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Kinetics of the Disproportionation of Complexes of Di-μ-oxo-bis[oxomolybdate(V)] in the Presence of Cyanide Ion

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Complexes of $[Mo_2O_4]^{2+}$ – $[Mo_2O_4(EDTA)]^{2-}$, $[Mo_2O_4(CYS)_2]^{2-}$, $[Mo_2O_4(HIS)_2]$, $[Mo_2O_4(CIT)_2]^{4-}$ *and* $[Mo_2O_4(HP_3O_{10})_2]^{6-}$ – *react with* CN^- *in aqueous solution to produce molybdate and* $[Mo(O)(OH)(CN)_4]^{3-}$. *The rate law for these reactions is rate* = $k[Mo_2O_4^{2+}\text{-complex}][OH^-]$, *where* $k = 0.020$ M^{-1} s^{-1} *for the EDTA complex,* 77 M^{-1} s^{-1} *for the cysteine (CYS) complex, and about 150* M^{-1} s^{-1} *for the other complexes at 25 °C. A mechanism for these reactions is proposed which is consistent with the observed rate law and the known chemistry of Mo(V) in solution.*

Introduction

Acetylene is reduced non-catalytically to ethylene, 1,3-butadiene, and other hydrocarbons in aqueous alkali by dioxotetracyanomolybdate(IV), $[Mo(O)_2(CN)_4]^{4-}$, and by several complexes of di-μ-oxo-bis[oxomolybdate(V)], $[Mo_2O_4]^{2+}$ [1, 2]. The rate of acetylene reduction in all of these systems is dependent on the concentration of hydroxide ion in solution. In the presence of cyanide ion, hydroxide causes the disproportionation of $[Mo_2O_4]^{2+}$ complexes into molybdate, $[MoO_4]^{2-}$, and $[Mo(O)_2(CN)_4]^{4-}$. Because of its possible relationship to the mechanism of acetylene reduction by Mo(V) complexes, we decided to examine the kinetics of the OH^- induced disproportionations of $[Mo_2O_4]^{2+}$ complexes in the presence of cyanide.

Experimental

Preparation of Aquated Di-μ-oxo-bis[oxomolybdate(V)] Ion, $[Mo_2O_4]^{2+}$

Aquated $[Mo_2O_4]^{2+}$ was prepared by the reduction of 0.5*M* solutions of sodium molybdate with metallic mercury in 3*M* HCl under an atmosphere of $N_{2(g)}$ [3]. Aliquots were removed and filtered for use in some of the preparations which are described below.

Preparation of Sodium μ-(Ethylenediaminetetraaceto)-di-μ-oxobis[oxomolybdate(V)] Trihydrate, $Na_2[Mo_2O_4(EDTA)]\cdot 3H_2O$

The procedure described by Pecsok and Sawyer [4] was used to prepare this salt. Recrystallization was performed twice by dissolution of the compound in water, followed by precipitation with 95% ethanol at 0 °C. The purified solid was washed with diethyl ether and dried under vacuum for 24 hours at 25 °C. *Anal.* Calcd. for $Na_2[Mo_2O_4(C_{10}H_{12}N_2O_8)]\cdot 3H_2O$: Mo, 29.8; C, 18.63; H, 2.80; N, 4.35. Found [5]: Mo, 29.5; C, 17.95; H, 2.77; N, 4.56. The infrared spectrum of this salt agreed with that reported previously [6].

Preparation of Sodium Di-μ-oxo-bis[(L-cysteinato)-oxomolybdate(V)] Hexahydrate, $Na_2[Mo_2O_4(CYS)_2]\cdot 6H_2O$

The procedure described by Kay and Mitchell [7] was used to prepare this complex. *Anal.* Calcd. for $Na_2[Mo_2O_4(C_3H_5NO_2S)_2]\cdot 6H_2O$: Mo, 30.5; C, 11.43; H, 3.49; N, 4.44; S, 10.2. Found: Mo, 31.5; C, 11.72; H, 3.20; N, 4.40; S, 9.8. The infrared spectrum of this salt agreed with that reported previously [6].

Preparation of Di-μ-oxo-bis[(L-histidinato)oxomolybdate(V)] Dihydrate, $[Mo_2O_4(HIS)_2]\cdot 2H_2O$

The method of Melby [8] was used to prepare the histidine complex. This insoluble compound was purified by heating a suspension of it in distilled water at 50 °C for one hour. The mixture was filtered while still hot, and the solid was washed with acetone. The product was then dried under vacuum for 24 hours at 25 °C. *Anal.* Calcd. for $[Mo_2O_4(C_6H_9N_3O_2)_2]\cdot 2H_2O$: Mo, 31.9; C, 23.93; H, 3.68; N, 13.69. Found: Mo, 31.9; C, 23.99; H, 3.52; N, 13.55.

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Preparation of a Bis-Citrato Complex of $[Mo_2O_4]^{2+}$

We found no previous mention of the isolation of a bis-citrato complex of $[Mo_2O_4]^{2+}$, which we prepared in the following manner: A 100 ml aliquot of aquated $[Mo_2O_4]^{2+}$ was filtered under nitrogen and treated with a three-fold molar excess (15g) of solid citric acid. Aqueous sodium hydroxide (3*M*) was added to bring the pH of the solution to about 5. Methanol was added to remove the product from solution as an oil, which was treated with additional methanol to yield a brown powder. The solid was recrystallized twice from water and methanol, washed with diethyl ether, and vacuum-dried. *Anal.* Calcd. for $Na_4[Mo_2O_4(C_6H_5O_7)_2]\cdot 5H_2O$: Mo, 23.5; C, 17.66; H, 2.47. Found: Mo, 23.4; C, 18.48; H, 2.38. A spectrum of this complex in solution showed an intense charge-transfer band in the ultraviolet, upon which is superimposed a band at 33,900 cm^{-1} (ϵ = 5500). This closely resembles the spectra of $[Mo_2O_4]^{2+}$ complexes of the type represented in Figure 2A [6], and we propose a similar structure for this compound.

Preparation of Sodium Di-μ-oxo-bis[(monohydrogentriphosphato)oxomolybdate(V)] Hexahydrate, $Na_6[Mo_2O_4(HP_3O_{10})_2]\cdot 6H_2O$

The preparation of the triphosphate complex has been reported recently by So, *et al.* [9]. It is analogous to the procedures which are described above for the citrate complex. *Anal.* Calcd. for $Na_6[Mo_2O_4(HP_3O_{10})_2]\cdot 6H_2O$: Na, 13.7; Mo, 19.0; H, 1.39; P, 18.40. Found: Na, 13.4; Mo, 19.1; H, 1.27; P, 18.32. Phosphorus-31 nmr shows that the central phosphate group in $HP_3O_{10}^{4-}$ binds *trans* to the molybdenyl oxygen, while the terminal phosphates bind *trans* to the bridging oxygens of the $[Mo_2O_4]^{2+}$ group.

Preparation of (Partially Hydrated) Potassium Dioxotetracyanomolybdate(IV), $K_4[Mo(O)_2(CN)_4]\cdot \frac{1}{4}H_2O$

This salt was prepared according to the method described by van de Poel and Neumann [10] as modified by Robinson, *et al.* [11]. It was used as a starting material for the preparation of solutions of $K_3[Mo(O)(OH)(CN)_4]$ and $K_2[Mo(O)(H_2O)(CN)_4]$. *Anal.* Calcd. for $K_4[Mo(O)_2(CN)_4]\cdot \frac{1}{4}H_2O$: Mo, 24.4; C, 12.22; N, 14.25; H, 0.13. Found: Mo, 24.5; C, 12.16; N, 13.90; H, 0.13. The infrared spectrum of this salt agreed with that published previously, as did the visible spectrum in aqueous solution [10, 11].

Kinetic Measurements

The appearance of the product, tetracyanooxomolybdate(IV), was measured spectrophotometrically at 575 nm, the isosbestic point for $[Mo(O)_2(CN)_4]^{4-}$ and $[Mo(O)(OH)(CN)_4]^{3-}$ [2]. Neither CN^- nor $[Mo_2O_4(EDTA)]^{2-}$ absorbs significantly at this wavelength, where the molar absorptivity for the tetracyano species is 35.6 ± 0.4 M^{-1} cm^{-1}. A Bausch and Lomb Spectronic 20 equipped with a thermal controller was used for preliminary kinetic runs, and a Gilford Model 2000 spectrophotometer was used to obtain the final data.

Reactions were initiated by the simultaneous addition of solutions of NaCN and NaOH to freshly prepared solutions of the complexes of $[Mo_2O_4]^{2+}$. Sodium cyanide solutions were freshly prepared also, to minimize the hydrolysis of the cyanide ion in alkaline solution [12]. The ionic strength of all reaction media was kept at 1.0 *M* by the addition of appropriate amounts of $NaClO_4$.

The presence of molybdate in the reacted solutions was determined qualitatively by precipitation of $Ba[MoO_4]$ with 0.1*M* $BaCl_2$.

Results

Addition of a 20-fold excess of NaCN to 0.1*M* aqueous solutions of $[Mo_2O_4(CYS)_2]^{2-}$ $[Mo_2O_4(CIT)_2]^{4-}$, or $[Mo_2O_4(HP_3O_{10})_2]^{6-}$ at 25 °C initiates the disproportionation of these orange complexes into $[MoO_4]^{2-}$ and the blue tetracyano species; all of these reactions are half-complete within 5s. A suspension of the insoluble $[Mo_2O_4(HIS)_2]$ reacts with CN^- at a similar rate. Only the EDTA complex disproportionates more slowly. The disproportionation of a 0.01*M* solution of $[Mo_2O_4(EDTA)]^{2-}$ in the presence of 0.2*M* NaCN is half-complete in about 4 h at 25 °C. Spectrophotometric analyses show that one mol of Mo(IV)-cyanide is produced from each mol of $[Mo_2O_4]^{2+}$-complex. Equivalent amounts of $Ba[MoO_4]$ could not be precipitated from the reaction solutions, presumably because the $[MoO_4]^{2-}$ was complexed with EDTA and the other appropriate ligands. The consumption of 3 molecules of OH^- per molecule of $[Mo_2O_4(EDTA)]^{2-}$ which is shown in Equation 1 was not determined experimentally, but was required to balance the chemical equation.

$$\begin{aligned}&[Mo_2O_4(EDTA)]^{2-} + 4CN^- + 3OH^- \rightarrow \\ &\quad MoO_4^{2-} + [Mo(O)(OH)(CN)_4]^{3-} + EDTA^{4-} + H_2O\end{aligned} \tag{1}$$

The observed rate law for the reaction with the EDTA complex is:

$$\text{rate} = k_{obs}[(Mo_2O_4(EDTA))^{2-}][OH^-] \tag{2}$$

where k = (2.00 ± 0.21) × 10^{-2} M^{-1} s^{-1} at 25 °C. Figure 1 illustrates this with plots of $\ln([Mo(IV)]_\infty - [Mo(IV)]_t)$ *vs.* time at various concentrations of OH^-. The data in Table I show that the rate of reaction is not inhibited by excess $[MoO_4]^{2-}$ or excess

TABLE I. Rate of Disproportionation of $[Mo_2O_4(EDTA)]^{2-}$ under Various Reaction Conditions.

$[Mo_2O_4(EDTA)^{2-}]_o$	$[OH^-]_o$	$[CN^-]_o$	[Reagent]	Temp.	k_{obs}, s^{-1}	k_{rate}[b], M^{-1} s^{-1}
0.011 *M*	2.89×10^{-3} *M*[a]	0.333 *M*	–	25.0 °C	5.51×10^{-5}	0.019
"	0.013[a]	"	–	"	1.96×10^{-4}	0.019
"	0.133	"	–	"	2.79×10^{-3}	0.021
"	0.200	"	–	"	4.60 "	0.023
"	0.267	"	–	"	5.34 "	0.020
"	0.333	"	–	"	6.49 "	0.019
"	0.400	"	–	"	8.00 "	0.020
"	0.540	"	–	"	10.4 "	0.019
"	0.667	"	–	"	12.0 "	0.018
"	0.200	0.167	–	"	3.76 "	0.019
"	0.200	0.333	–	"	4.60 "	0.023
"	0.201[a]	0.500	–	"	4.54 "	0.023
"	0.202[a]	0.667	–	"	4.40 "	0.022
"	0.203[a]	0.800	–	"	4.80 "	0.024
"	0.200	0.333	MoO_4^{2-} 0.033	"	4.14 "	0.021
"	"	"	" 0.100	"	3.80 "	0.019
"	"	"	" 0.167	"	3.30 "	0.016
"	"	"	" 0.233	"	4.30 "	0:022
"	"	"	" 0.316	"	4.04 "	0.020
"	0.193[c]	0.333	EDTA 0.0033	"	3.60 "	0.019
"	0.180[c]	"	" 0.010	"	3.26 "	0.018
"	0.173[c]	"	" 0.0167	"	2.92 "	0.017
"	0.153[c]	"	" 0.0233	"	3.01 "	0.020
"	0.200	0.333	–	1.9 °C	4.6×10^{-4}	0.0023
"	"	"		11.0 °C	1.44×10^{-3}	0.0072

[a] In these runs, $[OH^-]$ includes contribution from hydrolysis of cyanide ion. [b] The average $k_{rate} = (2.00 \pm 0.21) \times 10^{-2}$ M^{-1} s^{-1}. [c] The $[OH^-]$ in these runs was corrected for reaction with H_4EDTA.

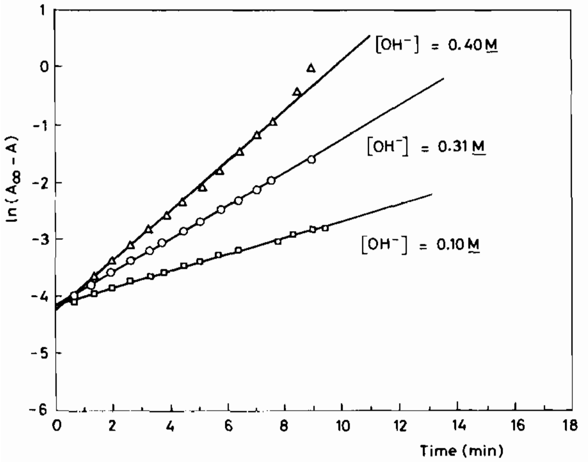


Figure 1. First-order plots for production of tetracyanomolybdate(IV) at three different OH^- concentrations.

EDTA rate has no dependence on $[CN^-]$, unless the $[OH^-]$ produced by hydrolysis of CN^- is significant with respect to the $[OH^-]$ from NaOH. If less than four equivalents of CN^- are present, the addition of NaOH leads to the decomposition of the complex and the precipitation of polymeric Mo(V) hydroxide, $Mo(O)(OH)_3$ (Equation 3).

$$[Mo_2O_4(EDTA)]^{2-} + 2OH^- + 2H_2O \rightarrow$$

$$2Mo(O)(OH)_{3(s)} + EDTA^{4-} \qquad (3)$$

The disproportionation is "reversible" in the sense that if the pH of a disproportionated solution is brought to 5 with 3*M* acetic acid, the $[Mo(O)(H_2O)(CN)_4]^{2-}$ loses cyanide as HCN (*CAUTION!*), and $[Mo_2O_4(EDTA)]^{2-}$ reforms along with some $Mo(O)(OH)_3$. The same products form if $[Mo(O)(H_2O)(CN)_4]^{2-}$, $[MoO_4]^{2-}$, and Na_2EDTA are mixed in a 1:1:2 ratio and treated with 3*M* acetic acid. This reaction takes 8–12 h at pH 5; more acidic conditions lead to the formation of more $Mo(O)(OH)_{3(s)}$ and less EDTA-complex.

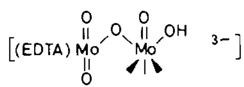
Calculations based on rate measurements at 275°, 284.1°, and 298.1 °K yield an apparent Arrhenius activation energy of 15.5 kcal mol^{-1} (Table I).

Initial experiments with the other complexes of $[Mo_2O_4]^{2+}$ show that their reactions with CN^- are qualitatively similar to those just described for the EDTA complex, *i.e.*, their rate laws are of similar form, their disproportionations are reversible at pH 5, and they decompose upon the addition of NaOH in the absence of cyanide. For the reaction of the cysteine complex with CN^-, $k = (77 \pm 15)$ M^{-1} s^{-1}; the rates of disproportionation for the triphosphato and citrato complexes are somewhat faster – $k = ca.\ 150 M^{-1} s^{-1}$.

Discussion

The observed rate law (Equation 2) implies that the rate-limiting step in this reaction involves the addition of one hydroxide ion to one molecule of $[Mo_2O_4(EDTA)]^{2-}$ (Equation 4). Subsequent reactions with OH^- and CN^- produce $[MoO_4]^{2-}$ and $[Mo(O)(OH)(CN)_4]^{3-}$ (Equation 5).

$$[Mo_2O_4(EDTA)]^{2-} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$



$$\left[(\mathrm{EDTA})\underset{O}{\overset{O}{\mathrm{Mo}}}{-}O{-}\overset{O}{\mathrm{Mo}}{-}OH\right]^{3-\,\ddagger} \qquad (4)$$

(*A*)

$$A^{\ddagger} + 2OH^- + 4CN^- \xrightarrow{k_2}$$

$$[MoO_4]^{2-} + EDTA^{4-} + [Mo(O)(OH)(CN)_4]^{3-} \qquad (5)$$

Compound *A* or some similar complex is proposed as an intermediate because 1) the similarities between the disproportionations of the various $[Mo_2O_4]^{2+}$ complexes indicate that (with the exception of the EDTA complex) differences in the ligands do not affect the reaction rates, and 2) because of several facts which indicate that substitution at $[Mo_2O_4]^{2+}$ involves the bridging oxygens. These include the following: a) Treatment of $[Mo_2O_4]^{2+}$ complexes with sulfide yields sulfur-bridged $[Mo_2O_3S]^{2+}$ and $[Mo_2O_2S_2]^{2+}$ complexes quite readily, while the formation of thiomolybdenyl groups occurs very slowly, if at all [13]. b) Oxygen-18 exchange for dithiocarbamato complexes of $[Mo_2O_4]^{2+}$ in dichloromethane occurs at the bridging oxygens only [14], and preliminary $^{18}OH_2$ exchange kinetics for $[Mo_2O_4(EDTA)]^{2-}$ and $[Mo_2O_4(CYS)_2]^{2-}$ show that the rate of exchange of the oxo- groups with water increases with increasing pH [15]. c) Certain $[Mo_2O_4]^{2+}$ complexes form blue-green species at pH 9–12 which may by mono-oxygen bridged Mo(V) dimers [16], whose formation may involve the attack of a single OH^-. d) Epr shows that $[Mo_2O_4(CYS)_2]^{2-}$ [17] and other $[Mo_2O_4]^{2+}$ complexes [18] dissociate into paramagnetic Mo(V) monomers in this pH range, but that the Mo(V)-EDTA complex does not dissociate.

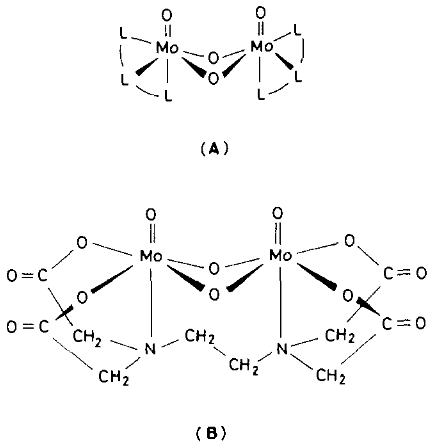


Figure 2. Schematic representations of the structures of (A) $[Mo_2O_4(CYS)_2]^{2-}$, $[Mo_2O_4(HIS)_2]$, $[Mo_2O_4(CIT)_2]^{4-}$, $[Mo_2O_4(HP_3O_{10})_2]^{6-}$ and (B) $[Mo_2O_4(EDTA)]^{2-}$.

A mechanism which requires an initial opening of the μ-di-oxo bridge also explains the fact that the EDTA complex disproportionates about 5000 times more slowly than the others. Figure 2 compares the structure of the EDTA complex with the structures of the other species. The bridging of the two molybdenum atoms by the $>N–CH_2CH_2–N<$ backbone of the ligand provides added stability for the $[Mo_2O_4]^{2+}$ core. This is shown by the slower replacement of the bridging oxygens in the EDTA complex by S^{2-} and $^{18}OH_2$ [13, 15]. For the reaction to go to completion, the $[Mo_2O_4]^{2+}$ group must be divided; in the EDTA complex three other bonds must also be broken – the N–Mo bond and two $–CO_2–Mo$ bonds. Therefore, this greater structural stability markedly decreases the rate of reaction of the EDTA complex with CN^- and OH^-. According to the mechanism suggested in Equations 4 and 5, the effect of EDTA could be either to decrease k_1 or to increase k_{-1}. We prefer the former explanation, since the formation of Mo(V) dimers from $[MoO_4]^{2-}$ and $[Mo(O)(H_2O)(CN)_4]^{2-}$ occurs at about the same rate for all of the complexes which we examined. In this reaction, the loss of CN^- as HCN is comparatively rapid (*i.e.*, it is complete within about 2 h at 25 °C), so the rate-limiting step may be the k_{-1} reaction (Equation 4) whose rate is independent of the nature of the ligand. More definitive evidence is the fact that the EDTA complex does not exchange with $^{18}OH_2$ at all within 24 h in neutral solutions at 25 °C [15], while the rate of exchange with $[Mo_2O_4]^{2+}$ and $[Mo_2O_4(CYS)_2]^{2-}$ occurs with a half-time of less than 1 h under similar conditions. A decrease in k_1 caused by the complexation of EDTA is consistent with this observation.

In summary, the disproportionation of $[Mo_2O_4(EDTA)]^{2-}$ and other complexes of $[Mo_2O_4]^{2+}$

in the presence of CN^- proceeds via an initial attack by OH^-. The reactive intermediate which results may be a mono-oxygen bridged Mo(V) dimer, which can react with either CN^- to produce $[MoO_4]^{2-}$ and tetracyanomolybdates, or, if no CN^- is present, with additional hydroxide ions to form $Mo(O)(OH)_{3(s)}$.

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