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Kinetics of the Oxidation of the Nitrite Ion by 1,2-Diaminocyclohexanetetraacetatomanganate(III)

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The reaction between the manganese(III) complex of 1,2-diaminocyclohexanetetraacetic acid and the nitrite ion was studied at 25.0° over the concentration ranges $[Mn^{III}CyDTA^-]_0 = (1.9–13) \times 10^{-4}$ *M*, $[NO_2^-] = (5.0–51) \times 10^{-3}$ *M*, and $[Mn^{II}CyDTA^{2-}]_0 = (5.0–24) \times 10^{-3}$ *M*. The kinetics were found to be independent of $[H^+]$ over the pH range 4.5 to 7.5. The experimental rate law was found to be:

$$-\frac{d[Mn^{III}CyDTA^-]}{dt} = \frac{k_a[Mn^{III}CyDTA^-]^2[NO_2^-]^2}{k_b[Mn^{II}CyDTA^{2-}]^2 + [Mn^{II}CyDTA^{2-}]}$$

Values for $k_a = (7.13 \pm 0.56) \times 10^2\ M^{-2}\ sec^{-1}$ and $k_b = (2.72 \pm 0.27) \times 10^2\ M^{-1}$ were determined. Possible mechanisms for this reaction are discussed. Between pH 2.5 and 4, $Mn^{II}CyDTA^{2-}$ was found to catalyze the disproportionation of nitrous acid. In this pH range and in the presence of oxygen, the overall reaction is the oxidation of nitrite to nitrate by molecular oxygen.

Over the past few years the oxidation state III of manganese has received much attention.[1,2] Moderately stable solutions of aquomanganese(III) species can be prepared by working at high acidities and high manganese(II) concentrations. These conditions are necessary to suppress the disproportionation of aquomanganese(III). A number of kinetic studies using aquomanganese(III) in perchloric acid medium have been published. These were the subject of a recent review by Davies.[1] The oxidation state III of manganese can also be stabilized with the aid of complexing agents. It has been suggested that many of these manganese complexes are likely to have biological relevance as model systems.[2a] The manganese(III)–porphyrin complexes have been widely studied[2] as possible models for the closely related and biologically important Fe system and have been studied also because of the manganese dependence of oxygen evolution in green plant photosynthesis.[3] Recently the enzyme superoxide dismutase from bacteria was found to contain manganese.[4] The available evidence suggests that manganese is in oxidation state III in the resting enzyme.

A number of polyaminocarboxylic acid complexes of manganese(III) have been reported.[5-7] Of those the Mn(III) complex of *trans*-1,2-diaminocyclohexanetetraacetic acid ($Mn^{III}CyDTAOH_2^-$) is the most stable.[6] This complex has been reported to be seven-coordinate in aqueous solution with the CyDTA acting as a hexadentate ligand and a labile water molecule occupying a seventh coordination site.[6] Recently the same interpretation has been made for this complex in methanol.[8] Kinetic studies using $Mn^{III}CyDTA$[9] and $Mn^{III}EDTA$ as oxidizing agents have been reported for the oxidation of $C_2O_4^{2-}$,[10] N_3^-,[11] VO^{2+},[12] and H_2O_2,[13] as well as the oxidation of a series of hindered phenols in methanol solvent.[14]

In this paper, the results of a study of the stoichiometry and kinetics of the oxidation of the nitrite ion by $Mn^{III}CyDTA$ are reported. Kinetic studies of metal ion oxidations of nitrous acid include Ce(IV),[15] Mn(III),[16] Mn(VII),[17] and Cr(VI).[18] In these studies only the oxidation of nitrous acid is involved because of the high hydrogen ion concentration necessary for the stability of the metal ions. Kinetic studies involving oxidations by nonmetals include the reactions with Cl_2,[19] Br_2,[20] I_2,[21] H_2O_2,[22] and the OH radical.[23]

This system is a possible model for the oxidation of nitrite to nitrate in biological systems. It is also of interest to compare the results of this study with those involving oxidation of nitrite or nitrous acid by other one electron oxidants.

Experimental Section

All solutions were prepared with deionized water which had been doubly distilled from alkaline permanganate solution. Nitrite solutions were prepared from reagent grade sodium nitrite obtained from Allied Chemical and were standardized prior to each set of runs by pipetting the nitrite solution into an excess of standard Ce(IV) solution and back-titrating the excess Ce(IV) with standard Fe(II) solution using ferroin as the indicator. The $Mn^{III}CyDTA$ complex and other solutions were prepared and standardized as previously described.[13]

Reaction Stoichiometry. The ratio of moles of $Mn^{III}CyDTA$ consumed to moles of nitrite consumed was determined by adding weighed amounts of $KMn^{III}CyDTA \cdot 2.5H_2O$ to known amounts of excess sodium nitrite solution in both the absence and the presence of acetate buffer. In all cases the pH was kept greater than 5.0. The change in nitrite concentration was determined from the difference in absorbance before and after the reaction at 355 nm ($\epsilon_{NO_2^-} = 23.3$ M^{-1} cm^{-1})[24] since neither $Mn^{III}CyDTA$ nor nitrate absorbed appreciably at that wavelength. Beer's law was obeyed over the region $[NO_2^-] = (5.0–90) \times 10^{-3}$ *M*, in agreement with previously reported results.[24] Strong absorption by the $Mn^{II}CyDTA$ ion precluded use of the more intense nitrite peak in the 210–230-nm region.

The ratio of moles of $Mn^{III}CyDTA$ consumed to moles of hydrogen ion produced was determined by adding weighed amounts of the complex to known amounts of sodium nitrite solution in the absence of any buffer. During this reaction, the mixture was titrated with 0.020 *F* sodium hydroxide to keep the pH between 5.5 and 6.0. After the completion of the reaction, the mixture was titrated back to the original pH (approximately 7.2). The reaction was carried out under a stream of nitrogen to minimize any problem with absorption of carbon dioxide from the air.

Reaction Rate. Apparent rate constants were determined by following the decrease in absorbance of $Mn^{III}CyDTA$ at 510 nm as a function of time. Solutions containing nitrite, $Mn^{II}CyDTA$, and sodium perchlorate[25] were thermostated to 25.0°. The kinetic run was initiated by injecting a solution of $Mn^{III}CyDTA$, also thermostated to 25.0°. Initial concentrations and ionic strength were calculated using the final volume of the solution. The $Mn^{III}CyDTA$ solutions were prepared immediately before the kinetic run. For all runs $[Mn^{III}CyDTA]_0$ was much less than $[Mn^{II}CyDTA]_0$ and $[NO_2^-]_0$.

The reaction was studied over the concentration ranges $[NO_2^-] = (5.0–51) \times 10^{-3}$ *M*, $[Mn^{II}CyDTA] = (5.0–24) \times 10^{-3}$ *M*, and $[Mn^{III}CyDTA] = (1.9–13) \times 10^{-4}$ *M*. The ionic strength was maintained at 0.25 *M* with $NaClO_4$ or $NaNO_3$.

Results

Stoichiometry. The ratio of moles of $Mn^{III}CyDTA$ consumed to moles of nitrite consumed was found to be 1.93 ± 0.14 (five determinations). The ratio of moles of hydrogen

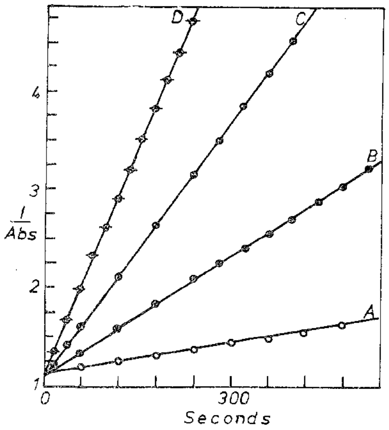

Figure 1. Plots of inverse absorbance *vs.* time for the reaction between Mn^{III}CyDTA and the nitrite ion. Nitrite concentrations: A, 0.0101 *M*; B, 0.0202 *M*; C, 0.0303 *M*; D, 0.0403 *M*. [Mn^{II}CyDTA] = 0.00997 *M*, temperature is 25.0°, and ionic strength is 0.25; pH varied from an initial value of 7.8 to *ca.* 5.2.

ions produced to moles of Mn^{III}CyDTA consumed was found to be 0.999 ± 0.011 (three determinations). These results agree with the overall reaction

$$2Mn^{III}CyDTAOH_2^- + NO_2^- \rightarrow 2Mn^{II}CyDTA^{2-} + NO_3^- + 2H^+ + H_2O \tag{1}$$

Kinetics. Under conditions where both Mn^{II}CyDTA and nitrite were in large excess over Mn^{III}CyDTA plots of 1/Abs *vs.* time (where Abs represents the absorbance) were linear over 75–80% of the reaction as shown in Figure 1 where $k_{app} = \epsilon b\Delta(1/\text{Abs})/\Delta t$, $\epsilon = 407\ M^{-1}\ \text{cm}^{-1}$, and *b* is cell thickness in centimeters. Data in Figure 1 and Table I indicate that the reaction is second order in both $[Mn^{III}CyDTA]_0$ and $[NO_2^-]$. Plots of $k_{app}/[NO_2^-]$ *vs.* $[NO_2^-]$ (data in Table I) are linear with a zero intercept (within experimental error) where other variables are held constant. The rate was found to be independent of $[H^+]$ above pH 4.5. This is in agreement with Figure 1 where the lines are straight but the pH changed from *ca.* 7.8 to *ca.* 5.2 during the runs. Because the rate was pH independent and acetate buffer appeared to give a slight rate enhancement, most of the runs reported in this paper were made in the absence of any buffer.

Figure 2 shows the dependence of k_{app} on Mn^{II}CyDTA. The apparent rate constant, k_{app}, was found to be unaffected by using $NaNO_3$ to adjust ionic strength. Flushing solutions with nitrogen prior to the kinetic runs made no apparent difference in the results.

These results can be expressed in the rate law

$$\frac{d[Mn^{III}CyDTA^-]}{dt} = \frac{k_a[Mn^{III}CyDTA^-]^2[NO_2^-]^2}{k_b[Mn^{II}CyDTA^{2-}]^{2-} + [Mn^{II}CyDTA^{2-}]} \tag{2}$$

where

$$k_{app} = \frac{k_a[NO_2^-]^2}{k_b[Mn^{II}CyDTA^{2-}]^2 + [Mn^{II}CyDTA^{2-}]} \tag{3}$$

Values for k_a and k_b were calculated from eq 3 using a nonlinear least-squares program written by Dye and Nicely.[26] Data are shown in Table I. Values were found to be $k_a = (7.13 \pm 0.56) \times 10^2\ M^{-2}\ \text{sec}^{-1}$ and $k_b = (2.72 \pm 0.27) \times 10^2\ M^{-1}$.

Table I. Experimental and Calculated Rates of Reaction between Mn^{III}CyDTA and Nitrate at 25.0° and Ionic Strength 0.25 *M*[a]

	$k_{app}, M^{-1}\ \text{sec}^{-1}$	
$10^2[NO_2^-]$,[c] *M*	Exptl	Calcd[b]
5.04	48.8 48.7	49.0
4.03	31.3 31.8	31.3
3.30	20.1 20.4	20.9
3.02	17.8 17.7	17.6
2.02	8.25 8.05	7.83
1.01	2.02 2.01	1.96
0.50	0.55 0.53	0.48

	$k_{app}, M^{-1}\ \text{sec}^{-1}$	
$10^3[Mn^{II}CyDTA]$,[d] *M*	Exptl	Calcd[b]
4.99	10.1[e] 10.8[e]	9.75
8.11	31.8 31.2	29.9
9.97	20.1 20.4	20.9
12.0	15.3 15.3	15.3
13.3	12.5 12.5	12.7
16.0	8.25 9.12	9.12
19.9	6.05 6.01	6.07
23.9	4.42 4.43 4.36	4.32

[a] $[Mn^{III}CyDTA]_0$ varied in the range (5.2–5.8) × 10^{-4} *M*. [b] k_{app} was calculated using eq 3 where $k_a = (7.13 \times 10^2\ M^{-2}\ \text{sec}^{-1}$ and $k_b = 2.72 \times 10^2\ M^{-1}$. [c] $[Mn^{II}CyDTA] = 9.97 \times 10^{-3}\ M$. [d] $[NO_2^-] = 3.30 \times 10^{-2}\ M$. [e] For these two runs [nitrite] = 1.27 × 10^{-2} *M*.

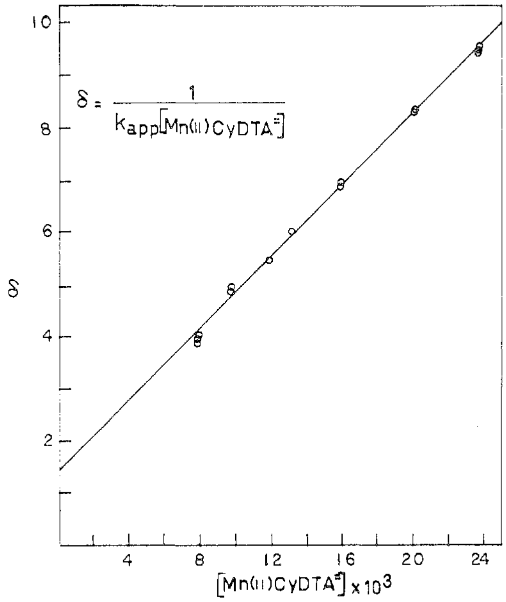

Figure 2. Relationship between k_{app} and Mn^{II}CyDTA concentration. [Nitrite] = 0.0330 *M*, temperature is 25.0°, and ionic strength is 0.25.

Dependence of k_{app} on $[Mn^{III}CyDTA]$. It was found that k_{app} showed a slight inverse dependence in initial Mn^{III}CyDTA concentration as shown by Table II. This slight dependence was noted at all concentrations of Mn^{II}CyDTA and nitrite studied and in the presence and absence of acetate buffer. The possibility that the reaction was photosensitive was ruled out by making parallel runs from the same reaction mixture where one solution was kept in the light path of the spectrophotometer almost continually while the other solution was kept in the dark

Table II. Dependence of k_{app} on $[\mathrm{Mn^{III}CyDTA}]_0$[a] at 25.0° and Ionic Strength 0.30 M

$10^4[\mathrm{Mn^{III}CyDTA}]_0$, M	k_{app}, M^{-1} sec^{-1}	$10^4[\mathrm{Mn^{III}CyDTA}]_0$, M	k_{app}, M^{-1} sec^{-1}
6.55	5.12	3.39	5.70
5.58	5.29	2.46	6.03

[a] $[NO_2^-] = 0.0114\ M$, $[\mathrm{Mn^{II}CyDTA}] = 7.58 \times 10^{-3}\ M$, $[\mathrm{OAc^-}] = 0.25\ M$, pH 5.53.

except for making quick absorbance readings. Results for the runs were identical. Values for $[\mathrm{Mn^{III}CyDTA}]_0$ calculated by extrapolating to zero time were always within experimental error of those calculated from dilution of the stock $\mathrm{Mn^{III}}$CyDTA solution. Repetitive scans of the spectra during a kinetic run showed only a decrease in the absorbance with no evidence of a shift in the peaks. These experiments tend to show that the inverse dependence in $[\mathrm{Mn^{III}CyDTA}]_0$ is experimentally valid although it is only a small perturbation on the system.

Initially one is tempted to explain the inverse dependence of k_{app} on $[\mathrm{Mn^{III}CyDTA}]_0$ by adding a $[\mathrm{Mn^{III}CyDTA}]$-dependent term to the denominator of eq 2, but this assignment is not consistent with observations made during the study. Plots of 1/Abs *vs.* time became nonlinear sooner at *high* concentrations of $\mathrm{Mn^{II}}$CyDTA, *low* concentrations of NO_2^-, and in runs made in a 10-cm cell where the initial concentration of $\mathrm{Mn^{III}}$CyDTA was the *lowest*. Any experimental conditions which caused k_{app} to be small increased the inverse dependence of k_{app} and showed greater earlier nonlinearity in plots of 1/Abs *vs.* time. An explanation that is more consistent with these observations is to propose a parallel path involving a first-order decomposition of $\mathrm{Mn^{III}}$CyDTA. When $\mathrm{Mn^{II}}$CyDTA and nitrite are in large excess the rate law would have the form

$$-\frac{\mathrm{d}[\mathrm{Mn^{III}CyDTA}]}{\mathrm{d}t} = k_{app}[\mathrm{Mn^{III}CyDTA}]^2 + k'[\mathrm{Mn^{III}CyDTA}]$$

The rate constants were evaluated by numerically integrating the above equation using the Dye and Nicely program.[26] It was found that in cases where plots of 1/Abs had considerable nonlinearity, the absorbance *vs.* time data could be fitted to eq 4 and gave a value for k' of about 3.1×10^{-4} sec^{-1}. For the data in Table II a value of 4.74 M^{-1} sec^{-1} was obtained for k_{app}.

Under the conditions of this study the inverse dependence in $[\mathrm{Mn^{III}CyDTA}]_0$ was not large enough to be evaluated with any confidence. Therefore no attempt was made to correct k_{app} values for this effect, and this is reflected in the relatively large overall standard deviation if the values of k_a and k_b.

Discussion

The kinetics and mechanisms of redox reactions of nitrogen(III) were the subject of a recent review.[27] For all the reactions discussed the order with respect to the metal ion oxidant varied between 0 and 1, inclusively, and in all cases the concentration of hydrogen ion appears in the rate law. The results reported in this paper appear to be unique in that it is second order in the metal ion oxidant and independent of pH. A second-order dependence in nitrite or nitrous acid is not uncommon and indicates that a dimeric nitrogen intermediate is involved as a reactive species. This is the third reported case of a redox reaction involving a second-order dependence in Mn(III) and the second case where both reactants are second order.[13,28] The previous case involved the oxidation of hydrazoic acid by aquomanganese(III) in perchloric acid medium. The overall stoichiometry of that reaction is 2 mol of HN_3 consumed by 2 mol of $\mathrm{Mn^{III}(aq)}$ to produce 3 mol of nitrogen.

The second-order dependence in nitrite as shown in eq 2 can be explained by proposing a mechanism that involves N_2O_4 as an intermediate with hydrophylic dismutation of this intermediate as the last slow step.[23] Such an intermediate will also explain the lack of hydrogen ion dependence in the rate law. The second-order dependence in $\mathrm{Mn^{III}}$CyDTA and inverse second-order dependence on $\mathrm{Mn^{II}}$CyDTA as well as an inverse first-order term in $\mathrm{Mn^{II}}$CyDTA suggest that a number of rapid equilibrium steps are involved in the mechanism prior to the rate-determining step. A mechanism that is consistent with these observations is

$$\mathrm{Mn^{III}CyDTA(OH_2)^-} + \mathrm{NO_2^-} \overset{K_1}{\rightleftharpoons} \mathrm{Mn^{III}CyDTA(NO_2)^{2-}} + \mathrm{H_2O} \quad (4)$$

$$2\mathrm{Mn^{III}CyDTA(NO_2)^{2-}} + \mathrm{H_2O} \overset{K_2}{\rightleftharpoons} \mathrm{Mn^{II}CyDTA(OH_2)^{2-}} + \mathrm{Mn^{III}CyDTA(N_2O_4)^{2-}} \quad (5)$$

$$\mathrm{Mn^{III}CyDTA(N_2O_4)^{2-}} + \mathrm{H_2O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mn^{II}CyDTA(OH_2)^{2-}} + \mathrm{N_2O_4} \quad (6)$$

$$\mathrm{N_2O_4} + \mathrm{H_2O} \xrightarrow{k_3} \mathrm{NO_2^-} + \mathrm{NO_3^-} + 2\mathrm{H^+} \quad (7)$$

Assuming a steady-state approximation for N_2O_4

$$-\frac{\mathrm{d}[\mathrm{Mn^{III}CyDTA(OH_2)^-}]}{\mathrm{d}t} = \frac{K_1{}^2K_2k_1[\mathrm{Mn^{III}CyDTA(OH_2)^-}]^2[\mathrm{NO_2^-}]^2}{(k_2/k_3)[\mathrm{Mn^{II}CyDTA(OH_2)^{2-}}]^2 + [\mathrm{Mn^{III}CyDTA(OH_2)^{2-}}]} \quad (8)$$

where

$$k_{app} = \frac{K_1{}^2K_2k_1[\mathrm{NO_2^-}]^2}{(k_2/k_3)[\mathrm{Mn^{II}CyDTA(OH_2)^{2-}}]^2 + [\mathrm{Mn^{II}CyDTA(OH_2)^{2-}}]} \quad (9)$$

and $k_a = K_1{}^2K_2k_1$ and $k_b = k_2/k_3$. A value of k_3 has been independently reported to be 1.0×10^3 sec^{-1}.[23] Therefore k_2 can be estimated to be $2.7 \times 10^5\ M^{-1}$ sec^{-1}. Since the value of k_2 is 10^3 smaller than the expected rate of water exchange[29] for $\mathrm{Mn^{II}CyDTA(OH_2)^{2-}}$, one must conclude that intermolecular electron transfer is rate determining for that step. Further analysis of the kinetic data yields little insight into the early steps of the mechanism.

The kinetics of the oxidation of nitrous acid by $\mathrm{Mn^{III}(aq)}$ showed a first-order dependence in both reactants[16] with no retarding effects on the rate with increasing $[\mathrm{Mn^{II}}]$ as was found with the oxidation of both H_2O_2 and HN_3 by $\mathrm{Mn^{III}(aq)}$. It was suggested that the radical(s) formed in the oxidation of nitrous acid by $\mathrm{Mn^{III}(aq)}$ was (were) much weaker oxidizing agent(s) than those formed in the previously studied systems. Since the $\mathrm{Mn^{III}}$CyDTA reduction potential is much less than that of aquomanganese(III) (0.81 *vs.* 1.51),[1,6] it would be expected that $\mathrm{Mn^{II}}$CyDTA would be readily oxidized by some radicals that would not oxidize $\mathrm{Mn^{II}(aq)}$. This explains the more complex kinetics observed in redox studies of complexed Mn(III) as compared to the aquomanganese(III) ion.

Reaction between HNO_2, $\mathrm{Mn^{II}}$CyDTA, and $\mathrm{Mn^{III}}$CyDTA. Below pH 4 the concentration of nitrous acid becomes significant. Between pH 2.5 and 4.0 it was found that $\mathrm{Mn^{II}}$CyDTA was rapidly oxidized to $\mathrm{Mn^{III}}$CyDTA by nitrous acid. This reaction leads to a much more complicated system. The reactions believed to be important are listed in Table III. When nitrite solutions with pH between 2.5 and 4.0 are mixed with either $\mathrm{Mn^{II}}$CyDTA or $\mathrm{Mn^{III}}$CyDTA, the $\mathrm{Mn^{III}}$CyDTA concentration rapidly comes to a pseudoequilibrium and then decreases very slowly with time. As expected such reactions are air sensitive. When left open to the air, the reaction mixture will remain colored for several days. When the reaction was run under nitrogen, the solution became decolorized

Table III. Reactions of Importance in the pH range 2.5–4.0

(1) $HNO_2 \rightleftharpoons H^+ + NO_2^- \quad pK_a = 2.95^a$
(2) $nH^+ + Mn^{II}CyDTA \rightleftharpoons Mn^{2+} + H_nCyDTA^b$
(3) $HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O \quad E^\circ = 1.00^c$
(4) $Mn^{III}CyDTA + e^- \rightleftharpoons Mn^{II}CyDTA \quad E^\circ = 0.81^d$
(5) $Mn^{II}CyDTA + HNO_2 + H^+ \rightleftharpoons Mn^{III}CyDTA + NO + H_2O^e$
(6) $2NO + O_2 \rightleftharpoons 2NO_2{}^f$
(7) $N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad k = 1.0 \times 10^3\ sec^{-1\ g}$
(8) $2NO_2 \rightleftharpoons N_2O_4 \quad K = 6.5 \times 10^{4\ g}$
(9) $2Mn^{III}CyDTA + NO_2^- + H_2O \rightleftharpoons 2Mn^{II}CyDTA + NO_3^- + 2H^+$

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after 1 day but the $Mn^{III}CyDTA$ could be regenerated by exposing the solution to air. This cycle could be repeated several times. These results suggest that, in the absence of oxygen, $Mn^{II}CyDTA$ simply catalyzes the disproportionation of nitrous acid, and, in the presence of oxygen, the overall reaction is the oxidation of nitrite to nitrate by molecular oxygen.

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Registry No. $Mn^{III}CyDTA^-$, 54182-32-0; NO_2^-, 14797-65-0; $Mn^{II}CyDTA^{2-}$, 14650-07-8.

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Dissociative–Associative Crossover for the Ligand-Substitution Mechanism in Octahedral Adducts of Niobium(V) and Tantalum(V) Halides[1,2]

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The neutral ligand-exchange reaction $MX_5 \cdot L + L^* \rightleftharpoons MX_5 \cdot L^* + L$ for the octahedral adducts $MX_5 \cdot L$ (M = Nb, Ta; X = Cl, Br) proceeds *via* a dissociative mechanism when L = Me_2O and *via* an associative mechanism when L = Me_2S, Me_2Se, Me_2Te. A different rate law is observed in each case and on going from Me_2O to the other ligands, activation parameters change abruptly (ΔH^* decreases by 11 kcal/mol and ΔS^* by 30–40 eu). Reaction rates vary according to the change in effective charge on the metal and obey the following reactivity sequences: dissociative mechanism, $MCl_5 << MBr_5$; associative mechanism, $MF_5 > MCl_5 > MBr_5$. For the associative mechanism, the reaction center exerts discrimination between the various nucleophiles. The proposed dissociative and associative reactions are respectively accelerated and slowed down when the ligand is sterically hindered.

Introduction

Substitution processes on octahedral systems were believed for many years to be exclusively dissociative. However, a number of reactions were then investigated which seemed to be best explained by an associative mechanism.[3-14] For these reactions which have not eventually been explained by another mechanism, the conclusions often are based on one type of evidence only (*i.e.*, either activation parameters, or rate law, or steric effects, etc.), this being usually due to difficulties inherent to the system under study.

We wish to report here on a system for which it was possible to collect a wide variety of data which are consistent with an associative mechanism. If a change in ligand occurs however, the same system can react according to a dissociative mechanism.

In dichloromethane and in chloroform, the dimeric niobium(V) and tantalum(V) halides react quantitatively with Lewis bases to form monomeric nonelectrolyte[15,16] adducts with 1:1 stoichiometry.[17] The ligand-exchange reactions examined can be described by the equation

$$MX_5 \cdot L + L^* \rightleftharpoons MX_5 \cdot L^* + L \quad (1)$$

where M = Nb, Ta; X = Cl, Br; L = Me_2O, Me_2S, Me_2Se, Me_2Te, Et_2O, Et_2S. The two sites of free and complexed