

COMMUNICATIONS TO THE EDITOR

A Kinetic Study on the Oxidation of Aquaoxomolybdenum(V) Dimer by Vanadium(V)

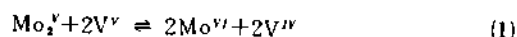
Chang-Su Kim and Moon-Pyoung Yi

Department of Chemistry Education, College of Education, Taegu University,
Taegu 634. Received February 17, 1986

It is known that oxo-molybdenum(V) ions such as $\text{Mo}_2\text{O}_7^{2+}$ and $\text{Mo}_2\text{O}_6^{2+}$ in solution are obtained as hydrogen-ion concentration of pentachlorooxomolybdate(V) solution decreases.¹⁻⁵ The reactions between aquaoxomolybdenum(V) dimer,⁶ $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$, and $[\text{IrCl}_6]^{2-}$ were explained by a rate law, rate = $k_1[\text{Mo}_2\text{O}_4^{2+}] + k_2[\text{oxidant}][\text{Mo}_2\text{O}_4^{2+}]$ (oxidant = $[\text{IrCl}_6]^{2-}$, $[\text{Fe}(\text{phen})_3]^{3+}$), that showed a pathway independent of oxidants and another pathway that involved the oxidizing agents. The oxidation of $\text{Mo}_2\text{O}_4^{2+}$ by Ce(IV) was studied in perchloric acid media by stopped-flow technique.⁷ The Mo(V) dimer reacts rapidly via an inner-sphere mechanism with Ce(IV). The oxidations of $[\text{Mo}_2\text{O}_4(\text{edta})]^{2+}$ by $[\text{IrCl}_6]^{2-}$ and $[\text{Fe}(\text{phen})_3]^{3+}$ provided evidence for the involvement of a Mo(V,VI) dimer as a kinetically significant intermediate.^{8,9} Kinetics of VO_2^+ oxidation of $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ which were carried out of perchlorate media are discussed in this paper.

The stoichiometry for the reaction of VO_2^+ oxidation on $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ was determined at 25°C by measuring the absorbance of the $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ at constant acidity. This was done in 0.03 M $[\text{HClO}_4]$ by adding varying amounts of

VO_2^+ to $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+} = 2.47 \times 10^{-4} \text{M}$ and adjusting to constant volume. Curvatures in the plots of the absorbance against the $[\text{VO}_2^+]$ occurred at $[\text{VO}_2^+] = 4.99 \times 10^{-4} \text{M}$. From this result the mole ratio of VO_2^+ to $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$ was 2.0 ± 0.2 consistent with the stoichiometry given in



In the presence of excess $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$, the dependence of the observed rate constants (k_{obsd}) on $[\text{VO}_2^+]$ at fixed conditions was a straight line passing through the origin, denoting a first order dependence on $[\text{VO}_2^+]$. This result was shown in Figure 1.

The effect of hydrogen-ion concentration was studied at constant concentration of the other reactants. Figure 2 shows a plot of the observed rate constants against $[\text{H}^+]$. The rate increases with increasing $[\text{H}^+]$. A straight line of Figure 2 gives k_{obsd} to be first-order function of hydrogen-ion concentration. From the results of Figures 1 and 2 an experimental equation may be expressed as

$$\begin{aligned} -\frac{d[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}]}{dt} &= k_{\text{obsd}}[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}] \\ &= \{k_0 + k_H[\text{H}^+]\} [\text{VO}_2^+] \\ &\quad [\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}] \end{aligned} \quad (2)$$

where $k_{\text{obsd}} = \{k_0 + k_H[\text{H}^+]\} [\text{VO}_2^+]$. k_0 and k_H obtained from

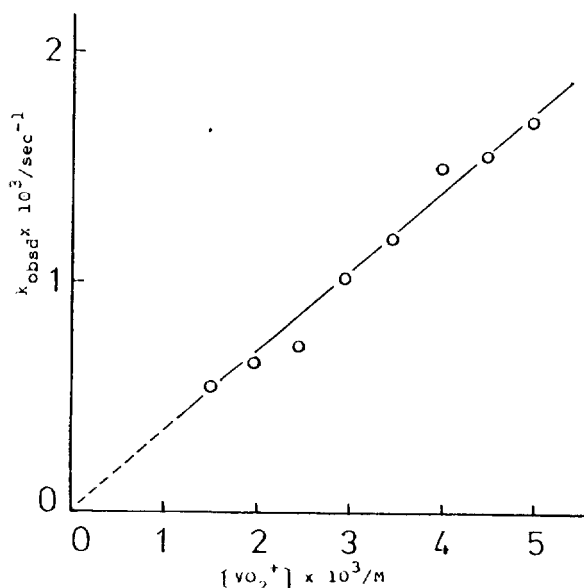


Figure 1. Dependence of k_{obsd} on $[\text{VO}_2^+]$ for the VO_2^+ oxidation of $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ at 25°C. $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+} = 1.85 \times 10^{-4} \text{M}$. $[\text{HClO}_4] = 0.023 \text{M}$.

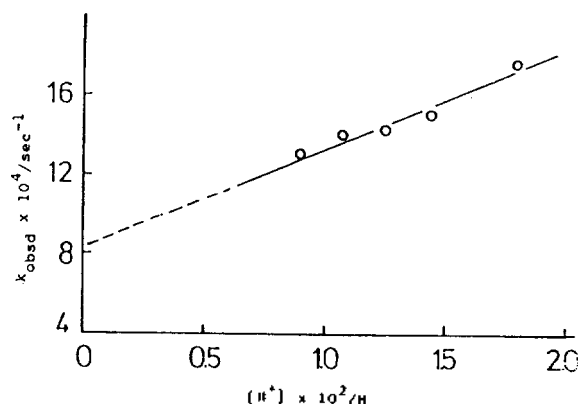
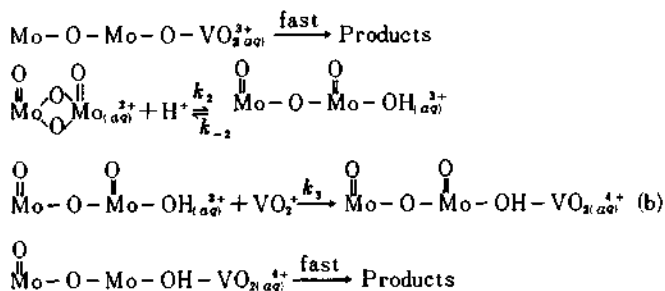
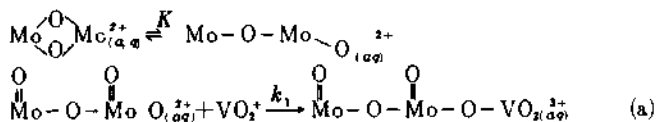


Figure 2. $[\text{H}^+]$ dependence of k_{obsd} for the VO_2^+ oxidation of $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ at 25°C. $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+} = 1.48 \times 10^{-4} \text{M}$, $[\text{VO}_2^+] = 3.96 \times 10^{-3} \text{M}$, $[\text{ClO}_4^-] = 1.80 \times 10^{-2} \text{M}$.

intercept and slope of Figure 2 were $8.34 \times 10^{-4} \text{ sec}^{-1}$ and $4.92 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. Rate equation (2) shows two terms involving $[\text{H}^+]$ -dependent and -independent rates. The $[\text{H}^+]$ -independent term indicates the presence of a dimeric Mo(V) species in which one of the oxo bridges was broken.^{6,8} The $[\text{H}^+]$ dependence is due to catalytic ring-opening of Mo_2O_7 , forming $\text{Mo}-\text{O}-\text{Mo}-\text{OH}^{2+}$ which is much more reactive than Mo_2O_7 . In the oxidation of the $[\text{Mo}_2\text{O}_4(\text{edta})]^{2-}$ and $[\text{Mo}_2\text{O}_4(\text{hedta})(\text{H}_2\text{O})]^-$ (H_3 hedta = N-(2-hydroxyethyl) ethylenediamine-N,N',N'-triacetic acid) by oxidants, molybdenum(V, VI) atoms were held together by edta^{4-} and hedta^{3-} , and thus formed $\text{Mo}^{\text{V}}-\text{Mo}^{\text{V}}-\text{edta}$ or $\text{Mo}^{\text{V}}-\text{Mo}^{\text{V}}-\text{hedta}$ as an intermediate.⁶ However, in the oxidation of $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ it is considered that there is fast dissociation of $\text{Mo}^{\text{V}}-\text{Mo}^{\text{V}}$. 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 seem energetically prohibitive.¹⁰

The mechanism for the oxidation of the aqua-oxomolybdenum(V) dimer by VO_2^+ may be described by the steps



Assuming steady state for the concentration of $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{Mo} - \text{O} - \text{Mo} \end{array} \text{O}_{(\text{aq})}^{2+}$ in mechanism (b) we obtain

$$-\frac{d[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}]}{dt} = \{k_1K + \frac{k_2k_3[\text{H}^+]}{k_{-2} + k_3[\text{VO}_2^+]}\} [\text{VO}_2^+][\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}] \quad (3)$$

Under the condition $k_{-2} \gg k_3[\text{VO}_2^+]$, rate equation (3) reduces to equation (4).

$$-\frac{d[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}]}{dt} = \{k_1K + (k_2k_3/k_{-2})[\text{H}^+]\} [\text{VO}_2^+][\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}] \quad (4)$$

From this equation $k_{\text{obs}} = \{k_1K + (k_2k_3/k_{-2})[\text{H}^+]\} [\text{VO}_2^+][\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}]$, $k_1K = k_0$, and $k_2k_3/k_{-2} = k_H$.

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

References

1. C.S. Kim and C.W. Kim, *Bull. Korean Chem. Soc.*, **7**, (1986) in press.
2. C.S. Kim and R.K. Murmann, *Inorg. Chem.*, **23**, 263 (1984).
3. C.S. Kim, C.W. Kim, C.Y. Kwon, and M.P. Yi, *J. Korean Chem. Soc.*, **29**, 510 (1985).
4. C.S. Kim, R.K. Murmann, and E.O. Schlemper, *Transition Met. Chem.*, **9**, 260 (1984).
5. M.F. Rudolf and A. Wolniak, *Z. anorg. alleg. Chem.*, **408**, 214 (1974).
6. G.R. Cayley, R.S. Taylor, R.K. Wharton, and A.G. Sykes, *Inorg. Chem.*, **16**, 1377 (1977).
7. G.A. Chappelle, A. MacStay, S.T. Pittenger, K. Ohashi, and K.W. Hicks, *Inorg. Chem.*, **23**, 2768 (1984).
8. Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **50**, 1939 (1977).
9. R.K. Wharton, J.F. Ojo, and A.G. Sykes, *J. Chem. Soc. Dalton Trans.*, 1526 (1975).
10. J.P. Birk and S.V. Weaver, *Inorg. Chem.*, **11**, 95 (1972).

Temperature Variation of the Polycrystalline EPR Spectrum of α -1,2,3- $[\text{H}_2\text{PV}(\text{IV})\text{V}_2\text{W}_9\text{O}_{40}]^{5-}$ Doped into $\text{K}_5[\text{H}_2\text{SiV}_3\text{W}_9\text{O}_{40}]$

Chul Wee Lee and Hyunsoo So*

Department of Chemistry, Sogang University, Seoul 121. Received March 15, 1986

Recently we have reported the polycrystalline electron paramagnetic resonance (EPR) spectrum of α -1,2,3- $[\text{H}_2\text{PV}(\text{IV})\text{V}_2\text{W}_9\text{O}_{40}]^{5-}$ doped into $\text{K}_5[\text{H}_2\text{SiV}_3\text{W}_9\text{O}_{40}]$ and its solution spectrum at room temperature.^{1,2} The solution spectrum consists of fifteen lines, indicating that the unpaired electron is hopping fast between the two vanadium ($I = 7/2$) atoms of the OH-V-O-V-OH group. The V-OH-V bridge prevents effectively the electron transfer between the vanadium atoms. The polycrystalline spectrum consists of three sets of fifteen lines and it was analyzed as a spectrum of an $I = 7$ system.

Now we have measured EPR spectra of the polycrystalline sample at low temperatures and found that the behavior of this complex, in which the VO_6 octahedra are corner-shared,³ is quite different from that of $[\text{P}_2\text{V}(\text{IV})\text{VW}_9\text{O}_{40}]^{9-}$ and related complexes in which the VO_6 octahedra are edge-shared.⁴

Three EPR spectra measured at 300, 200, and 100K are shown in Figure 1. The 300K spectrum may be interpreted as consisting of x-, y-, and z-components, each component showing fifteen lines. In fact, only nine outer lines of the z component can be clearly seen; inner lines are overlapped with x-