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- (21) If it is assumed that the proton adds to the carbon atom in reaction 31a, a considerably lower rate of reaction is expected.²² However, in this case it would be difficult to explain the relatively "small" difference between k_{FL}^0 and k_{FL}^{22} and the very large differences in rates for the consecutive ligands.
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- (23) One of the reviewers has pointed out that "reaction 30b might be a two-step process, protonation and dissociation, where the first step may be a fast established equilibrium", and therefore the estimate of K_{30a} might be wrong. The data obtained in this study are insufficient to prove or disprove this hypothesis.

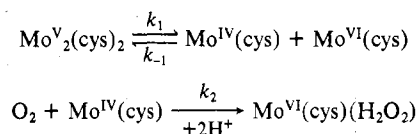
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The Di- μ -oxo-bis[oxo(L-(+)-cysteinato)molybdate(V)](2-)-Dioxygen Reaction

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The reaction of di- μ -oxo-bis[oxo(L-(+)-cysteinato)molybdate(V)](2-), Mo₂O₄(cys)₂²⁻, I \equiv Mo^V₂(cys)₂, with O₂ has been studied in HPO₄²⁻-H₂PO₄⁻ and HN₃-NH₄⁺ buffers. In HPO₄²⁻-H₂PO₄⁻ buffer at pH 6.5, excess O₂ reacted with I according to the mechanism



where at least one phosphate is bound to Mo^V₂(cys)₂. When a steady-state condition is imposed on Mo^{IV}(cys), the rate law becomes $-d[\text{Mo}^{\text{V}}_2(\text{cys})_2]/dt = \{k_2k_1[\text{O}_2][\text{Mo}^{\text{V}}_2(\text{cys})_2]\}/\{k_{-1}[\text{Mo}^{\text{VI}}(\text{cys})] + k_2[\text{O}_2]\}$ and $k_1 = (1.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$, $k_{-1}k_2^{-1} = 0.9 \pm 0.2$ at 25.0 ± 0.2 °C. In excess I, the disappearance of O₂ follows strict first-order kinetics under all conditions. The rate constant k_{obsd} decreases with increasing [O₂] (10^{-6} - 10^{-4} M) and increases with increasing [I], the best linear plot of the data being k_{obsd}^{-1} vs. [I]⁻¹. A mechanism is proposed involving a Mo^V₂(cys)₂-O₂ complex which yields Mo^{VI} and H₂O₂. The resulting H₂O₂ can oxidize Mo^V₂(cys)₂ or be catalytically decomposed. The excess I-O₂ reaction was investigated at pH 9.8 in NH₃-NH₄⁺ buffer. It was found that NH₃ enhances the reactivity of I toward O₂. The rate law is assumed to be rate = $\{k_{\text{OH}^-} + k_{\text{NH}_3}[\text{NH}_3]\}[\text{I}][\text{O}_2]$, where $k_{\text{OH}^-} = 5.5 \pm 0.5 \text{ s}^{-1} \text{ M}^{-1}$ and $k_{\text{NH}_3} = (1.8 \pm 0.4) \times 10^2 \text{ s}^{-1} \text{ M}^{-2}$ at 25.0 ± 0.2 °C and [O₂]_{init} = 4.1×10^{-5} M. It should be noted that k_{obsd} for the reaction is also dependent upon [O₂]_{init}. The enhancement of I-O₂ reaction by the bases phosphate, ammonia, and hydroxide is explained as the addition of these bases to I, which causes a coordination asymmetry, resulting in an asymmetry in oxidation state: IV-VI vs. V-V. Such asymmetric species can be reactive toward dioxygen and possibly dinitrogen.

Introduction

The importance of molybdenum to the activity of a number of oxidation-reduction enzymes has been established for some time.¹ Complexes of molybdenum and L-(+)-cysteine, cys, have long been proposed as models for molybdenum-containing enzymes.^{2,3} The participation of the complex di- μ -oxo-bis[oxo(L-(+)-cysteinato)molybdate(V)](2-), Mo₂O₄(cys)₂²⁻, I \equiv Mo^V₂(cys)₂, in the reduction of dinitrogen and a series of dinitrogen analogues has been demonstrated by Schrauzer and co-workers.⁴ However, a recent study suggests that I is not a good model compound for the molybdenums present in nitrogenase.⁵ Due to the interest in molybdenum chemistry, the oxidation-reduction reactions of complex I warrant investigation in order to determine the reacting species. A study of the kinetics of reactions involving the oxidation of this complex by dioxygen in different media is reported here.

Experimental Section

UV-visible spectral observations were performed on Cary Model 14 and 17 spectrophotometers. Kinetic studies were executed on Cary 14 and 17 spectrophotometers and stopped-flow instruments. The stopped-flow apparatus included a Gibson-Durrum and a Durrum Model D-40 which was fitted to a Beckman UV-visible spectrophotometer. Oxygen concentrations were measured by a Beckman Fieldlab oxygen analyzer, Model 1008, which employs a polarographic oxygen sensor electrode that is sensitive to the oxygen fugacity. A

Beckman Expandomatic pH meter, which was calibrated against standard buffers, was used in all pH measurements. Temperature control for all experiments was achieved through the use of either a Haab constant-temperature circulator, Model F, with Lumo contact thermometers, providing thermoregulation, or a Therimstep temperature controller, Model 71, connected to a heating coil.

Materials. Na₂[Mo₂O₄(SCH₂CHNH₂CO₂)₂]-5H₂O \equiv I. I was synthesized according to literature methods.⁵ Bright orange crystals were recrystallized from ethanol-water mixed solvent (50/50 by volume). C, H, N, and S were determined by Galbraith Laboratories, Inc., Knoxville, Tenn. Molybdenum was determined according to a literature method.⁶ Anal. Calcd: C, 11.4; H, 3.2; N, 4.5; S, 10.1; Mo, 30.5. Found: C, 11.6; H, 3.2; N, 4.5; S, 10.0; Mo, 32.2.

All phosphate salts used for making buffer solutions were obtained from Mallinckrodt Chemical Works and were used without further purification. Aqueous solutions were prepared with distilled water which was further purified by passing through a deionizing system.

Kinetic Method. Dioxygen Reaction of I. Dioxygen reactions were run in 0.5 M phosphate buffer (HPO₄²⁻-H₂PO₄⁻). The pH of such a solution was 6.5 ± 0.1 . All stock solutions of I were prepared by adding an appropriate amount of deaerated buffer solution to a volumetric flask that contained a weighed amount of I (solution I). The flask itself was flushed with purified N₂ or Ar gas. Plastic syringes fitted with Teflon tubing were used to transfer the solution in order to avoid metal contamination. Reactions with excess dioxygen were initiated by injecting 0.2 mL of solution I (ca. 2×10^{-3} M) into 30.0 mL of a dioxygen- or an air-saturated solution contained in a 10-cm quartz cell. The rate of reaction was monitored by following the

Table I. Kinetic Data for the I, HPO_4^{2-} - H_2PO_4^- Reaction^a

[P], ^b M	k_{obsd} , s ⁻¹	[P], ^b M	k_{obsd} , s ⁻¹
0.500	0.53 ± 0.1	0.150	0.13 ± 0.02
0.400	0.37 ± 0.05	0.125	0.06 ± 0.01
0.300	0.26 ± 0.03		

^a [I] = 2.0×10^{-5} M, $t = 25.8 \pm 0.2$ °C, and pH 6.5 ± 0.1 .

^b [P] = $[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-]$.

disappearance of the 305-nm peak. Reactions in which Mo(VI) and cysteine were present were initiated by adding 0.2 mL of solution I to an air- or oxygen-saturated solution that contained these two species. The molybdenum(VI)-cysteine solution was freshly prepared and used within 2 h. The rate constant for the molybdenum(VI)-cysteine reaction to give Mo(V) and cystine, which may have an inhibitory effect, is small, and our experiments show no reduction of Mo(VI) by cysteine in the time period the solution was used.

Reactions with I in excess over dioxygen were initiated by injecting 7.5 mL of solution I ($\sim 10^{-3}$ M) into a 15.5-mL reaction flask containing 8 mL of an air-saturated solution. The reaction flask was equipped with a Beckman Fieldlab oxygen analyzer. The rate of reaction was monitored by following the change of dioxygen concentration in the solution. Dioxygen concentrations were altered by mixing different volumes of an air-saturated solution and deaerated buffer solution.

Reaction with I in excess over dioxygen in the presence of NH_3 were initiated by adding appropriate amounts of $\text{NH}_3(\text{aq})$, NH_4Cl , and NaCl in solution and H_2O to 4 mL of I to bring the final volume to 13 mL. The pH of the solution was 9.75, buffered by NH_3 - NH_4^+ that was present in the solution. The solution was left to equilibrate at 25 °C for 5 min. Three milliliters of an air- or O_2 -saturated solution was injected into the reaction flask (16.0 mL) to initiate the reaction. The rate of reaction was monitored as previously described.

Results

The rate of the I- O_2 reaction is strongly dependent on the supporting electrolyte and solvent. In water around neutral pH values the reaction proceeds at an appreciable rate in the presence of phosphate but not in the presence of chloride, sulfate, or perchlorate or in the absence of a supporting electrolyte. In a more basic medium a path involving hydroxide ion appears, and ammonia accelerates the reaction. In propylene carbonate, a polar but poor coordinating solvent, no reaction is observed. Studies of the I- O_2 reaction were undertaken in HPO_4^{2-} - H_2PO_4^- buffer at pH 6.5 because of the proximity of the pH to biological pH's and the requirement for phosphate (as ATP) in the process of nitrogen fixation and in a more basic medium at pH 9.8 using NH_3 - NH_4^+ buffer because of the involvement of I in the reduction of N_2 to NH_3 .

O_2 -I Reaction in HPO_4^{2-} - H_2PO_4^- Buffer at pH 6.5. In the absence of dioxygen, complex I dissolves in phosphate buffer yielding a spectrum having a maximum at 305 nm.⁷ The observed extinction coefficient at λ 305 nm, ϵ_{305} , decreases with increasing buffer concentration. At [I] = 2.0×10^{-5} M, the following results are typical. Total phosphate concentration, [P] (M), ϵ_{305} ($\text{M}^{-1} \text{cm}^{-1}$): 0, 1.4×10^4 ; 0.025, 1.1×10^4 ; 0.500, 5.9×10^3 . Stopped-flow experiments monitored at 305 nm show that when excess HPO_4^{2-} - H_2PO_4^- buffer was mixed with I at the same pH, a reaction occurred which conformed to the rate law rate = $k[\text{I}][\text{P}]$. Typical data at 25.8 ± 0.2 °C are listed in Table I. The data showed no effect of ionic strength. If we assume that $k_{\text{obsd}} = k[\text{P}]$, the average k is 1.06 ± 0.03 s⁻¹ M⁻¹. The rate law is consistent with a mechanism involving addition of at least one molecule of a phosphate species to one molecule of I. This species, I with at least one phosphate bound, is an important reactive species toward O_2 .

When I was dissolved in phosphate buffer and dioxygen passed through the solution, the absorption at the 305-nm maximum decreased and the maximum shifted to 310 nm, ϵ_{301} $1400 \text{ M}^{-1} \text{cm}^{-1}$. The spectral properties of an O_2 -oxidized solution of I in an unknown buffer and at an unknown pH have been reported to be λ_{max} 316 nm, ϵ_{316} $5000 \text{ M}^{-1} \text{cm}^{-1}$.⁷ The

Table II. Kinetic Data for the I-Excess O_2 Reaction^a

run	10^5 [I], M	10^4 [O_2], M	$\frac{10^4 \times [\text{Mo}^{\text{VI}}]}{[\text{cys}]}$, ^b M	$10^3 k_{\text{obsd}}$, s ⁻¹
1	1.5	2.2		1.32 ± 0.08
2	0.81	9.9		2.15 ± 0.08
3	1.42	9.9		2.03 ± 0.08
4	1.5	9.9		2.03 ± 0.08
5	1.5	2.2	0.765	1.18 ± 0.02
6	1.5	2.2	0.97	1.03 ± 0.02
7	1.5	2.2	1.31	1.03 ± 0.02
8	1.5	2.2	1.44	1.02 ± 0.02
9	1.5	2.2	2.32	0.63 ± 0.03
10	1.5	2.2	2.90	0.70 ± 0.03
11	1.5	2.2	3.04	0.82 ± 0.03
12	1.5	2.2	4.96	0.58 ± 0.02
13	1.5	2.2	9.85	0.32 ± 0.05
14	1.5	9.9	0.762	1.83 ± 0.08
15	1.5	9.9	0.997	1.50 ± 0.02
16	1.5	9.9	1.00	1.61 ± 0.03
17	1.5	9.9	1.33	1.68 ± 0.02
18	1.5	9.9	2.3	1.21 ± 0.02
19	1.5	9.9	2.98	1.02 ± 0.02
20	1.5	9.9	9.88	0.87 ± 0.02
21	1.62	9.9	2.06	1.13 ± 0.08
22	3.22	9.9	2.56	1.03 ± 0.08

^a $t = 25.0 \pm 0.2$ °C, pH 6.5 ± 0.1 , and $[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] = 0.5$ M. ^b 1:1 molybdenum(VI)-cysteine.

spectrum of the product was independent of how much excess O_2 was used. When H_2O_2 is used as the oxidizing agent, the spectrum of the product is the same as that obtained in the O_2 reaction. The same product spectrum can be produced by adding H_2O_2 to a molybdenum(VI)-cysteine solution (10^{-3} M) which contains phosphate buffer. If H_2O_2 is added to a solution containing only Mo(VI) or cysteine, no new species is formed. These experiments suggest that the product of the I-excess O_2 reaction is a $\text{Mo}^{\text{VI}}(\text{cys})(\text{H}_2\text{O}_2)$ species.

The H_2O_2 formed can react with I, and our experiments show that H_2O_2 reacts at least 20 times faster than O_2 with I. However, in the case where the [I] is small, viz., the I-excess O_2 reaction, the I- H_2O_2 reaction is not important. The possibility of the oxidation of cysteine to cystine was excluded because no cystine was isolated.

The I-Excess O_2 Reaction. Table II presents data for the first-order disappearance of [I], as represented by the absorbance at 305 nm in excess $[\text{O}_2]$. The observed rate constant, k_{obsd} , increases with increasing $[\text{O}_2]$ and at a constant dioxygen concentration is independent of [I] (runs 2, 3, 21, and 22). The rate constant is decreased by the addition of Mo(VI), 1:1 molybdenum(VI)-cysteine, but not cysteine itself. One-to-one molybdenum(VI)-cysteine is more effective than Mo(VI) alone in inhibiting the reaction. Spence and Chang reported,⁸ for a solution that contains equivalent amounts of Mo(VI) and cysteine, various species can form. When the concentration is below 5×10^{-3} M, a 1:1 complex is the major species. The results (runs 5-20) show a decreasing k_{obsd} with increasing 1:1 molybdenum(VI)-cysteine and indicate a path involving the disproportionation of I into a Mo(IV) species and a 1:1 molybdenum(VI)-cysteine species. Plots of absorption at 350 nm/cell length vs. [I] are not linear (λ 350 nm is used in order to include a wider range of concentrations) and indicate a dissociation or disproportionation process involving $\text{Mo}^{\text{V}}_2(\text{cys})_2$. The presence of a 1:1 molybdenum(VI)-cysteine species as a product of a disproportionation was tested by diluting 0.2 mL of a solution containing 2.0×10^{-3} M I and $(4-6) \times 10^{-3}$ M Mo(VI) and cysteine, individually or combined, to 30 mL in deaerated buffer and observing whether a change in absorption other than that due to dilution occurred. In every case except 1:1 molybdenum(VI)-cysteine, dilutions resulted in a rapid, small decrease in the absorption at 305 nm in

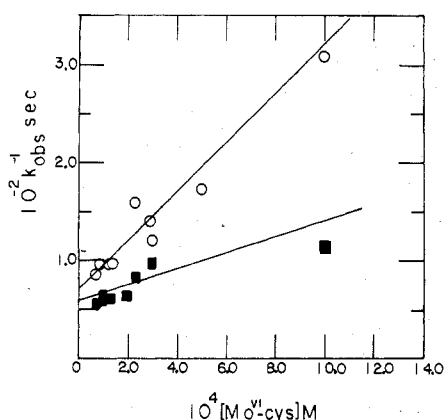
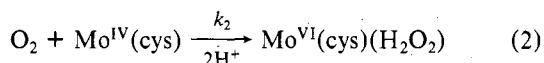
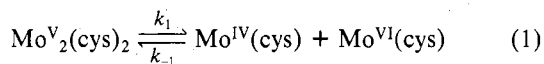


Figure 1. Plot of k_{obs}^{-1} vs. $[\text{Mo}^{\text{VI}}(\text{cys})]$ for the excess O₂-I reaction: $[\text{O}_2] = 2.2 \times 10^{-4}$ M (O) and 9.9×10^{-4} M (■) at 25.0 ± 0.2 °C and pH 6.5.

addition to that resulting from dilution.

On the basis of this observation and the data for the dioxygen reaction, the mechanism of eq 1 and 2 is proposed,



where $\text{Mo}^{\text{V}}_2(\text{cys})_2$ has at least one bound phosphate. In step 1 it is not known whether phosphate is bound to $\text{Mo}^{\text{IV}}(\text{cys})$, $\text{Mo}^{\text{VI}}(\text{cys})$, or both.

$\text{Mo}^{\text{IV}}(\text{cys})$ can be oxidized by O₂ through a two-electron oxidation or by a series of one-electron oxidations to a $\text{Mo}^{\text{VI}}(\text{cys})(\text{H}_2\text{O}_2)$ species. When a steady-state condition is imposed on the $\text{Mo}^{\text{IV}}(\text{cys})$ species, the rate law becomes

$$-\frac{d[\text{Mo}_2(\text{cys})_2]}{dt} = \frac{k_2 k_1 [\text{O}_2] [\text{Mo}_2(\text{cys})_2]}{k_{-1} [\text{Mo}^{\text{VI}}(\text{cys})] + k_2 [\text{O}_2]} = k_{\text{obs}} [\text{Mo}_2(\text{cys})_2]$$

the expression for k_{obs} can be rearranged to

$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1}}{k_2 k_1 [\text{O}_2]} [\text{Mo}^{\text{VI}}(\text{cys})] + \frac{1}{k_1}$$

The relation of k_{obs} to the molybdenum(VI)-cysteine and dioxygen concentrations is shown in Figure 1. From the intercept one can calculate k_1 to be $(1.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ and from the slope combined with k_1 , $k_{-1} k_2^{-1}$ is 0.9 ± 0.2 at 25.0 °C. Other mechanisms are possible such as one in which $\text{Mo}^{\text{VI}}(\text{cys})$ forms a complex with $\text{Mo}^{\text{V}}_2(\text{cys})_2$ reducing the former's reactivity toward O₂.

The Excess I-O₂ Reaction. The consumption of dioxygen under conditions of excess I was investigated. In this study, experimental conditions for the reaction were 0.5 M total phosphate buffer, pH 6.5 ± 0.1 , and $t = 25.0 \pm 0.2$ °C, and $[\text{I}]$ was in at least 10-fold excess over $[\text{O}_2]$. The disappearance of O₂ follows strict first-order kinetics and its consumption is represented by the rate constant k_{obs} . The data in Table III summarize the dependence of k_{obs} upon $[\text{I}]$. The rate of reaction is unaffected by the addition of 1:1 molybdenum(VI)-cysteine. In a typical experiment the concentration of molybdenum(VI)-cysteine was 7.1×10^{-4} M, $[\text{I}] = 7.9 \times 10^{-3}$ M, and $[\text{O}_2] = 5.1 \times 10^{-4}$ M.

Figure 2 is a plot of k_{obs}^{-1} vs. $[\text{I}]^{-1}$ at $[\text{O}_2] = 1.14 \times 10^{-4}$ M (runs 1-8). The slope of this linear plot is $2.26 \pm 0.03 \text{ s}$, and the intercept is $(1.8 \pm 0.3) \times 10^2 \text{ s}$. $[\text{I}]$ was maintained constant at 8.2×10^{-3} M, and the initial $[\text{O}_2]$, $[\text{O}_2]_{\text{init}}$, was varied from 10^{-6} to 10^{-4} M. The dependence of k_{obs} upon $[\text{O}_2]_{\text{init}}$ is summarized by runs 9-17 in Table III. Notice that

Table III. Kinetic Data on the Excess I-O₂ Reaction^a

run	$10^3 [\text{I}], \text{M}$	$10^4 [\text{O}_2], \text{M}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$
1	1.30	1.14	0.52 ± 0.05
2	2.13	1.14	0.85 ± 0.02
3	2.40	1.14	0.85 ± 0.10
4	3.05	1.14	1.08 ± 0.1
5	4.14	1.14	1.50 ± 0.03
6	6.15	1.14	2.0 ± 0.2
7	8.25	1.14	2.0 ± 0.2
8	12.7	1.14	2.52 ± 0.02
9	8.2	0.071	7.3 ± 0.2
10	8.2	0.142	4.8 ± 0.3
11	8.2	0.284	4.7 ± 0.2
12	8.2	0.422	3.3 ± 0.5
13	8.2	0.517	3.3 ± 0.5
14	8.2	1.14	2.1 ± 0.1
15	8.2	1.88	1.2 ± 0.1
16	8.2	2.55	1.4 ± 0.1
17	8.2	5.10	1.4 ± 0.3

^a $[\text{I}] = 8.2 \times 10^{-3}$ M, $t = 25.0 \pm 0.2$ °C, pH 6.5 ± 0.1 , and $[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] = 0.5$ M.

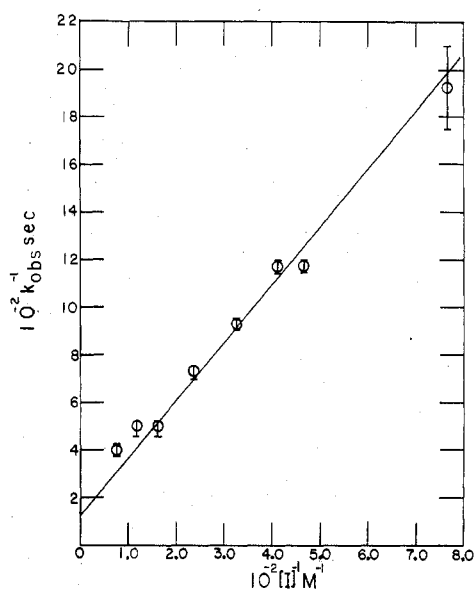
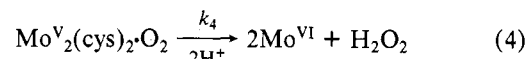
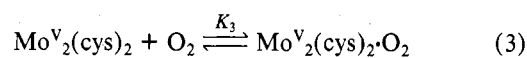


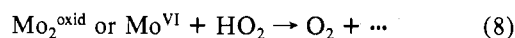
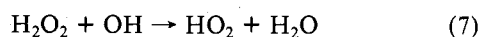
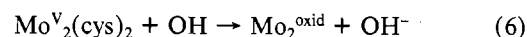
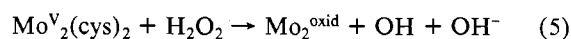
Figure 2. Plot of k_{obs}^{-1} vs. $[\text{I}]^{-1}$ for the excess I-O₂ reaction at 25.0 ± 0.2 °C with $[\text{O}_2]_{\text{init}} = 1.14 \times 10^{-4}$ M and pH 6.5.

as the concentration of dioxygen increases, k_{obs} decreases. At large $[\text{O}_2]_{\text{init}}$, k_{obs} is about $1.4 \times 10^{-3} \text{ s}^{-1}$. The disappearance of dioxygen with respect to time still follows first-order kinetics.

The data are consistent with a mechanism in which $\text{Mo}^{\text{V}}_2(\text{cys})_2$ reacts reversibly with dioxygen to give a dioxygen adduct:



followed by



Dioxygen, O₂, is rapidly produced when excess $\text{Mo}^{\text{V}}_2(\text{cys})_2$ reacts with H₂O₂: $[\text{Mo}^{\text{V}}_2(\text{cys})_2] = 8 \times 10^{-3}$ M, $[\text{H}_2\text{O}_2]_{\text{init}} = 2.2 \times 10^{-4}$ M, $[\text{O}_2]$ generated $\approx 1.1 \times 10^{-5}$ M. No cystine was formed in this process. It should be noted that the

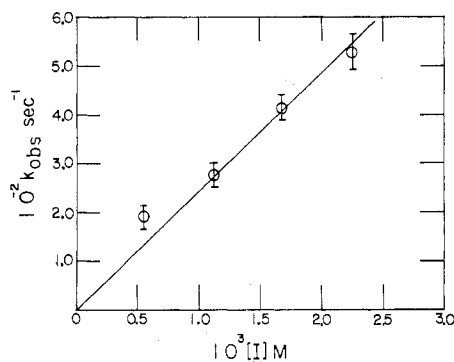


Figure 3. Plot of k_{obsd} vs. $[I]$ for the excess I- O_2 reaction at 25.0 ± 0.2 °C with $[O_2]_{\text{init}} = 4.1 \times 10^{-5}$ M and pH 9.75.

proposed mechanism is speculative but consistent with the rate law.

When (4) is considered rate determining and a steady-state condition is applied to H_2O_2 , HO_2 , and OH , rate law 9 results,

$$-\frac{d[O_2]}{dt} = \frac{k_4 K_3 [Mo^V_2(cys)_2] [O_2]}{1 + K_3 [Mo^V_2(cys)_2]} \left(1 - \frac{k_7 [H_2O_2]}{k_6 [Mo^V_2(cys)_2] + 2k_7 [H_2O_2]} \right) \quad (9)$$

which indicates that, at constant $[Mo^V_2(cys)_2]$, as $[H_2O_2]$ increases, the observed rate constant decreases. A complex relationship exists between $[H_2O_2]$ and $[O_2]$ at any time, and the increase in k_{obsd} with decreasing $[O_2]_{\text{init}}$ may reflect indirectly this relationship or the fact that a small amount of a Mo(V) species is initially present that reacts directly with O_2 generating an intermediate in an amount proportional to $[O_2]_{\text{init}}$. When the slope and intercept from Figure 2 and the rate law when it is independent of $[H_2O_2]$ or $[O_2]_{\text{init}}$ are used, $K_3 = 80 \pm 10$ M $^{-1}$ and $k_4 = (6 \pm 1) \times 10^{-3}$ s $^{-1}$ at 25 °C.

The Excess I- O_2 Reaction in $NH_3-NH_4^+$ Buffer at pH 9.8.

The reaction between excess I and O_2 was investigated at pH 9.8 in $NH_3-NH_4^+$ buffer. The disappearance of O_2 is first order with a rate constant k_{obsd} . Figure 3 represents k_{obsd} vs. $[I]$ and shows that k_{obsd} is first order in $[I]$. As was the case with the I- O_2 reaction in $HPO_4^{2-}-H_2PO_4^-$ at pH 6.5, k_{obsd} increases with decreasing $[O_2]_{\text{init}}$. Typical rate constants at $[I] = 2.2 \times 10^{-3}$ M and $[NH_3] = 0.1$ M are as follows. k_{obsd} (s $^{-1}$), $[O_2]_{\text{init}}$ (M): 0.032 ± 0.004 , 18.6×10^{-5} ; 0.051 ± 0.003 , 4.1×10^{-5} ; 0.077 ± 0.004 , 2.7×10^{-5} .

The effect of NH_3 and OH^- on the reaction was investigated. Figure 4 is a plot of k_{obsd} vs. $[NH_3]$, where $[NH_3] = [NH_4^+]$ (pH 9.8). Sodium chloride was added to the buffer to maintain constant ionic strength and did not affect the rate constant for the reaction. The reactions were performed by allowing the buffer to equilibrate with I for 5 min before the introduction of O_2 . If this procedure was not employed, the disappearance of O_2 was not first order. Subsequently it was found that $NH_3-NH_4^+$ interacts with I and that the spectral change accompanying this interaction is accomplished in less than 5 min: presumably this reaction involves an equilibration of NH_3 and OH^- (vide infra) with I. The extrapolation of $[NH_3] \rightarrow 0$ in Figure 4 yields an intercept k_{OH^-} which coincides within experimental error with the rate constant determined for the first-order disappearance of O_2 in the I- O_2 reaction at the same $[I]$ and at pH 9.8 in the absence of $NH_3-NH_4^+$. In the latter case the pH was adjusted with H^+ and OH^- . The path was investigated between pH 9.3 and 11.1 in order to establish k_{OH^-} at pH 9.8. It is clear at pH 6.5 that k_{OH^-} does not contribute appreciably to the rate. The value of k_{obsd} is first order in $[NH_3]$ suggesting the addition of at least one NH_3 to I in the reaction forming $NH_3Mo_2(cys)_2$. If

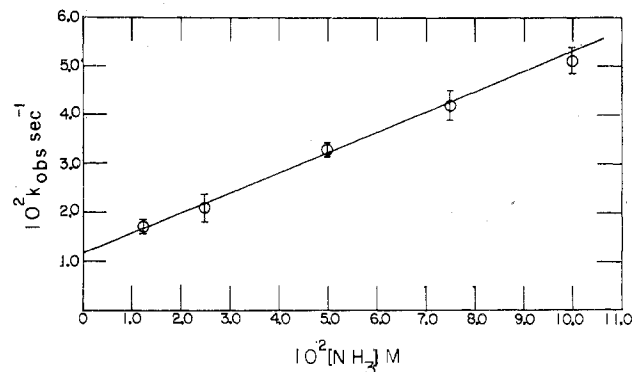
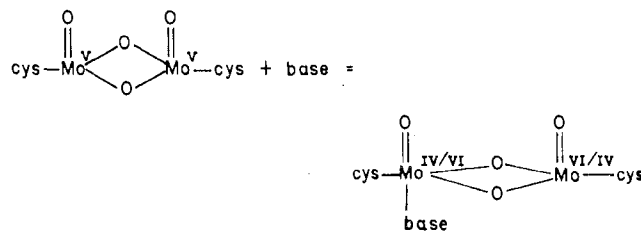


Figure 4. Plot of k_{obsd} vs. $[NH_3]$ for the excess I- O_2 reaction at 25.0 ± 0.2 °C with $[O_2]_{\text{init}} = 4.1 \times 10^{-5}$ M, $[I] = 2.2 \times 10^{-3}$ M, and pH 9.75.

$[O_2] = 4.1 \times 10^{-5}$ M and the rate law is assumed to be $-d[O_2]/dt = k_{\text{obsd}}[O_2] = (k_{OH^-} + k_{NH_3}[NH_3])[I][O_2]$, the $k_{OH^-} = 5.5 \pm 0.5$ s $^{-1}$ M $^{-1}$ and $k_{NH_3} = (1.8 \pm 0.4) \times 10^2$ s $^{-1}$ M $^{-2}$ (25.0 ± 0.1 °C, pH 9.8). It should be recalled that these rate constants are defined at a specific $[O_2]_{\text{init}}$. It is likely that the reason for the increasing value of k_{obsd} with decreasing $[O_2]_{\text{init}}$ in the $NH_3-NH_4^+$ case is the same as that for the $HPO_4^{2-}-H_2PO_4^-$ case.

Discussion

It is clear that I is unreactive toward O_2 unless activated by the introduction of at least one, but possibly more than one, base. From this study the bases that complex and activate I are found to be phosphate, ammonia, and hydroxide but not chloride, sulfate, or perchlorate. Ott and Schultz⁹ have proposed complexation of buffers with I to account for the effect of buffers on the electrochemical reduction of I. The unreactive character of I unless coordinated by an external base is consistent with Kroneck and Spence's study on the reaction of I with flavin mononucleotide.¹⁰ The question is how does the base enhance the reactivity of I toward dioxygen. It seems reasonable that the addition of a base to I creates a coordination asymmetry in the complex which can result in an asymmetry in oxidation states: IV-VI vs. V-V:



This asymmetry can enhance the reactivity of I or facilitate its disproportionation to a more reactive species.

Under experimental conditions where the concentration of I is low the base-coordinated dimer species dissociates and disproportionates (reaction 1). The formation of a monomeric Mo(IV) species is not only important in the dioxygen reaction but also in the reaction of I with acetylene,¹¹ and molybdenum(IV)-cysteine has been proposed as a reactive species toward various substrates.⁴ The value of k_1 is of considerable interest. Guymon and Spence¹² reported a disproportionation rate constant for the $Mo^V_2(aq)$ species to give $Mo^{IV}(aq)$ and $Mo^{VI}(aq)$ species of 1.8×10^{-3} s $^{-1}$ at 20 °C and pH 6.5, which is amazingly close to the value of k_1 reported here, 1.5×10^{-3} s $^{-1}$.

It is also found that I can catalyze the decomposition of H_2O_2 . It is likely that this process is important in the I- O_2 reactions, where it is found in excess $Mo^V_2(cys)_2-O_2$ reactions such a decomposition offers one possible explanation of the variation of k_{obsd} with $[O_2]_{\text{init}}$. Several attempts have been

made to search for the existence of the dioxygen adduct proposed. No convincing evidence besides the reported kinetic data have yet been found, but it should be pointed out that dioxygen-molybdenum complexes are known to exist.¹³

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Registry No. I, 25604-33-5; O_2 , 7782-44-7.

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Kinetics of Oxidation of Hydrazinium Ion by Hexachloroiridate(IV)

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Kinetics of the oxidation of hydrazinium ion by hexachloroiridate(IV) have been studied spectrophotometrically in perchloric acid medium in the temperature range 30–45 °C. The reaction is first order with respect to iridium(IV) whereas the order with respect to hydrazinium ion is less than 1. Hydrogen ion decreases the rate of oxidation. The additions of salts have accelerating effects on the rate of reaction. The rate also increases with decreasing dielectric constant. The reaction is not retarded by the hexachloroiridate(III) ions produced in the reaction. The empirical rate equation is $-d[\text{IrCl}_6^{2-}]/dt = kK[\text{IrCl}_6^{2-}][\text{N}_2\text{H}_5^+]/([\text{H}^+] + K[\text{N}_2\text{H}_5^+])$. E_a and ΔS^\ddagger were found to be 96.8 kJ mol⁻¹ and -1.2 J K⁻¹, respectively. ΔH and ΔS° associated with K were found to be -69 kJ mol⁻¹ and -205 J K⁻¹, respectively.

Introduction

Hydrazinium ion is known to be a very powerful reducing agent.¹ The thermodynamic reducing strength of hydrazine is dependent on the nitrogen species to which hydrazine is oxidized. Hydrazine is quantitatively oxidized to nitrogen gas by 2-equiv oxidants^{2,3} whereas 1-equiv oxidation of hydrazine is approached⁴⁻⁶ when Mn^{III} , Fe^{III} , and Co^{III} are used as oxidants. However, the kinetics of the oxidation of hydrazinium ion by Ir(IV) has not been reported although the kinetics of the oxidation of cyclohexanone⁷ and some substituted phenols⁸ and quinols⁹ by Ir(IV) has been studied. The kinetics of oxidation of hydrazinium ion by PtCl_6^{2-} has been studied¹⁰ in the acid medium. The reaction has been shown to proceed through the formation of intermediate platinum(III) followed by the reaction of platinum(III) with another hydrazinium ion to give products of reaction. The present reaction was undertaken in view of the interesting results obtained with PtCl_6^{2-} . The oxidation of hydrazinium ion by IrCl_6^{2-} was carried out under various experimental conditions with a view to suggesting a possible reaction mechanism.

Experimental Section

Reagents. All inorganic materials were of AnalaR (BDH) grades. Hydrazine solution was standardized under the usual Andrews conditions¹¹ by using potassium iodate as mentioned in an earlier communication.¹⁰ Sodium hexachloroiridate, $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (Johnson-Mathey), was used to prepare solutions of iridium(IV), and such solutions in perchloric acid (0.1–1.0 M) were stable over periods of 24 h.^{12b} These were stored in the dark and used under subdued lighting conditions generally within 5–6 h of preparation. Standardization of hexachloroiridate(IV) solutions was effected spectrophotometrically at 488 nm (ϵ 4050 M⁻¹ cm⁻¹). Sodium perchlorate was prepared by the neutralization of perchloric acid with sodium hydroxide. All solutions were made in doubly distilled water. We purified the dioxane by distilling twice with metallic sodium, each time collecting the middle fraction.

Absorption Spectra. The absorption spectra of iridium(IV) solutions (in 0.1 M perchloric acid) in the concentration range (0.283–2.41) $\times 10^{-4}$ M were recorded in the visible region. The spectral pattern remained unaltered with changes in concentration of iridium(IV). An absorption maximum at 488 nm and a minimum at 460 nm were in good agreement with literature values.¹³ Beer's law has been found to be valid in this concentration range. The spectra of 1.0×10^{-4} M iridium(IV) were also recorded at different concentrations (viz., 0.04–2.24 M) of perchloric acid but without any change in the absorption maximum and minimum. It may be mentioned that the spectral pattern as well as λ_{max} of $\text{Ir}(\text{OH}_2)\text{Cl}_5^-$ is different from that of IrCl_6^{2-} indicating that IrCl_6^{2-} and not $\text{Ir}(\text{OH}_2)\text{Cl}_5^-$ acts as the oxidizing species. The IrCl_6^{3-} ion and its hydrolyzed product $\text{Ir}(\text{OH}_2)\text{Cl}_5^{2-}$ ion are transparent in the region of maximum absorption of IrCl_6^{2-} as indicated by Poulson and Garner.^{12a}

Kinetic Measurements. The reactions were studied under pseudo-first-order conditions, i.e., in the presence of a large excess of hydrazinium ion. Kinetic runs were performed at constant concentrations of iridium(IV), N_2H_5^+ , and HClO_4 at 1.04×10^{-4} , 8.0×10^{-3} , and 1.0×10^{-1} M, respectively, and measurements were carried out at 35 °C unless otherwise mentioned. The rate of the reaction was followed from the decrease in iridium(IV) concentration, the latter being reflected in the measurements of absorbance at 488 nm. The reactions were studied in the thermostated cell compartment of a Beckman DU spectrophotometer. Iridium(III) at that low concentration of 1.0×10^{-4} M and other products of the reaction were transparent at this wavelength. The cell compartment of the spectrophotometer was kept at constant temperature by circulating water from the thermostat into the surrounding water jackets. The reaction mixtures containing the oxidant in perchloric acid (and salt or solvent, if any) in one vessel and hydrazinium ion in the other vessel were separately equilibrated to bath temperature, mixed externally, and immediately transferred into a cell of path length 1 cm. The rate of decrease of iridium(IV) was followed for 50–80% conversion of the initial iridium(IV) concentration depending upon the concentration of hydrazinium ion and on the temperature. Generally, 6–8 readings were noted for each set with change in time, and pseudo-first-order rate constants (k_{obsd}) were obtained graphically from $\log A$ ($A =$