and Cu(dien)$^{2+}$ thermodynamics are very different, then the ligand-substitution reactions of the protein and Cu(dien)$^{2+}$ must be different, possibly reflecting the protein's direct influence on metal ion reactivity.

It is clear that the similarity of the equilibrium constants for anion binding to SOD and Cu(dien)$^{2+}$ is very misleading, since the relative contributions from ΔH° and ΔS° differ greatly. ΔH° and ΔS° for the SOD reaction with thiocyanate were measured under various conditions in addition to those cited in Table I. Assuming $\Delta\epsilon \simeq 200$ M^{-1} cm^{-1}, $\Delta H^\circ = 16 \pm 2$ kJ mol^{-1} and $\Delta S^\circ = 70 \pm 5$ J mol^{-1} K^{-1} in the standard buffer at relatively high thiocyanate concentrations, [SCN$^-$] = 0.40 M. In 5.0 mM PIPES, 0.3 M NaCl, and 0.1 M KSCN (pH 7.0), $\Delta H^\circ = 6.0 \pm 1$ kJ mol^{-1} and $\Delta S^\circ = 30 \pm 2$ J mol^{-1} K^{-1}. Independent of any assumptions about the magnitudes of K and $\Delta\epsilon$, the temperature dependence of the SOD LMCT transition establishes that ΔH°(SCN$^-$) is unambiguously positive. Absorbance changes displayed by the SOD–SCN$^-$ complex in the ligand-field region were nearly independent of temperature (Figure 4), which rules out the possibility that the SOD–Cu(II)–NCS$^-$ geometry is significantly temperature dependent over the range examined. Positive enthalpies and large positive entropies were consistently observed for SCN$^-$ binding under all conditions employed. The thermodynamic data also suggest that the structures of the Cu(dien)$^{2+}$–anion and SOD–Cu(II)–anion complexes may not be the same (e.g. nonidentical leaving groups or final coordination numbers/geometries). Entropy effects are far more important in the SOD reactions and may reflect the influence of the protein structure on metal ion reactivity. Indeed, ΔS° can be readily interpreted by reference to the Cu,Zn-SOD crystal structure. The active-site channel, including the metal ion ligands and three buried water molecules, is very highly ordered.[13] Anion binding displaces at least some of the ordered water molecules and possibly disrupts the structure of the Cu(II) ligands and neighboring residues. Both effects should contribute to a positive ΔS°. The more positive enthalpies for anion binding to SOD, compared to Cu(dien)$^{2+}$, may reflect histidine displacement[2c] or protein conformational changes. Further, the thermodynamics of N_3^- and SCN$^-$ binding to bovine Cu,Zn-SOD are qualitatively different, in contrast to the Cu(dien)$^{2+}$ ligand-substitution reactions, where N_3^- and SCN$^-$ coordination are thermodynamically very similar. Two possible sources for thermodynamic differences between azide and thiocyanate binding to the SOD are as follows: (1) N_3^- and SCN$^-$ coordinate to Cu(II) in different ways; (2) protein structural perturbations (associated, for example, with the anions' relative sizes and the narrow width (<4 Å)[13] of the active-site channel) may be a function of the bound ions.[16] Experiments designed to test these possibilities (including experiments on modified SODs) are feasible. Thermodynamic measurements clearly will be quite helpful in understanding the active-site coordination chemistry of Cu,Zn-SOD. Moreover, our results indicate that thermodynamics measurements, combined with structural information, are a useful approach to identifying ways in which proteins modulate or control metal ion reactivity.

Acknowledgments. This research was supported by the American Heart Association with funds contributed in part by the Massachusetts Affiliate (Grant 82-972) and by the NIH (Grant GM 27659). We are grateful to Phoebe Mix and Cheryl Cotê for their assistance and to Joan Valentine, Ivano Bertini, Claudio Luchinat, and Joe Rotilio for helpful discussions.

Registry No. SOD, 9054-89-1; N_3^-, 14343-69-2; SCN$^-$, 302-04-5; Cu(dien)$^{2+}$, 45520-77-2.

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(16) A definitive explanation for the complex behavior associated with the SOD–thiocyanate reaction is not yet available. One reviewer suggested that SCN$^-$ may bind to charged groups on the protein. This is certainly a reasonable proposal that is not excluded by our data, although one might expect similar behavior with azide, which was not observed. Until the interactions(s) between Cu,Zn-SOD and thiocyanate are better understood at the molecular level, the thermodynamic quantities for this reaction should be regarded as applicable only under conditions that closely correspond to those used here.

Contribution from the Department of Chemistry,
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Oscillating Reactions Involving a Nickel Complex with a 13-Membered Tetraaza Macrocyclic Ligand in Acidic Bromate Medium

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Received December 10, 1984

New oscillating reactions with the participation of a macrocyclic nickel(II) complex ion [Ni(ATH)]$^{2+}$ as catalyst in acidic bromate medium are described. This complex ion contains the ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene. The [Ni(ATH)]$^{2+}$ ion can undergo an irreversible oxidation reaction of Ni(II) → Ni(III). The reduction potential of the couple [Ni(ATH)]$^{3+}$/[Ni(ATH)]$^{2+}$ in a 9:1 ethanol–acetonitrile mixture is found to be 1.32 V. The concentration oscillations of this system are damped rapidly due to the consumption of the catalyst and are inhibited by I$^-$ ion, if the I$^-$ ion concentration exceeds 2×10^{-3} mol L^{-1}, but they are promoted somewhat, if the I$^-$ concentration is below 1.2×10^{-3} mol L^{-1}. Acrylamide or acetonitrile cannot entirely inhibit the oscillation. In the absence of malonic acid or other organic substrate, the catalyst itself may serve as organic substrate to produce a few oscillations. In some respects, the [Ni(ATH)]$^{2+}$-catalyzed oscillating reactions behave similarly to the ferroin-catalyzed ones. The reaction trajectories of the [Ni(ATH)]$^{2+}$-catalyzed system are spiral, which may provide some useful information about the details of the chemical mechanism.

Introduction

Yatsimirskii et al.[1-5] have recently reported that several hexamethyl tetraaza macrocyclic complexes can act as catalysts in Belousov–Zhabotinskii[6,7] (B–Z) oscillating reactions. They also described new oscillating reactions, viz. the oxidation of Me$_6$-[14]-4,14-dieneN$_4$ complexes of copper and nickel by acidic bromate. However, the mechanisms of these oscillating reactions have not been discussed in detail. Until now, the oscillating reactions involving other polyaza macrocyclic complexes have not yet been reported.

In order to search for the possibilities that other polyaza macrocyclic complexes may participate in oscillating reactions,

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(1) Yatsimirskii, K. B.; Zakrevskaya, L. N.; Kolchinskii, A. G.; Tikhonova, L. P. *Dokl. Akad. Nauk SSSR* **1980**, *251*, 132.

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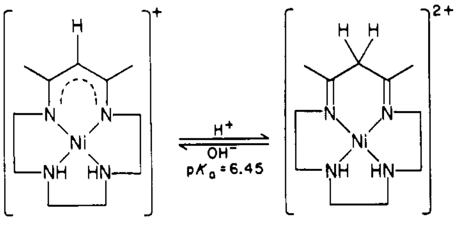
we have investigated the nickel complexes with 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene, [Ni(AT)]X (X = ClO_4^-, NO_3^-, Br^-, I^-).

Noyes[8] has pointed out that all presently known catalysts in B-Z oscillating reactions involve reduction potentials of about 1.0–1.5 V. According to the literature,[9,10] the $[Ni(AT)]^+$ ion undergoes an electrochemically irreversible one-electron-oxidation reaction at +0.27 V vs. Ag/Ag^+ (0.1 mol L^{-1} in acetonitrile) reference electrode in acetonitrile medium, and it can be protonated and converted to $[Ni(ATH)]^{2+}$ in acidic medium:



$[Ni(AT)]^+$ $[Ni(ATH)]^{2+}$

Obviously, the protonation of $[Ni(AT)]^+$ will change its electrochemical behavior. However, the oxidation potential of its protonated product has not yet been reported.

Since $[Ni(ATH)]^{2+}$ has a methylene group similar to the "active methylene group" in malonic acid, we expect that if the reduction potential of the redox pair $[Ni(ATH)]^{3+}/[Ni(ATH)]^{2+}$ lies in the range of 1.0–1.5 V and $[Ni(ATH)]^{2+}$ acts as a catalyst in oscillating reactions, the $[Ni(ATH)]^{2+}$-catalyzed systems will show some interesting features.

Experimental Section

Electrochemical measurements were performed at 25 ± 1 °C, with a three-electrode configuration consisting of a glassy-carbon-disk working electrode, a platinum-wire auxiliary electrode, and a Ag/Ag^+ (0.1 mol L^{-1}) in acetonitrile) reference electrode. Voltammograms were obtained with a 79-1 voltammeter and a Da Hua LZ-3 x-y recorder. All oscillation experiments were performed in a closed glass container with a magnetic stirrer at 30 ± 0.5° regulated by a thermostat. The redox potential and instantaneous bromide concentration were monitored by a platinum-wire electrode and a bromide-selective electrode, respectively. The reference electrode was a saturated calomel electrode connected via a salt bridge containing 10% KNO_3. The bromide-selective electrode was calibrated according to the literature[11,12] so that the absolute bromide concentration could be read directly. The potentials of these two electrodes were measured and recorded by using two ion meters (Model PXD-2) connected to a y-t or x-y recorder.

The catalysts [Ni(AT)]X (X = Br^-, ClO_4^-, NO_3^-, I^-) were prepared by the method of Cumming and Sievers[10] and identified by their IR spectra and elemental analyses. The solutions of [Ni(AT)]X to be used were prepared daily. Bromomalonic acid was prepared as described by Zaikin and Zhabotinskii.[13] The solvent anhydrous ethanol and other chemicals were analytical reagent grade and were used without further purification.

Results and Discussion

Electrochemical Behavior of $[Ni(AT)]^+$ and $[Ni(ATH)]^{2+}$ Ions. We observed that the $[Ni(AT)]^+$ ion undergoes irreversible oxidation at +0.25 V vs. Ag/Ag^+ (0.1 mol L^{-1} in acetonitrile) reference electrode in 9:1 ethanol–acetonitrile solution (0.1 mol L^{-1} $LiClO_4$ as supporting electrolyte). When H_2SO_4 was added to this solution, the cyclic voltammograms of it showed that the oxidation peak of $[Ni(AT)]^+$ disappeared and a new oxidation peak with a higher positive potential, which we designated as the oxidation peak of $[Ni(ATH)]^{2+}$, appeared instead. The reduction potential of the couple $[Ni(ATH)]^{3+}/[Ni(ATH)]^{2+}$ is found to be +1.32 V (+0.68 V vs. Ag/Ag^+ (0.1 mol L^{-1})). This potential can lead to Belousov–Zhabotinskii oscillating chemical reactions involving this redox pair as catalyst.

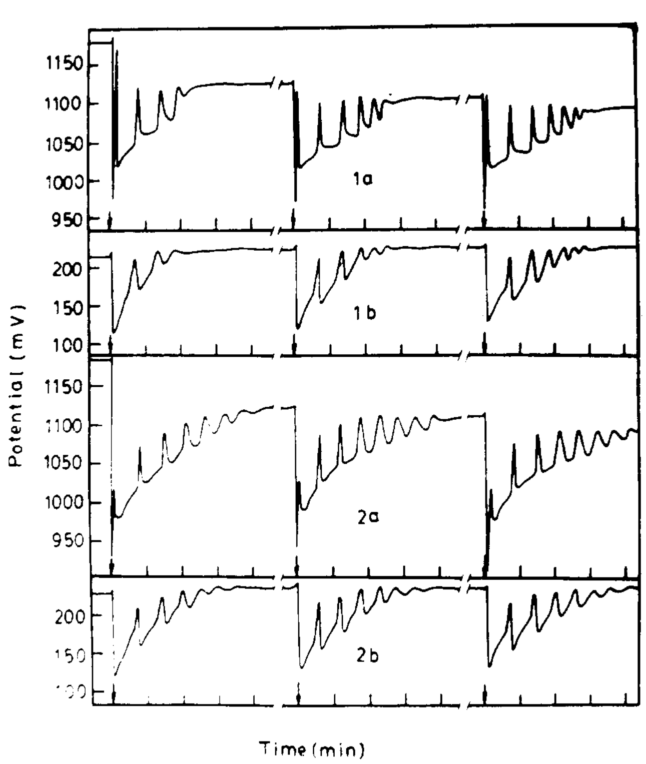


Figure 1. Potential traces of platinum (a) and bromide-selective (b) electrodes in the reaction of the $KBrO_3$–H_2SO_4–$[Ni(AT)]ClO_4$–$CH_2(COOH)_2$ system and the effects of $[CH_2(COOH)_2]_0$ on the potential traces: (1) $[CH_2(COOH)_2]_0$ = 0.063 mol L^{-1}; (2) $[CH_2(COOH)_2]_0$ = 0.013 mol L^{-1}. The potential of the bromide-selective electrode becomes more positive when the bromide concentration decreases (the same is true for the other figures). The arrows on the diagram indicate the addition of 0.4 mL of 0.1 mol L^{-1} $[Ni(AT)]ClO_4$ solution. Concentrations: $[KBrO_3]_0$ = 0.063 mol L^{-1}; $[H_2SO_4]_0$ = 0.8 mol L^{-1}.

$[Ni(ATH)]^{2+}$-Catalyzed Oscillating Reactions. When catalytic quantities of [Ni(AT)]X (X = Br^-, NO_3^-, ClO_4^-, I^-) were added to the homogeneous solution containing $KBrO_3$, H_2SO_4, and malonic acid, damped concentration oscillations without induction period were observed (Figure 1). A characteristic green color of Ni(III) species appeared periodically in the solution. The visible spectrum of the green solution was consistent with the spectrum of $[Ni(ATH)]^{3+}$ published in the literature. The periods of oscillation of the system were proportional to the initial concentrations of [Ni(AT)]X within a certain range, while the initial concentrations of malonic acid, $KBrO_3$, and H_2SO_4 were fixed. In the case of using bromomalonic acid instead of malonic acid in the system, similar results were obtained but the oscillating frequency increased.

When several aliquots of solutions of [Ni(AT)]X were successively added to the reaction solution in which the oscillation had ceased, oscillation took place again and the periods of oscillation increased (Figure 1). This phenomenon indicated that the damping of oscillations was neither due to the depletion of BrO_3^- and malonic acid nor due to the accumulation of reaction products that inhibit oscillations.

The $[Ni(ATH)]^{3+}$ ion undergoes decomposition at a certain rate in solution.[14] Therefore, it is reasonable to presume that as the oscillation proceeds, catalyst in the solution would deplete gradually; hence, damping in oscillations was observed.

When [Ni(AT)]X (X = Br^-, NO_3^-, ClO_4^-, I^-) catalysts were added to the homogeneous solution containing $KBrO_3$, H_2SO_4, and acetone, similar oscillations were also observed. The characteristic green of Ni(III) species appeared periodically, and bromoacetone, which has an irritating odor as a tear gas, was liberated. When the concentration of acetone was varied from

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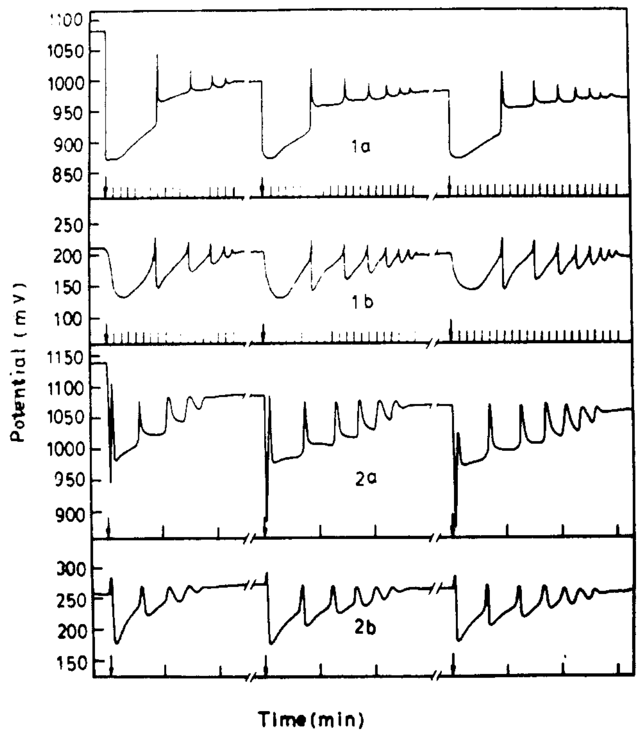

Figure 2. Effects of $[H_2SO_4]_0$ on the potential traces of platinum (a) and bromide-selective (b) electrodes: (1) $[H_2SO_4]_0 = 0.3$ mol L^{-1}; (2) $[H_2SO_4]_0 = 0.8$ mol L^{-1}. The arrows on the diagram indicate the addition of 0.4 mL of 0.1 mol L^{-1} $[Ni(AT)]ClO_4$ solution. Concentrations: $[CH_2(COOH)_2]_0 = 0.063$ mol L^{-1}; $[KBrO_3]_0 = 0.063$ mol L^{-1}.

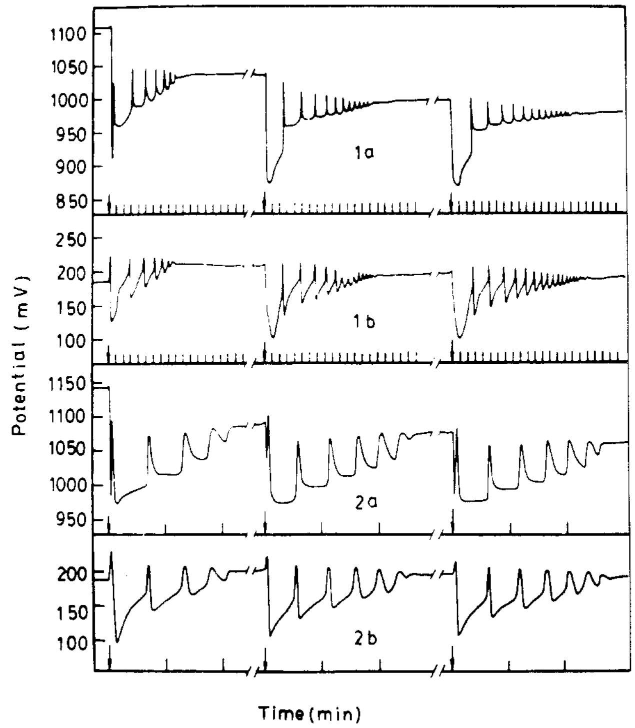

Figure 3. Effects of $[KBrO_3]_0$ on the potential traces of platinum (a) and bromide-selective (be) electrodes: (1) $[KBrO_3]_0 = 0.032$ mol L^{-1}; (2) $[KBrO_3]_0 = 0.063$ mol L^{-1}. The arrows on the diagram indicate the addition of 0.4 mL of 0.1 mol L^{-1} $[Ni(AT)]ClO_4$ solution. Concentrations: $[CH_2(COOH)_2]_0 = 0.063$ mol L^{-1}; $[H_2SO_4]_0 = 0.8$ mol L^{-1}.

0.17 to 1.7 mol L^{-1}, the periods of oscillation were almost unchanged. It seems that acetone acts merely as an absorbent of bromine in the system.

When $[Ni(AT)]X$ ($X = ClO_4^-$, NO_3^-) catalysts were added to the homogeneous solution containing only $KBrO_3$ and H_2SO_4, the system could oscillate for a short duration (three to four periods). As the oscillation proceeded, elementary bromine was liberated. At the end of oscillation the reaction mixture turned turbid and then some precipitate of a light cream color formed. When acetone or malonic acid was added to the system as soon as the oscillation had ceased, the oscillation could be revived to some extent, but the addition of $[Ni(AT)]X$ could not revive the oscillation at all. The oscillations die out much more rapidly, probably due to the fact that the macrocycle was destroyed more rapidly under the effects of oxidation, bromination, and decomposition at the same time.

Characters of $[Ni(ATH)]^{2+}$-Catalyzed Oscillation. Period Dependence on Initial Concentration of Reactants. Noyes[8] has classified the bromate-driven oscillators into five distinct classes. In class 1, i.e., the classical B–Z reactions, there are two kinds of catalysts. The oxidized forms of Ce(III) or Mn(II) are substitution-labile with reduction potentials of about 1.5 V. The oxidized forms of $[Fe(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ are inert to substitution and have reduction potentials of 1.0–1.3 V. The mechanisms for ferroin- and cerous-catalyzed oscillations do not coincide since their periods show a different dependence on initial concentrations.[15]

For the $[Ni(ATH)]^{2+}$-catalyzed system, in which the oxidized form of the catalyst, $[Ni(ATH)]^{3+}$, is substitution-inert, the influence of the initial concentrations of malonic acid, H_2SO_4, and $KBrO_3$ on the potentials of platinum and bromide-selective electrodes is shown in Figures 1–3, respectively.

Figure 2 represents two systems with different concentrations of H_2SO_4. From top to bottom, $[H_2SO_4]_0 = 0.30$ and 0.80 mol L^{-1}. Because of the great difference in periods, two times scales have to be used. With the decrease in $[H_2SO_4]_0$, there is a decrease in frequency.

Figure 3 shows the changes in waveform due to a change in the initial concentration of bromate. With a decrease in $[BrO_3^-]_0$, there is a decrease in frequency.

We observed that the dependence of the mean period of $[Ni(ATH)]^{2+}$-catalyzed oscillations on the initial concentrations of $KBrO_3$ and H_2SO_4 is similar to that of ferroin-catalyzed ones. However, different from the case of the ferroin-catalyzed system, the influence of initial concentration of malonic acid on the mean period of the $[Ni(ATH)]^{2+}$-catalyzed system is not obvious. It is worth noticing that as the initial concentration of malonic acid decreases within the range of 0.005–0.25 mol L^{-1}, the periods of oscillation increase as shown in Figure 1.

Influence of Different Anions. Experiments showed that the amplitude of oscillation of $[Ni(AT)]X$-catalyzed systems changed in the order $[Ni(AT)]Br >> [Ni(AT)]NO_3 > [Ni(AT)]ClO_4 >> [Ni(AT)]I$. This fact indicates that the Br^- ion plays a particular role in oscillation. We observed that I^- ion at high concentration (above 2×10^{-3} mol L^{-1}) will inhibit the oscillation, but the periods of oscillation increase somewhat in the presence of lower concentration (2.5×10^{-4}–1.2×10^{-3} mol L^{-1}) of I^- (Figure 4). The promoting action of I^- ion may be due to the fact that, at lower concentration, the reductive iodide ion decreases the irreversibly oxidized fraction of the catalyst during the oscillation, so that the "lifetime" of the catalyst is prolonged and the periods of oscillation increase.

Effect of Acrylamide and Acetonitrile. Varadi and Beck[16] have reported that the periodic reactions of the B–Z system were inhibited by acetonitrile and they occurred by a free-radical mechanism.

The oscillations of $[Ni(ATH)]^{2+}$-catalyzed $KBrO_3$–H_2SO_4–malonic acid and $KBrO_3$–H_2SO_4–acetone systems were not entirely inhibited by acetonitrile or acrylamide, but the periods of oscillation were decreased if the concentration of acrylamide was higher than 4×10^{-3} mol L^{-1}, as shown in Figure 5. This phenomenon may be explained in the following way: when the macrocyclic complex ions of Ni(II) are attacked by 1-equiv oxidants, the spins on the resulting species are probably too diffuse

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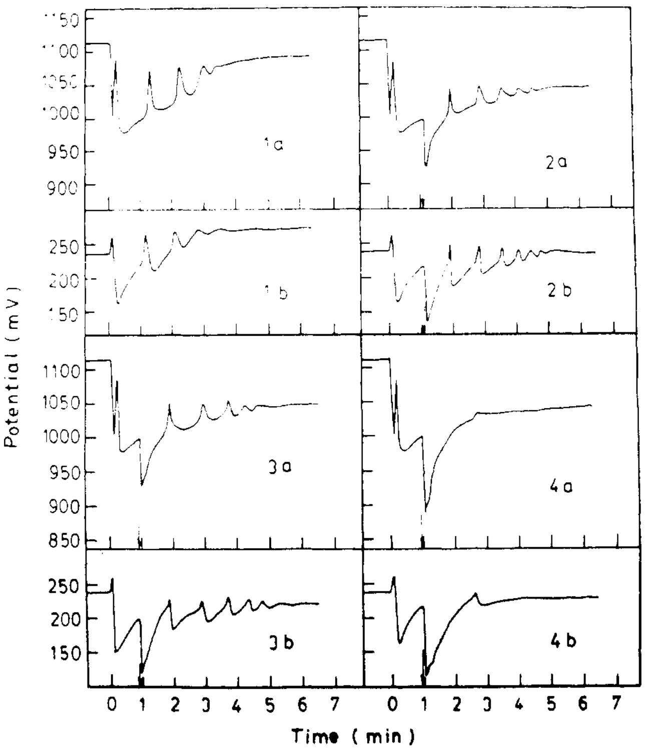

Figure 4. Effects of iodide ion on the potential traces of platinum (a) and bromide-selective (b) electrodes: (1) no KI; (2) 0.1 mL of KI; (3) 0.2 mL of KI; (4) 0.5 mL of KI. The arrows on the diagram indicate the addition of 0.2 mol L^{-1} KI solution. Concentrations: $[CH_2(COOH)_2]_0$ = 0.063 mol L^{-1}; $[KBrO_3]_0$ = 0.063 mol L^{-1}; $[H_2SO_4]_0$ = 0.8 mol L^{-1}. The initial volume was 40 mL.

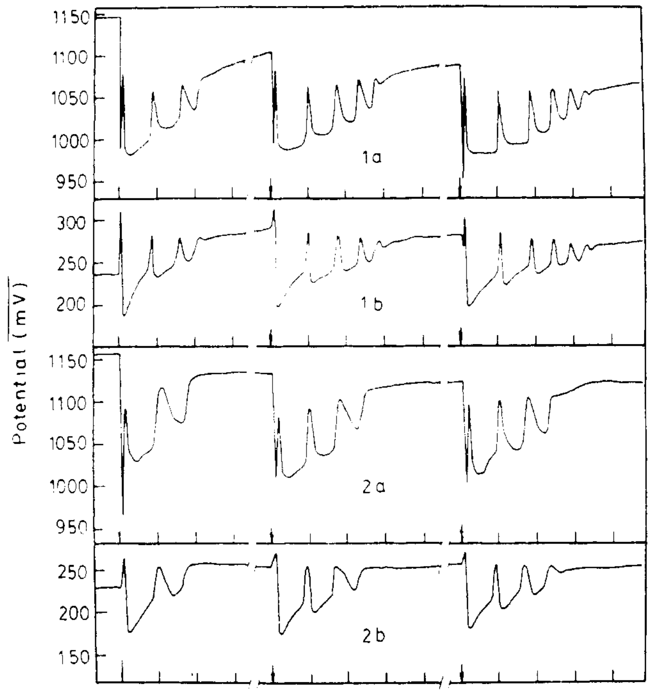

Figure 5. Effects of acrylamide concentrations on the potential traces of platinum (a) and bromide-selective (b) electrodes. The arrows on the diagram indicate the additionof 0.4 mL of 0.1 mol L^{-1} $[Ni(AT)]ClO_4$ solution: (1) no $CH_2{=}CHCONH_2$; (2) $[CH_2{=}CHCONH_2]_0 = 2.5 \times 10^{-3}$ mol L^{-1}. Concentrations: $[CH_2(COOH)_2]_0$ = 0.063 mol L^{-1}; $[KBrO_3)_0$ = 0.063 mol L^{-1}; $[H_2SO_4]_0$ = 0.8 mol L^{-1}.

to attack acrylamide effectively.

Effect of $AgNO_3$. Noszticzius[12] has reported that the addition of silver nitrate to a cerium-catalyzed B–Z system can temporarily suppress the potential oscillations of a bromide-selective electrode while the potential of a platinum electrode still oscillates in a non-Br^--controlled mode.

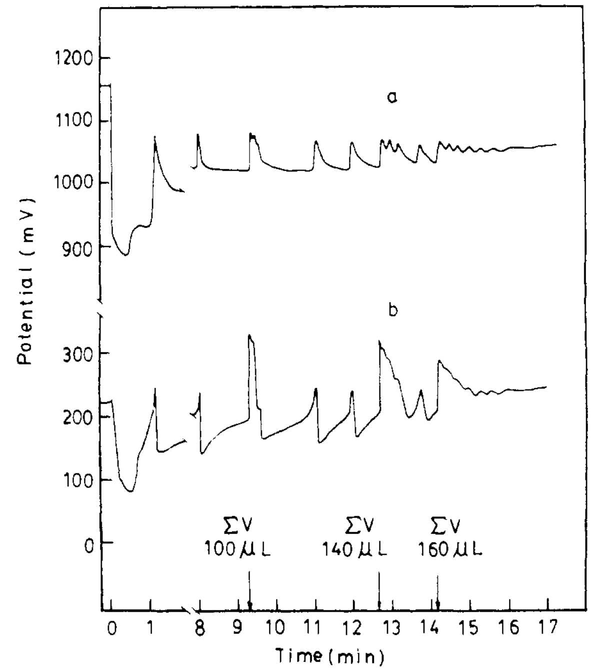

Figure 6. Potential traces of platinum (a) and bromide-selective (b) electrodes in an oscillating reaction mixture before and after $AgNO_3$ addition. Concentrations: $[KBrO_3]_0$ = 0.063 mol L^{-1}; $[CH_2(COOH)_2]_0$ = 0.063 mol L^{-1}; $[H_2SO_4]_0$ = 0.8 mol L^{-1}; $[Ni(AT)ClO_4]_0$ = 0.005 mol L^{-1}. The initial volume was 40 mL. At the moments indicated by arrows on the diagram, 0.04797 mol L^{-1} $AgNO_3$ solution was added to the system. A cumulative variable $\sum v$ shows the sum of the added volumes.

When silver nitrate was added to an oscillating $[Ni(ATH)]^{2+}$-catalyzed $KBrO_3$–H_2SO_4–malonic acid system, "abnormal" potential oscillations occurred on both platinum and bromide-selective electrodes (Figure 6). The amplitudes of these potential oscillations were decreased by about 60–80% and the frequency increased by about 100–200%. The phenomena are analogous to the results of our experiments for ferroin-catalyzed systems. It is obvious that these "abnormal" oscillations are still controlled by the concentration of bromide, the variation of which can "turn on" and "turn off" certain chemical processes.

Trajectories of $[Ni(ATH)]^{2+}$-Catalyzed Oscillating Systems. We have recorded the reaction trajectories of potential of bromide-selective electrodes vs. those of platinum electrodes for $[Ni(ATH)]^{2+}$-catalyzed oscillating systems, which are spiral instead of limit cycles. In our resulting graph the abscissa scale has been calibrated and expressed in log $[Br^-]$. Since the platinum electrode measures the mixed potential effected by the concentrations of bromate as well as Ni(III) species in the system, the coordinate scale is not calibrated. However, the fluctuations of platinum electrode potentals at nearly constant bromate concentration are directly related to the changes in the $[Ni(ATH)]^{3+}/[Ni(ATH)]^{2+}$ ratio. Figures of this type will provide valuable information about the details of chemical mechanisms.

Conclusion

$[Ni(ATH)]^{2+}$ can act as a "catalyst" for acidic bromate driven oscillators. Its oxidized form is inert to substitution and has a reduction potential of 1.32 V in a 9:1 ethanol–acetonitrile mixture. The $[Ni(ATH)]^{2+}$-catalyzed oscillating reactions exhibit some interesting features. The oscillations die out much more rapidly. The reaction trajectory of the oscillating system is a spiral instead of a limiting cycle. In the absence of organic substrate, the catalyst itself may serve as organic substrate to produce a few oscillations. Acrylamide or acetonitrile cannot entirely inhibit the oscillating reaction. The iodide ion presents a dual effect—the oscillations are inhibited when the I^- concentration is above 2×10^{-3} mol L^{-1} but is promoted somewhat when the I^- concentration is below 1.2×10^{-3} mol L^{-1}. In some respects, the $[Ni(ATH)]^{2+}$-catalyzed 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.

Contribution from the Department of Chemistry, University of the Orange Free State,
Bloemfontein, 9301 Republic of South Africa

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

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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

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

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

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

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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