# A kinetic study of the aqueous phase oxidation of di-$\mu$-oxo-bis(L-cysteine)-oxomolybdenum(V) by molecular oxygen

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## Summary

The molecular oxygen-mediated decomposition of the binuclear complex, prepared from oxomolybdate(V) and L-(+)-cysteine, was studied spectrophotometrically at pH 3.5–5.6. The formation of $\mathrm{Mo^{VI}}$ was detected. The effects of pH and $[O_2]$ on the decomposition kinetics are given by the equation:

$$k_{\mathrm{obs}} = \frac{(0.19 \pm 0.01) + \{(6 \pm 1) \times 10^2 \times [\mathrm{H^+}]\}}{1 + \{(9.4 \pm 0.8) \times 10^4 \times [\mathrm{H^+}]\}} \times [\mathrm{O_2}]$$

with the apparent first order rate constant, $k_{\mathrm{obs}}$, expressed in $\mathrm{s^{-1}}$ and the concentrations in molar units.

## Introduction

Molybdenum-sulfhydryl complexes have received attention as inorganic models for the active site of electron transfer in molybdenum-containing enzymes(1). One of the most widely investigated model compounds has been the binuclear complex di-$\mu$-oxo-bis(L-(+)cysteine)-oxomolybdenum(V), $\mathrm{Na_2[Mo_2O_4(cyst)_2]}$(2-4). Alkaline solutions of this complex disproportionate to molybdenum(VI) and molybdenum(IV). The molybdenum(IV) complexes generated in this way act as two-electron reductants with respect to acetylene and nitrogen(5). However, there is no report on the stability of the complex in acid medium. In this study, we describe the kinetics of decomposition of di-$\mu$-oxo-bis(L-(+)-cysteine)-oxomolybdenum(V) in aqueous solutions (pH 3–6) saturated with different gases at room temperature.

## Experimental

$\mathrm{Na_2Mo_2O_4(cyst)_2.5H_2O}$ was prepared according to the literature procedure(2). All other chemicals (p.a. quality) were used without further purification. Water was distilled through a Millipore system.

Ir. spectra, measured with a Shimadzu IR-435 spectrometer in KBr discs, were coincident with the reported data for the complex(3). The complex was also characterized by X-ray diffraction [Philips PW1710, $\mathrm{K_\alpha}$ Cu ($\lambda$ = 1.54186 Å)]. From literature X-ray data obtained with a single crystal(4) and with the aid of the computer program Lazy Pulverix (1977)(6), good agreement was found between experimental and simulated difractograms for $\theta \leq 55°$. The discrepancy obtained for $\theta > 55°$ can be assigned to the limitations of the computer program.

The pH of solutions of the complex was controlled with NaOAc/AcOH buffer(7) and measured with a pHM82 Standard pH-meter (Radiometer Copenhagen). u.v-vis. measurements in aqueous solutions were carried out with a computer-controlled CARY 3 spectrophotometer.

In some experiments $\mathrm{O_2/N_2}$ mixtures obtained from a home-made gas mixer were bubbled into the solutions. The $O_2$ concentration was calculated using Henry's law and $[\mathrm{O_2}] = 2.65 \times 10^{-4}$ M(8) M as $O_2$ concentration in air-saturated water.

Oxygen consumption was measured *in situ* with a specific oxygen electrode (Orion 97-0899). The conventional tests used for detecting formation of $H_2O_2$ were the chromic acid test, the permanganic test and the iodide test(9).

## Results and discussion

Absorption maxima at 205 ($\varepsilon$ = 19000 $\mathrm{M^{-1}\ cm^{-1}}$) and 306 nm ($\varepsilon$ = 12000 $\mathrm{M^{-1}\ cm^{-1}}$) have been reported for the complex in aqueous solution(2). We calculated the absorption coefficient at 308 nm as $\varepsilon$ = 11900 $\mathrm{M^{-1}\ cm^{-1}}$ for solutions of pH = 5.3, in good agreement with the reported value. Freshly prepared air-saturated solutions show changes in their u.v.-vis. absorption spectra, as shown in Figure 1 for a $5 \times 10^{-5}$ M solution of the complex at pH = 5.3. Kinetic analysis of the absorption changes at 300 nm shows first order behavior (Figure 1, inset), with rate constant $k_{\mathrm{obs}} = 2.3 \times 10^{-5}\ \mathrm{s^{-1}}$.

On one hand, freshly prepared He or $N_2$ saturated solutions do not show changes in their absorption spectra. On the other hand, the changes observed with $O_2$-saturated solutions are qualitatively the same as with air-saturated solutions. In order to quantitatively analyze the oxygen concentration effect on $k_{\mathrm{obs}}$, $\mathrm{O_2/N_2}$ mixtures were bubbled through some of the solutions. Figure 2 shows the dependence of $k_{\mathrm{obs}}$ on $[\mathrm{O_2}]$.

$k_{\mathrm{obs}}$ was obtained for air-saturated solutions of the complex at different pH's. The effect of pH on $k_{\mathrm{obs}}$ is shown in Figure 3.

The dependence of $k_{\mathrm{obs}}$ on the concentration of oxygen and pH is well-fitted by equation (1).

$$k_{\mathrm{obs}} = \{\mathrm{a} + \mathrm{b}[\mathrm{H^+}]\} \cdot [\mathrm{O_2}]/(1 + \mathrm{c}[\mathrm{H^+}]) \qquad (1)$$

with a = (0.19 ± 0.01); b = (6 ± 1); c = $(9.4 \pm 0.8) \times 10^4$ for $k_{\mathrm{obs}}$ expressed in $\mathrm{s^{-1}}$ and the concentrations in molar units.

The shoulder at 230 nm, which appears in oxygen-containing solutions, is coincident with that reported for $\mathrm{MoO_4^{2-}}$ (10), suggesting that molybdenum(V) is oxidized to molybdenum(VI). In alkaline solutions the complex disproportionates into molybdenum(VI) and molybdenum(IV) derivatives(5). The disproportionation of irradiated solutions of $\mathrm{Na_2[Mo_2O_4(cyst)_2]}$ (11) and of other binuclear molybdenum(V) complexes(12-15) was proposed to account for the formation of molybdenum(VI) and $H_2$ as reaction products. However, under our experimental conditions the decomposition of the

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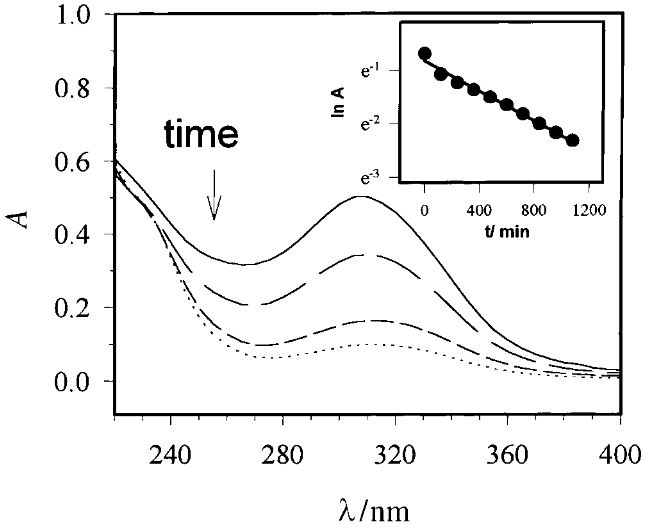

**Figure 1.** Changes in the absorption spectrum of an air-saturated $5 \times 10^{-5}$ M acid (pH = 5.3) solution of the complex at t = 0, 2, 12 and 18 h. Inset: Plot of ln *A versus* time for the air-saturated $5 \times 10^{-5}$ M acid (pH = 5.3) solution of the complex.

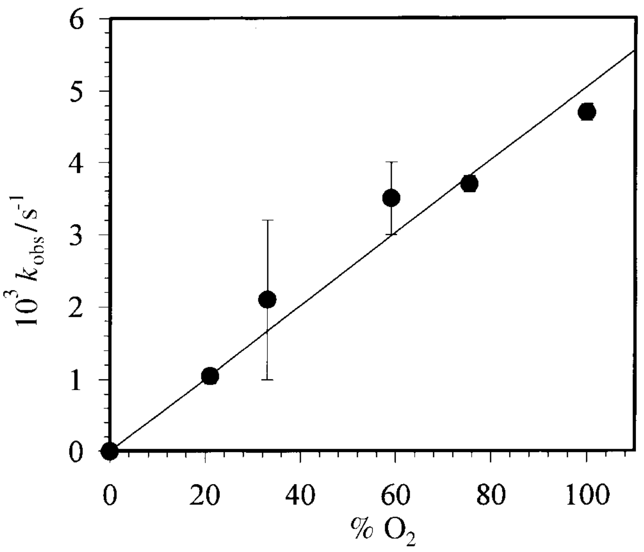

**Figure 2.** Oxygen effect on $k_{obs}$ for an acid (pH = 5.3) a $5 \times 10^{-5}$ M solution of the complex.

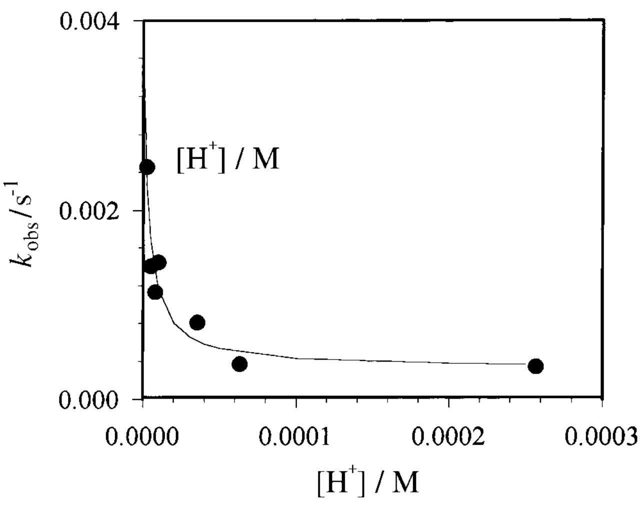

**Figure 3.** pH effect on $k_{obs}$ for an air-saturated $5 \times 10^{-5}$ M solution of the complex.

complex, *i.e.*, the formation of molybdenum(VI) is not observed in the absence of molecular oxygen. Thus, molecular oxygen should be directly involved in the reaction mechanism, as confirmed by the oxygen effect on $k_{obs}$ (*vide supra*). Moreover, measurements with the specific oxygen electrode showed that molecular oxygen is consumed during the reaction. The molar consumption of molecular oxygen after 34 min ($\Delta[O_2] = (3.7 \pm 0.1) \times 10^{-5}$ M) was measured in a closed vessel for a $5 \times 10^{-4}$ M acid (pH = 4) solution of the complex , which was initially air-saturated. $\Delta[O_2]$ was found to be equal, within the experimental error, to the decrease in molar concentration of the complex, as determined from its absorption at 300 nm. In order to determine the reduction product of molecular oxygen, tests for hydrogen peroxide formation were done. The negative results of these tests indicate that $O_2$ is reduced to $H_2O$.

The pH effect on $k_{obs}$ indicates that acid/base equilibria are involved. The mechanism shown in the following scheme considers both the pH and $[O_2]$ dependencies of $k_{obs}$.

$$\begin{array}{lll}
\mathrm{Mo_2O_4(cyst)_2^{-2}} & \xrightarrow{O_2} \longrightarrow \mathrm{Mo^{VI}} & k_1 \\
\mathrm{H^+} \uparrow\downarrow \mathrm{K} & & \\
A' & \xrightarrow{O_2} \longrightarrow \mathrm{Mo^{VI}} & k_2 \\
\mathrm{O_2 + 4H^+} \longrightarrow \mathrm{2H_2O} & &
\end{array}$$

From this mechanism, equation (2) is derived for $k_{obs}$;

$$k_{obs} = \frac{k_2 + \{(k_1/\mathrm{K})[\mathrm{H^+}]\}}{1 + [\mathrm{H^+}]/\mathrm{K}}[\mathrm{O_2}] \tag{2}$$

Comparison of equations (1) and (2) yields $k_1 = 6 \times 10^{-3}$ M$^{-2}$ s$^{-1}$, $k_2 = 0.19$ M$^{-1}$ s$^{-1}$ and K = $1.1 \times 10^{-5}$ (pK = 5.0 ± 0.2). This pK value does not correspond to the deprotonation of the molybdenum(V) moiety (pK = 2)(16-17) and thus, it should be related to ligand deprotonation. The pK value kinetically determined in this work is lower than that corresponding to the sulfhydryl group of free cysteine (pK = 8.33)(7). Although the pK values of $[\mathrm{Mo_2O_4(cyst)_2}]^{2-}$ are not known, the pK of the sulfhydryl group of cysteine is of the order of 6.30 for complexes with divalent transition metals(18). The decrease of the sulfhydryl pK when cysteine is complexed allows us to assume that the equilibrium shown in the Scheme involves the deprotonation of the sulfhydryl group in the $[\mathrm{Mo_2O_4(cyst)_2}]^{2-}$ complex.

We conclude that the two-electron oxidation of $\mathrm{Mo_2O_4(cyst)_2^{-2}}$ by molecular oxygen which takes place in acid aqueous solution can be interpreted by a reaction mechanism involving deprotonation of the sulfhydryl group of the ligand.

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