certainty. Assuming they are as indicated in equation (5), then $k_6 = (6.5 \pm 0.7) \times 10^{-3}$ M^{-1} s^{-1}. Interestingly when PTS^- is replaced by $TFMS^-$, k_4 and k_5 make no contribution and k_6 is lowered by greater than an order of magnitude. However k_1, k_2, and k_3 (as well as the rate constant for the NCS^- substitution reaction) are little affected by this change.

An additional feature of the $[Mo(H_2O)_6]^{3+}$ redox studies described is that an $[H^+]^{-1}$ dependence is here diagnostic of an outer-sphere reaction, whereas reaction independent of $[H^+]$ proceeds by an inner-sphere process. The opposite is the case in many other electron-transfer reactions, those between the V^{II} and Fe^{III} aqua ions[7] and Cr^{2+} with $[Co(NH_3)_5(H_2O)]^{3+}$[8] being particularly good examples. Indeed this pattern of behaviour appeared to be sufficiently established that an approach based on $[H^+]$ dependences has been used (with justification) as a means of distinguishing between inner- and outer-sphere mechanisms.[9]

Of further interest is whether the reaction of $[Mo(H_2O)_6]^{3+}$ with the two-equivalent oxidant NO_3^-[10] conforms to one or other of the above categories.

References

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