oscillating reactions behave similarly to the ferroin-catalyzed ones, such as the dependence of mean periods on the initial concentrations of $KBrO_3$ and H_2SO_4. However, it is difficult to study such an oscillating system quantitatively because the "catalyst" itself is irreversibly destroyed during the oscillations.

Acknowledgment. This research wa supported by a grant from the Science Foundation of Academia Sinica. We are indebted to the reviewers of thi spaper for their valuable suggestions and encouragments. We also wish to thank Ding Xiang and Hu Si-jiu for taking part in the experimental work.

Registry No. $Ni(ATH)^{2+}$, 55701-27-4; $Ni(ATH)^{3+}$, 81610-31-3; $KBrO_3$, 7758-01-2; $AgNO_3$, 7761-88-8; Br^-, 24959-67-9; I^-, 20461-54-5; ClO_4^-, 14797-73-0; NO_3^-, 14797-55-8; malonic acid, 141-82-2; acetonitrile, 75-05-8; acrylamide, 79-06-1.

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Kinetics and Salt Effects for the Oxidation of Octacyanomolybdate(IV) by Peroxydisulfate Ions

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Received July 8, 1985

The oxidation of octacyanomolybdate(IV) by peroxydisulfate ions shows a very strong alkali metal ion catalytic effect in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The alkali metal ion is considered part of the transition state with the rate law $r = k[Mo(CN)_8^{4-}][S_2O_8^{2-}][M^+]$. A linear relationship between the observed rate constant ($M^{-2}\ s^{-1}$ at 40 °C) [Li^+ (3.8×10^{-3}), Na^+ (7.6×10^{-3}), K^+ (18×10^{-3}), Rb^+ (32×10^{-3}), Cs^+ (64×10^{-3})] and the polarizability of the alkali metal ion shows the greater effectivity of the larger cation in forming a bridge for electron transfer. A Marcus relationship suggests an advantage of the electron transfer between $M(CN)_n^{4-}$ and $S_2O_8^{2-}$ over the hydrolysis of $S_2O_8^{2-}$ for these reactions (M = Mo, W, Fe; n = 8, 6).

Introduction

The peroxydisulfate ion is one of the strongest oxidizing agents known in aqueous solution. Uncatalyzed oxidation by peroxydisulfate is very slow at 25 °C despite a favorable free energy.

The kinetics and mechanisms[1] of the oxidation of a large variety of compounds by the peroxydisulfate ion, both catalyzed and uncatalyzed, have been investigated. The most commonly used catalyst for these reactions is the silver(I) ion, although reactions involving the copper(II) ion as catalyst have also been studied. The rates of these catalyzed reactions are, without exception, independent of the reductant concentration but are first order in peroxydisulfate and catalyst.

Characteristic of first-order uncatalyzed oxidations with peroxydisulfate is the aqueous decomposition to sulfate free radicals, which react with water molecules to produce hydroxyl free radicals. This rate-determining hydrolysis of $S_2O_8^{2-}$ in neutral or alkaline solutions can be represented by

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$$

$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + OH\cdot$$

$$2OH\cdot \rightarrow H_2O + {}^1/_2O_2$$

A specific salt effect found in the uncatalyzed oxidation of hexacyanoferrate(II)[2-4] and octacyanotungstate(IV)[5] ions by the peroxydisulfate ion suggests that the ion-pairs $MFe(CN)_6^{3-}$, $MW(CN)_8^{3-}$, and $MS_2O_8^-$ are the reactive species for these reactions. The reactions are also first order with respect to these species.

Several studies[6-13] on the redox properties of the cyano complexes of iron, molybdenum, and tungsten have shown the reaction mechanism of these cyanide complexes with a specific reactant to be similar, while others[14-20] showed the reaction mechanism to be different. In view of this, the oxidation of $Mo(CN)_8^{4-}$ was studied for a comparison with the peroxydisulfate oxidation of $Fe(CN)_6^{4-}$ and $W(CN)_8^{4-}$.

Table I. Rate of Oxidation of $Mo(CN)_8^{4-}$ by $S_2O_8^{2-\,a}$

$10^4 \times [Mo(CN)_8^{4-}]$, M	$10^2 \times [S_2O_8^{2-}]$, M	$10^4 \times k_{obsd}$, s^{-1}	$10^4 \times [Mo(CN)_8^{4-}]$, M	$10^2 \times [S_2O_8^{2-}]$, M	$10^4 \times k_{obsd}$, s^{-1}
5.0	2.5	1.10	5.0	1.3	0.55
4.5	2.5	1.08	5.0	1.5	0.63
4.0	2.5	1.07	5.0	1.8	0.76
3.5	2.5	1.10	5.0	2.0	0.90
3.0	2.5	1.23	5.0	2.3	1.01
2.5	2.5	1.16	5.0	2.5	1.08

^{a} μ = 0.4 M (K_2SO_4); [K^+] = 0.25 M; [OH^-] = 0.01 M (KOH); T = 40 °C.

Experimental Section

$K_4Mo(CN)_8 \cdot 2H_2O$ was prepared as described by Leipoldt et al.[21] and was used as a primary standard[22] after recrystallization. All other

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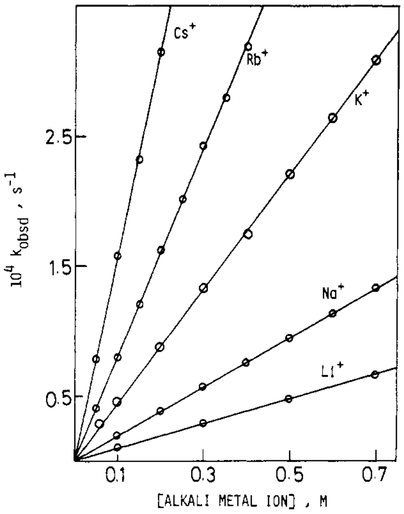

Figure 1. Dependence of the observed rate constant (s^{-1}) on the alkali metal ion concentration for the oxidation of $Mo(CN)_8^{4-}$ by $S_2O_8^{2-}$ ($[Mo(CN)_8^{4-}] = 5 \times 10^{-4}$ M; $[S_2O_8^{2-}] = 2.5 \times 10^{-2}$ M; $T = 40$ °C; μ varies between 0.1 and 1.0 M for each set of data).

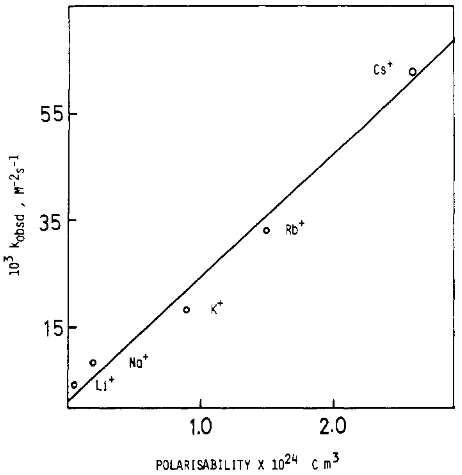

Figure 2. Plot of k_{obsd} (M^{-2} s^{-1}), for the oxidation of $Mo(CN)_8^{4-}$ by $S_2O_8^{2-}$, against the polarizability of the alkali metal ions.

Table II. Observed and Calculated Rate Constants for Variation of the Ionic Strength of the Reaction Mixture[a]

μ, M (K_2SO_4)	$10^2 \times k_{obsd}$, M^{-2} s^{-1}	$10^2 \times k_{calcd}$, M^{-2} s^{-1}	μ, M (K_2SO_4)	$10^2 \times k_{obsd}$, M^{-2} s^{-1}	$10^2 \times k_{calcd}$, M^{-2} s^{-1}
0.09	1.72	1.54	0.60	1.91	1.96
0.15	1.79	1.77	0.75	1.80	1.81
0.30	1.83	2.03	0.90	1.76	1.63
0.45	1.88	2.05	1.05	1.68	1.45

[a] $[Mo(CN)_8^{4-}] = 5 \times 10^{-4}$ M; $[S_2O_8^{2-}] = 2.5 \times 10^{-2}$ M; $[OH^-] = 0.01$ M; $T = 40$ °C.

reagents were of analytical grade, and redistilled water was used throughout.

Kinetic data were collected by monitoring the formation of the $Mo(CN)_8^{3-}$ ion at 390 nm with a Pye Unicam SP 1700 spectrophotometer. The temperature of reaction mixtures was controlled to within 0.1 °C. In all reaction mixtures $[S_2O_8^{2-}]$ was more than a factor of 10 in excess relative to $[Mo(CN)_8^{4-}]$ to obtain pseudo-first-order reaction conditions. Variation of the $[H^+]$ over the pH range 3–13 had no significant effect on the reaction rate, and all the reported runs were thus carried out in a convenient 0.01 M hydroxide medium.

The stoichiometry of the reaction was studied volumetrically by determining excess $Mo(CN)_8^{4-}$ with a standard $Ce(SO_4)_2$ solution and *N*-phenylanthranilic acid as indicator.[23] This confirmed the overall reaction to be

$$2Mo(CN)_8^{4-} + S_2O_8^{2-} \rightarrow 2Mo(CN)_8^{3-} + 2SO_4^{2-} \quad (1)$$

Results and Discussion

The oxidation of octacyanomolybdate(IV) by peroxydisulfate ions proceeds at a very low rate, and reactions were followed to approximately 50% conversion. The reaction was first order in $[Mo(CN)_8^{4-}]$. A strong alkali metal cation catalysis was also observed. The kinetic results (Table I; Figure 1) yield the experimental rate law

$$-\frac{d[Mo(CN)_8^{4-}]}{dt} = k[Mo(CN)_8^{4-}][S_2O_8^{2-}][M^+] \quad (2)$$

The alkali metal ion concentration was varied by addition of the alkali metal sulfate to the reaction mixture. A plot of k_{obsd} vs. the alkali metal ion concentration is linear with practically a zero intercept. The results in Figure 1 indicate a strong alkali metal ion catalytic effect in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Similar observations were previously reported.[3,8,13,19,24,25]

The first-order dependence of the reaction on the alkali metal ion concentration may be explained by ion-pair formation with any of the reacting species, $Mo(CN)_8^{4-}$ or $S_2O_8^{2-}$. The increase in rate constant with increasing size of the cation is in accordance with the known fact that larger ions have larger association constants. The large increase in reaction rates from Li^+ to Cs^+ ($k_{Li^+} = 3.8 \times 10^{-3}$, $k_{Na^+} = 7.60 \times 10^{-3}$, $k_{K^+} = 18 \times 10^{-3}$, $k_{Rb^+} = 32 \times 10^{-3}$, and $k_{Cs^+} = 64 \times 10^{-3}$ M^{-2} s^{-1} at 40 °C, a factor of about 17) cannot be attributed to the increase in K_{assn}[26] from Li^+ to Cs^+ (a factor of about 4). The association constant for $KS_2O_8^-$ has been reported by Chlebek and Lister[2] to be 3.3 M^{-1} for our experimental conditions, but the value of K_{assn} for $KMo(CN)_8^{3-}$ is not known. The association constants[2,13,29] for a few $M(CN)_n^{3-}$ ions were reported to be of the same magnitude. It is thus reasonable to accept that K_{assn} for $KMo(CN)_8^{3-}$ is approximately the same as the association constant[2,5,26] for $KFe(CN)_6^{3-}$ and $KW(CN)_8^{3-}$ ($K_{assn} \sim 25$ M^{-1}). These values suggest that for our experimental conditions, the species $S_2O_8^{2-}$ and $Mo(CN)_8^{4-}$ are more than 25% and 70% in the associated form, respectively. According to these values for K_{assn} a leveling effect should be observed and the reaction will not be first order in M^+ at all concentrations. The observed effect of the different alkali metal ions and the first-order dependence in alkali metal ion concentration thus cannot be explained by an ion-pair mechanism unless further association (with a small equilibrium constant) is considered.

Alternatively then, the alkali metal ion may actually facilitate the transfer of electrons by electrostatically forming a bridge between the reacting species, which means that the alkali metal ion is part of the transition state.[24] It must, however, be made clear that this bridge differs entirely from an inner-sphere halide[27,28] or cyano[26] bridge between metal centers.

Shporer et al.[30] suggested that the alkali metal cation fulfill two distinct parts during electron-transfer reactions of this type: (i) it can act as a bridge for electron transfer, and (ii) it can act as a charge buffer between the reacting species. The large increase in the reaction rates may thus be due to the greater effectivity of the larger alkali metal ion (due to its larger polarizability) as an actual bridge during electron transfer. The linear relationship between k_{obsd} and the polarizability[24] of the alkali metal cations (Figure 2) may serve as evidence for this view on the catalytic effect of the alkali metal ions.

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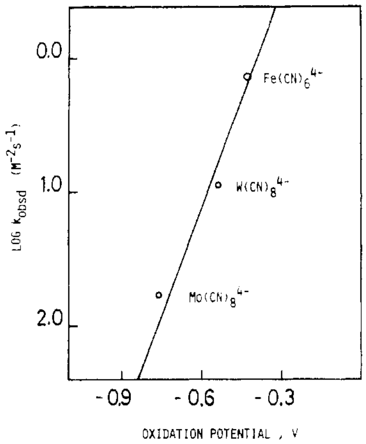

Figure 3. Plot of log k_{obsd} (M^{-2} s^{-1}; cation = K^+), for the oxidation of $M(CN)_n^{4-}$ by $S_2O_8^{2-}$, against the oxidation potential (vs. NHE) of the cyano complex (M = Fe, Mo, W). Values for $Fe(CN)_6^{4-}$ and $W(CN)_8^{4-}$ are from ref 3 and 5, respectively.

The variation in the ionic strength of the reaction mixture between 0.09 and 1.05 had very little effect on the rate constant (Table II). Application of the Davies equation[31]

$$-\log f^{\ddagger} = 0.5Z_1Z_2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \tag{3}$$

to the individual ion activities shows that the effect of the ionic strength on the rate constants is given by

$$\log k = \log k_0 + 0.5(\Delta Z)^2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \tag{4}$$

where

$$(\Delta Z)^2 = Z_x^2 - (pZ_p^2 + qZ_q^2 + rZ_r^2)^{32}$$

According to the observed rate law [Z_p, Z_q, Z_r, and Z_x are the electronic charges of $Mo(CN)_8^{4-}$, $S_2O_8^{2-}$, M^+, and the activated complex, respectively, and p, q, and r denote the order with respect to the species], $(\Delta Z)^2 = 4$ and

$$\log k = \log k_0 + 2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \tag{5}$$

According to eq 5 the value of k passes through a broad maximum at $\mu = 0.5$ M but varies only by about 20% between $\mu = 0.09$ M and $\mu = 1.05$ M. Our experimental observations (Table II) are in agreement with this calculated trend.

A correlation between the rate constants and the driving force for the reaction of peroxydisulfate with the cyano complexes of Fe, Mo, and W (Figure 3) was found. k_{obsd} is linearly dependent on the driving force, with a slope of 5.5 V^{-1}. The Marcus relation[33] (eq 6) predicts this type of linear behavior where k_{12} is the

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{6}$$

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \tag{7}$$

cross-reaction rate constant, k_{11} and k_{22} are self-exchange rate constants, and K_{12} is the equilibrium constant. This predicts a slope of 8.46 V^{-1} for a plot of log k_{12} vs. $E°$. Our experimental results are thus reasonably consistent with the Marcus theory.

The dependency of k_{obsd} on the driving force, $E°$ (Figure 3), indicates that the electron-transfer step is rate-determining. This, as well as the first-order dependence in both oxidant and reductant (eq 2), shows an advantage of the electron transfer between $M(CN)_n^{3-}$ and $S_2O_8^{2-}$ via an outer-sphere pathway over the hydrolysis of the peroxydisulfate ion for these reactions.

Acknowledgment. We are grateful to the South African CSIR and the Research Fund of this University for financial support.

Registry No. $Mo(CN)_8^{4-}$, 17923-49-8; $S_2O_8^{2-}$, 15092-81-6; Cs, 7440-46-2; Rb, 7440-17-7; K, 7440-09-7; Na, 7440-23-5; Li, 7439-93-2.

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Syntheses, Spectral Properties, and Substitution Reactions of $M(CO)_3(S_2CNC_4H_4)_2$ (M = Mo, W) Complexes Containing the Electronically Unique Pyrrole-*N*-carbodithioate Ligand

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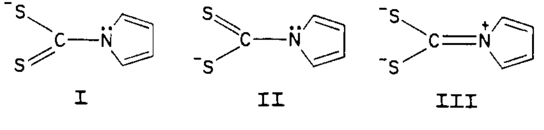
Received July 25, 1985

A series of seven-coordinate $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ (n = 0–2) molybdenum(II) and tungsten(II) complexes have been synthesized with the electronically unique pyrrole-*N*-carbodithioate chelating ligand [$M(CO)_2L(S_2CNC_4H_4)_2$: M = Mo, W, L = PPh_3, PEt_3, $P(OMe)_3$; M = Mo, L = OC_4H_8, SC_4H_8, $AsPh_3$, $SbPh_3$. $M(CO)L_2(S_2CNC_4H_4)_2$: M = Mo, W, L = $P(OMe)_3$; M = Mo, L = PEt_3, $^1/_2$ $Ph_2PCH_2CHPPh_2$. $[R_4N][M(CO)_2X(S_2CNC_4H_4)_2]$: M = Mo, W, X = F; M = Mo, X = Cl, Br, I]. The decreased electron donor ability of the pyrrole-*N*-carbodithioate ligand relative to alkyl analogues is evident in increased infrared ν_{CO} frequencies and in increased lability of carbon monoxide ligands in $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ complexes with n = 0 and 1. The 16-electron $Mo(CO)_2(S_2CNC_4H_4)_2$ complex is significantly more electrophilic than $Mo(CO)_2(S_2CNEt_2)_2$ as reflected in isolation of the stable halide complexes listed above. Carbon-13 enriched carbon monoxide ligands in $W(CO)_3(S_2CNC_4H_4)_2$ and $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$ have been used to probe intramolecular rearrangements by variable-temperature ^{13}C NMR. Two low-temperature fluxional processes are observed for the parent tricarbonyl; the first exchanges two of the three inequivalent carbonyl ligands, and the second averages all three carbonyl signals. The (triphenylphosphine)tungsten derivative exhibits a single carbon monoxide ^{13}C NMR signal at room temperature, which is frozen into two signals at low temperature.

Introduction

Dithiocarbamate anions can be represented by the three resonance forms shown in Chart I. Contributions from these resonance forms are relatively insensitive to alkyl substituent variations on the nitrogen atom.[1] The pyrrole-*N*-carbodithioate ligand ($^-S_2CNC_4H_4$) prepared by Kellner et al.[2] exhibits unusual bonding

Chart I



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