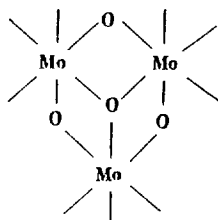# A Kinetic Study on the Oxidation of Aquaoxomolybdenum(IV) Trimer by Vanadium(V)

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The structure and ^{18}O exchange rates of the trimeric aquaoxomolybdenum(IV) ion, $[Mo_3O_4(H_2O)_9]^{4+}$, were reported by Murmann and Shelton[1]

Sykes and his coworkers[2] have indicated that the reaction of $[IrCl_6]^{2-}$ with $Mo_3{}^{IV}$ in large excess can be expressed as $Mo_3{}^{IV} + 6Ir^{IV} \rightleftharpoons 3Mo^{VI} + 6Ir^{III}$. They reported that the reaction of $[Fe (phen)_3]^{3+}$ with $Mo_3{}^{IV}$ occurred exclusively by an outer-sphere mechanism, while $[IrCl_6]^{2-}$ reacted via an inner-sphere mechanism. No oxidations of $Mo_3{}^{IV}$ by $[Co(C_2O_4)_3]^{3-}$ and $[PtCl_6]^{2-}$ were observed. We now report here our results of the reaction of $[Mo_3O_4(H_2O)_9]^{4+}$ with VO_2^+ in perchlorate media.

The stoichiometry of VO_2^+ oxidation of $[Mo_3O_4(H_2O)_9]^{4+}$ was determined at 25°C by measuring the absorbance of the $[Mo_3O_4(H_2O)_9]^{4+}$ at constant acidity. This experiment was done in 0.03M perchloric acid by adding varying amounts of VO_2^+ to $[Mo_3O_4(H_2O)_9^{4+}] = 3.57 \times 10^{-4}M$ and adjusting to constant volume. Curvature was obtained from plot of the absorbance against the $[VO_2^+]$ at $[Mo_3O_4(H_2O)_9^{4+}] = 3.57 \times 10^{-4}M$. From this result the mole ratio of VO_2^+ to $[Mo_3O_4(H_2O)_9]^{4+}$ was 5.9 ± 0.2 consistent with the stoichiometry given in

$$Mo_3{}^{IV} + 6V^V \rightleftharpoons 3Mo^{VI} + 6V^V \qquad (1)$$

The kinetics of the reaction were studied under conditions of the presence of excess VO_2^+ in order to maintain the pseudo-first order condition. Rates of oxidation of $[Mo_3O_4(H_2O)_9]^{4+}$ were measured by adding VO_2^+ of a given concentration with lambda pipette to reaction cell at constant temperature. The rate constants were obtained by a linear least-squares analysis of the absorbance against time. The relation between $\ln (A_t - A_\infty)$ versus t was a straight line for at least 3 half-lives. Rate constants for the oxidation of $[Mo_3O_4(H_2O)_9]^{4+}$ by VO_2^+ in perchlorate media were obtained spectrophotometrically at 340nm.

Figure 1 shows the dependence of the observed rate constants(k_{obsd}) on $[VO_2^+]$ at $[Mo_3O_4(H_2O)_9^{4+}] = 3.57 \times 10^{-4}M$ and $[HClO_4] = 0.57M$. This is a straight line through the origin, denoting a first-order dependence on $[VO_2^+]$ as shown in Figure 1.
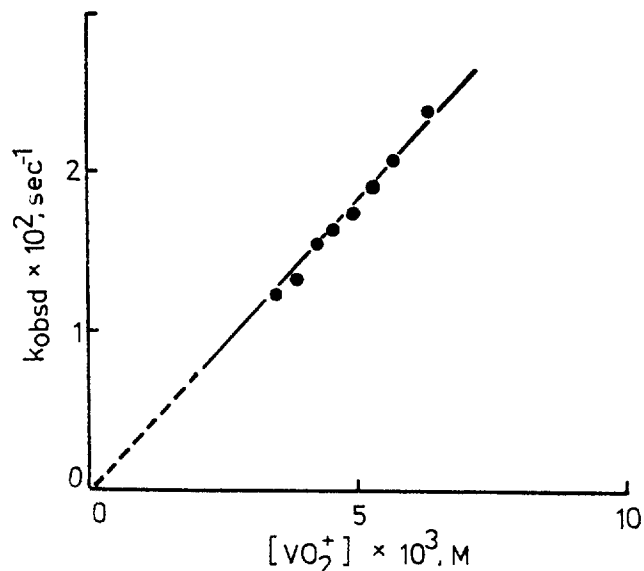
The effect of hydrogen-ion concentration was studied at

Figure 1. Dependence of k_{obsd} on $[VO_2^+]$ at 25°C. $[Mo_3O_4(H_2O)_9^{4+}] = 3.57 \times 10^{-4}M$, $[HClO_4] = 0.57M$.
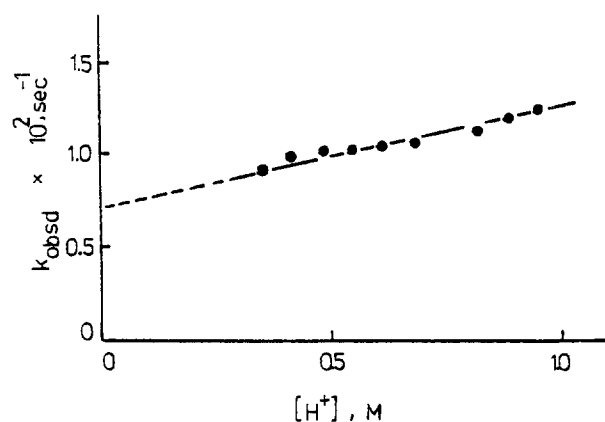
Figure 2. Hydrogen-ion dependence of k_{obsd} at 25°C. $[VO_2^+] = 3.53 \times 10^{-3}M$, $[Mo_3O_4(H_2O)_9^{4+}] = 2.14 \times 10^{-4}M$, $[ClO_4^-] = 0.66M$.

$[VO_2^+] = 3.53 \times 10^{-3}M$, $[Mo_3O_4(H_2O)_9^{4+}] = 2.14 \times 10^{-4}M$, and $[ClO_4^-] = 0.66M$. Figure 2 shows a plot of the pseudo-first order rate constants against $[H^+]$. The rate increases with increasing hydrogen-ion concentration. A straight line of Figure 2 shows k_{obsd} to be a first-order function of $[H^+]$.

From the results of Figure 1 and 2 an experimental equation was expressed as

where $k_{obsd} = \{k_o + k_h[H^+]\} [VO_2^+]$. k_o and k_h obtained from in-

$$-d\,[Mo_3O_4(H_2O)_9{}^{4+}]/dt = k_{obsd}\,[Mo_3O_4(H_2O)_9{}^{4+}] \qquad (2)$$
$$= \{k_o + k_h[H^+]\}\,[VO_2^+]\,[Mo_3O_4(H_2O)_9{}^{4+}]$$

tercept and slope of Figure 1 were $7.5 \times 10^{-3}\text{sec}^{-1}$ and $4.82 \times 10^{-3}\text{M}^{-1}\text{sec}^{-1}$, respectively. Rate equation shows two terms involving $[H^+]$-dependent and -independent rates. The $[H^+]$-independent term indicates substitution of a coordinated water of $Mo_3O_4^{2+}$. This makes bridge bond with OH^- of VO_2^+. The increase in the rate of oxidation with increasing hydrogen–ion concentration implies that the protonation of $Mo_3O_4^{4+}$ produces $Mo_3O_3(OH)^{5+}$ containing the OH^- group which is more strongly coordinated than water. It is not observed that the molybdenum(IV)–hydroxide species were formed by dissociation of proton from a coordinated water under the condition of this experiment.

Ratios of the rate constants for a series of oxidants reduced by two different reductants are often used as a diagnostic criterion for assigning redox reactions as proceeding by outer–sphere mechanisms or inner–sphere mechanisms.[3] Ratios (k_{Fe}/k_{Ir}) of the rate constants for the reactions of $Mo_2O_4(aq){}^{2+}$ and $[Mo_2O_4(edta)]^{2-}$ with $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ are 281,[4] while ratios of k_s/k_{Ir} for VO_2^+ oxidation of $Mo_2O_4(aq){}^{2+}$ and $Mo_3O_4(aq){}^{4+}$ are 6.3 and 3.0, respectively.[5] These ratios are not in agreement with that observed for the outer–sphere reactions of $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ with $[Mo_3O_4(H_2O)_9]^{4+}$.[2] This fact indicates that the aquaoxomolybdenum(IV) trimer reacts rapidly via an inner–sphere mechanism with VO_2^+. This aquaoxomolybdenum(IV) complex allows for complexation by the inner–sphere oxidant. We assume that rate determining step of the reaction(1) is the process which the coordination number of vanadium in aqueous solution is increased from four or five in V(V) to six in V(IV) since redox step accompanying structural change seems energetically prohibitive.[6]

The mechanisms for the oxidation of the aquaoxomolybdenum(IV) trimer by VO_2^+ may be described by the steps (a) and (b).

From this equations $k_{obsd} = \{k_1 + K_h k_2[H^+]\}\,[VO_2^+]$, $k_1 = k_o$, and $K_h k_2 = k_h$. These results are consistent with the empirical

$$Mo_3O_4{}_{(aq)}{}^{4+} + VO_2^+{}_{(aq)} \xrightarrow{\;k_1\;} O_4Mo_3\text{-OH-VO(OH)}_{(aq)}{}^{5+} \left.\right\}\;(a)$$
$$\text{(I)}$$
(I) *fast* products

$$Mo_3O_4{}_{(aq)}{}^{4+} + H^+ \underset{}{\overset{\;k_h\;}{\rightleftharpoons}} Mo_3O_3(OH)_{(aq)}{}^{5+}$$
$$Mo_3O_3(OH)_{(aq)}{}^{5+} + VO_2^+{}_{(aq)} \xrightarrow{\;k_2\;} O_3Mo_3\text{-OH-VO}_2{}^{6+}{}_{(aq)} \left.\right\}\;(b)$$
$$O_3Mo_3\text{-OH-VO}_2{}^{6+}{}_{(aq)} \xrightarrow{\;fast\;} \text{products}$$
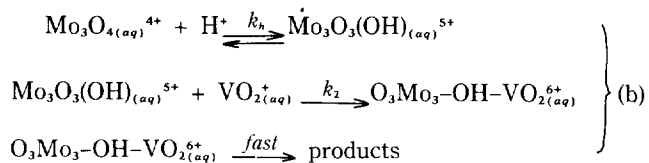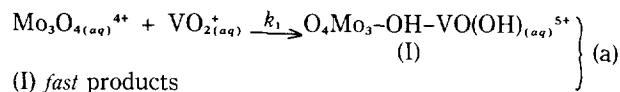
From mechanisms (a) and (b) we obtain
$$-d[Mo_3O_4(H_2O)_9{}^{4+}]/dt = \{k_1 + K_h k_2[H^+]\} \qquad (3)$$
$$[VO_2^+]\,[Mo_3O_4(H_2O)_9{}^{4+}]$$

rate equation. It is considered that the rate determining step for the reaction is the formation of the bridging complex between two reactants, Mo(IV) and V(V). The bridging ligand of an intermediate is donated by the reducing agent, $[Mo_3O_4(H_2O)_9]^{4+}$, as in the reactions of VO_2^+ with $[Fe(CN)_6]^{4-}$ and chromium(VI) with $[Fe(CN)_6]^{4-}$, $[Fe(bipy)(CN)_4]^{2-}$, and $[Fe(bipy)_2(CN)_2]$.[6,7]

Detailed mechanisms of the reaction should be the subject of further investigations.

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The Reductive N–Benzylation of Alkanolamines using Tetracarbonylhydridoferrate, HFe(CO)₄, as a Selective Reducing Agent

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The combination of two functionalities of alkanolamines having amino and hydroxyl group makes them versatile intermediates for countless industrial applications: they are of particular interest to the textile, pharmaceutical and household products industries[1]. Secondary alkylalkanolamines are generally prepared by the ring opening of an epoxides with an alkylamines[2]. The addition of imidoosmium reagents to alkenes[3] and methods for the alkylation of primary amines with 2-bromoalcohols[4] are also well established procedures for the preparation of N-alkyl-1, 2-alkanolamines. Cope et al[5] suc-