nmr spectra are recorded as a function of pH. A simple two-lined nmr spectrum corresponding to the uncomplexed ligand is observed for the clear, dark, red-brown solution at pH 0. A heavy, light brown precipitate forms at pH 1. Between pH 3 and 4 the precipitate changes to a darker brown and partially dissolves; the intensities of the free-ligand nmr peaks decrease and several relatively broad peaks appear between pH 4 and 9. Above pH 9 further precipitation occurs and only the free ligand peaks are observed.

Determination of the stoichiometry of the chelate by nmr techniques is complicated by partial molybdenum precipitation in the pH region where complex formation occurs. Calculations based on molybdenum titration data and the nmr spectral integral imply a 1:1 metal:ligand ratio in the complex. Although both *cis* and *trans* isomers of the dimeric complex are possible, inspection of molecular models of the isomers indicates that the two MIDA groups in the *trans* position should be more stable because steric repulsions exist between the methyl groups when the ligands are arranged in the *cis* configuration.

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A Kinetic and Equilibrium Study of the Reaction between Ethylenediaminetetraacetatomanganate(III) and Azide

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Ethylenediaminetetraacetatomanganate(III), $[\mathrm{Mn^{III}EDTA(OH_2)^-}]$, and azide were shown to react to form the complex azido(ethylenediaminetetraacetato)manganate(III), $[\mathrm{Mn^{III}EDTA(N_3)^{2-}}]$, with a formal equilibrium constant of 32.1 at 25° and an ionic strength of 0.25. The potassium salt, $\mathrm{K_2[Mn^{III}EDTA(N_3)]\cdot H_2O}$, was prepared and recovered for analysis. The infrared spectrum of the complex indicated that the compound was probably seven-coordinate. In solution this complex decomposed by an electron-transfer step to give ethylenediaminetetraacetatomanganate(II) and gaseous nitrogen. At $\mu = 0.25$ the kinetics of the formation of the azide complex and its decomposition were studied over the temperature range 6.5–30°. At all temperatures the ratio of the rate constants for the forward and backward reactions in the formation and decomposition of the azido complex was in good agreement with the equilibrium constant determined by an independent method.

Introduction

A few ethylenediaminetetraacetic acid (EDTA) type complexes of manganese(III) have recently been prepared.[1,2] They have been found to be quite stable in the crystalline form and to decompose only slowly in aqueous solution. These complexes are relatively strong oxidants and can be used to oxidize a variety of compounds. The mechanism of the oxidation of oxalate with *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III) has been investigated and was found to involve the interaction of the oxalate species with the manganese(III) complex as the rate-determining step rather than the electron-transfer step.[3] The reaction of $\mathrm{Mn^{III}EDTA}$ with excess ligand has been studied[4] and it was found that the complex oxidizes the excess free ligand rather than the coordinated ligand. This is just the opposite of what has been reported for most reactions of manganese(III) complexes[5] where the unimolecular decomposition of the complex is looked on as the rate-determining step.

The azide ion is quite unstable thermodynamically but is kinetically inert toward many oxidants. The azide ion is quantitatively oxidized by ceric ion to nitrogen gas,[6] while the reaction of azide with permanganate[7] is sluggish and gives a variety of products. Nitrous acid reacts with azide rapidly and completely to give nitrogen gas and nitrous oxide.[8]

Experimental Section

The EDTA was obtained from Geigy Chemical Corp. and was recrystallized twice from hot water and was air dried before use. Sodium azide from Eastman Organic Chemicals was used to prepare the stock solutions. The sodium azide was recrystallized and analyzed according to the methods given by Pepkowitz.[9] The recrystallized material was found to be 99.2% pure. Stock solutions of the sodium azide were prepared by adding weighed portions of sodium azide to distilled water and diluting to the mark in a volumetric flask.

The pH of solutions was adjusted with perchloric acid and carbonate-free sodium hydroxide solution. The ionic strength was

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[1] Y. Yoshino, A. Ouchi, Y. Tsunoda, and M. Kojima, *Can. J. Chem.*, **40**, 775 (1962).

[2] R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).

[3] M. A. Suwyn and R. E. Hamm, *ibid.*, **6**, 142 (1967).

[4] K. A. Schroeder and R. E. Hamm, *ibid.*, **3**, 391 (1964).

[5] W. A. Waters and J. S. Littler, "Oxidations in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 185–241.

[6] J. Martin, *J. Am. Chem. Soc.*, **49**, 2133 (1927).

[7] R. Dennis and D. Browne, *ibid.*, **26**, 577 (1904).

[8] G. Sommer, *Ber.*, **48**, 1843 (1915).

[9] L. P. Pepkowitz, *Anal. Chem.*, **24**, 900 (1952).

maintained at 0.25 with sodium perchlorate prepared by neutralizing perchloric acid with carbonate-free sodium hydroxide.

The potassium salt of ethylenediaminetetraacetatomanganate(III), $Mn^{III}EDTA(OH_2)^-$, was prepared as previously described.[2] The potassium salt of azido(ethylenediaminetetraacetato)manganate(III), $Mn^{III}EDTA(N_3)^{2-}$, was prepared in a manner similar to the preparation of the $Mn^{III}EDTA(OH_2)^-$ complex. One mole of potassium azide per mole of EDTA was added to an MnO_2–$Mn(NO_3)_2$–2(EDTA) slurry which had been cooled to −10°. Sufficient potassium hydroxide was slowly added to neutralize any excess acid as the mixture was allowed to stand at −10° in a cooler for 5 hr. After the excess MnO_2 was filtered off, an equal volume of cold ethanol was added to the remaining solution. The azido complex precipitated out immediately as a dark brown crystalline precipitate. The precipitate was washed with absolute ethanol and was air dried before analysis. The yield was about 65% based on the amount of potassium azide added. The salt was sent to Galbraith Laboratories for analysis. Duplicate analyses gave these results. *Anal.* Calcd for $K_2[Mn^{III}EDTA(N_3)] \cdot H_2O$: K, 16.23; Mn, 11.40; C, 24.93; H, 2.91; N, 14.55. Found: K, 16.20; Mn, 11.32; C, 24.97; H, 3.08; N, 14.49.

By dissolving the complex in 1 *M* azide solution at a pH of 4.5 the absorption spectrum of the azido complex was obtained. The complex was found to have an absorption maximum at 440 mμ which appeared as a shoulder on a larger charge-transfer band extending into the visible region from the ultraviolet. The molar absorptivity of the azido complex was obtained by dissolving constant weighed amounts of the potassium salt of the azido complex into azide solutions at a pH of 5 with increasing concentrations of azide ion. A plot of absorbance at 440 mμ *vs.* azide concentration leveled off at high azide concentrations to give a value of 1448 M^{-1} cm^{-1} as the molar absorptivity for the azido complex. The aquo complex had previously been found to have an absorption maximum at 397 mμ. Table I gives the molar absorptivities of the involved manganese compounds at the two wavelengths.

TABLE I

MOLAR ABSORPTIVITIES (M^{-1} CM^{-1})

	440 mμ	397 mμ
$Mn^{III}EDTA(N_3)^{2-}$	1448	855
$Mn^{III}EDTA(OH_2)^-$	226	345
$Mn^{II}EDTA(OH_2)^{2-}$ [a]	~0	~0

[a] The proof that the manganese(II) compound with EDTA is seven-coordinate in the solid has been given by S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964), and evidence that the compound also is seven-coordinate in solution has been given by L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5046 (1964). In this paper we shall therefore assume seven-coordination for this compound.

The reaction rate was determined by observing the change in absorbance at the absorption maximum of $Mn^{III}EDTA(OH_2)^-$ (497 mμ) and $Mn^{III}EDTA(N_3)^{2-}$ (440 mμ) with a Beckman Model DU spectrophotometer which was fitted with a constant-temperature cell block. The rates determined at both wavelengths were identical within experimental error; however, much better precision was obtained at 440 mμ because of the greater change in the absorption at this wavelength. The absorbance was measured against a blank having the same composition as the sample except for the manganese(III) complex. Solutions containing the azide ion at a given pH and ionic strength were prepared by adding the proper amount of sodium perchlorate to bring the ionic strength to 0.25 and the proper amount of stock azide solution and then by diluting to volume with distilled water. A 25-ml volume of the prepared solution was placed in each of the reaction flasks which were placed in a constant-temperature bath, maintained within ±0.02° of the desired temperature. Nitrogen gas which had been passed through a chromous ion scrubber was bubbled through the solution to remove the dissolved oxygen; weighed portions of the potassium salt of the complex were introduced into the flasks and they were stirred by means of a Teflon-coated stirring bar. An aliquot was then placed in a spectrophotometer cell which was placed in the constant-temperature cell block maintained at ±0.05° of the desired temperature.

Ionic strengths were calculated assuming a −1 charge for the $Mn^{III}EDTA(OH_2)^-$ complex and a −2 charge for the $Mn^{III}EDTA(N_3)^{2-}$ complex. The concentration of the azide ion was calculated by using dissociation constants calculated from the values reported by Hantzch.[10]

The reaction was studied in the pH range 3.0–5.0. The $Mn^{III}EDTA(OH_2)^-$ complex is in equilibrium with the hydroxo complex $Mn^{III}EDTA(OH)^{2-}$ and therefore the reaction had to be carried out at pH values less than 5.0 so that the hydroxo complex concentration does not become important. No reactions were carried out at pH values less than 3.5 since the azide ion concentration becomes vanishingly small in solutions more acid than this. All pH readings were made with a Beckman Research pH meter equipped with a calomel electrode filled with 4 *M* sodium chloride to prevent precipitation of potassium perchlorate.

No photochemical reaction was found to result when the sample was left in the path of the light beam in the spectrophotometer between readings. The products of the reaction were found to be nitrogen gas and $Mn^{II}EDTA(OH_2)^{2-}$. The $Mn^{II}EDTA(OH_2)^{2-}$ was determined by the addition of PbO_2 to completely reacted samples at 5°. This produced a red color which after filtering off the excess PbO_2 gave an absorption spectrum identical with that given by an $Mn^{III}EDTA(OH_2)^-$ complex. This complex then slowly reacted with the excess azide in the solution to form $Mn^{III}EDTA(N_3)^{2-}$ complex indicating that the manganese(II) species was the aquo rather than the azido complex. The gas liberated during the reaction was bubbled through a $Ba(OH)_2$ solution but no precipitate was formed. The gas was also passed through an Ascarite tube after being dried, but there was no noticeable increase in weight of the tube, indicating that there was no carbon dioxide produced in the reaction. A manometric method was used to determine the amounts of gas given off during the course of the reaction. Assuming this gas to be nitrogen, calculation of the results of five experiments gave 1.48 moles of N_2 per mole of $Mn^{III}EDTA(OH_2)^-$ with a standard deviation of 0.04.

No precipitation resulted when completely reacted samples were treated with semicarbazide hydrochloride or 2,4-dinitrophenylhydrazine indicating that formaldehyde was not a product in the reaction. A similar completely reacted solution when tested with *n*-butyraldehyde and acetone gave no indication of hydroxylamine as a product.

Results and Discussion

The identification of the products given above permits the writing of the stoichiometric reaction

$$2Mn^{III}EDTA(OH_2)^- + 2N_3^- \longrightarrow 2Mn^{II}EDTA(OH_2)^{2-} + 3N_2$$

The azide ion in the $K_2[Mn^{III}EDTA(N_3)] \cdot H_2O$ complex is believed to be coordinated to the manganese(III) ion due to the fact that the infrared spectrum of the complex shows a strong absorption in the 2040–2070-cm^{-1} region which is attributed to the asymmetric stretching motion of the azide ion. A noncoordinated azide ion should absorb in the 2140-cm^{-1} region.[11] The antisymmetric carboxylate stretching region is similar to that reported for the $K[Mn^{III}EDTA(OH_2)]$ complex.[1] A characteristic strong absorption of the carboxylate group is observed in the 1600–1700-cm^{-1}

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(10) A. Hantzch, *Ber.*, **32**, 3066 (1899).

(11) D. A. Dows, E. Whittle, and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1475 (1955).

region. The fine structure is rather complicated with three major peaks at 1620, 1640, and 1670 cm^{-1}. If one of the carboxylate groups were not coordinated to the manganese(III), an absorption would be expected to appear around 1750 cm^{-1} as is found in the Co^{III}-EDTABr^{2-} complex where one of the carboxylate groups is not coordinated.[12]

The above facts appear to be evidence for the existence of a seven-coordinated manganese(III) ion since it appears that all of the carboxylate groups and the azide ion are coordinated to the metal. If one looks at a model of the complex, it is readily apparent that it is unlikely that all of the carboxylate groups could be coordinated and still have one of the nitrogens of the EDTA not coordinated.

When the azido complex was added to a 0.3 *M* azide solution at a pH of 4.5 and a temperature of 25° and the absorbance at 440 mμ was recorded as a function of time, a plot of log (absorbance) *vs.* time had the appearance of the curve shown in Figure 1. The slow portion of the plot is linear, indicating a process that is first order in the absorbing species, which in this case is primarily Mn^{III}EDTA(N$_3$)$^{2-}$. When the pH, ionic strength, and the starting concentration of the azido complex were kept constant and the azide concentration was varied from 0.15 to 0.50 *M*, the slope of the straight-line portion of the plot did not vary, indicating that it was independent of the azide concentration. When the ionic strength, azide concentration, and starting concentration of the azido complex were held constant while varying the pH from 3.5 to 5.0, the slope also remained constant.

In order to look at the equilibrium step involved, K[Mn^{III}EDTA(OH$_2$)] was added to an azide solution at 20° and the absorbance at 440 mμ was recorded as a function of time. A plot of log (absorbance) *vs.* time for the data is shown in Figure 2. As can be seen, the absorbance increases rapidly and then falls off at a much slower rate. The slower portion of the plot is once again linear, indicating first order in the absorbing species. The straight-line segment was extrapolated to zero time and the logarithm of the difference between the experimentally observed absorbance and the extrapolated value at the same time was plotted *vs.* time. Figure 3 shows such a plot. The first portion of the plot is straight, only curving later where taking the differences would be inaccurate.

On the basis of the above observations, the mechanism is proposed

$$\mathrm{Mn^{III}EDTA(OH_2)^- + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{III}EDTA(N_3)^{2-} + H_2O} \quad (1)$$

$$\mathrm{Mn^{III}EDTA(N_3)^{2-} \xrightarrow{k_2} Mn^{II}EDTA(OH_2)^{2-} + N_3^0} \quad (2)$$

$$\mathrm{2N_3^0 \xrightarrow{k_r} 3N_2} \quad (3)$$

where k_r is very large compared to k_1, k_{-1}, and k_2. If k_1, k_{-1}, and k_2 do not differ greatly from one another, there is no simple integrated solution or quantities which may be plotted to solve for k_1 and k_{-1}. However, k_2 may be identified with the slow, linear portion of the log (absorbance) plots when either the axido complex or the aquo complex is dissolved in azide solution. It was found that at the same temperature the slopes of

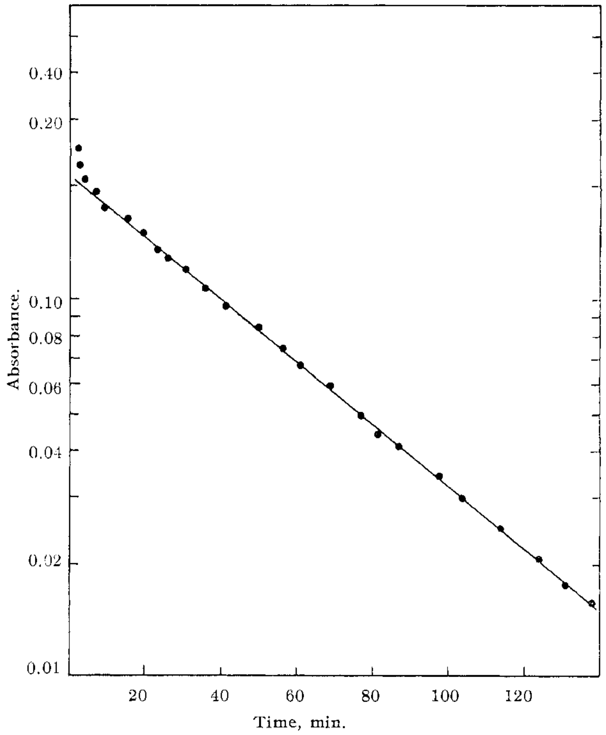

Figure 1.—Absorbance at 440 mμ (on a logarithmic scale) plotted against time for the reaction of 1.93 × 10^{-4} *M* [Mn^{III}-EDTA(N$_3$)$^{2-}$] in 0.3 *M* NaN$_3$ at 20° and pH 4.5.

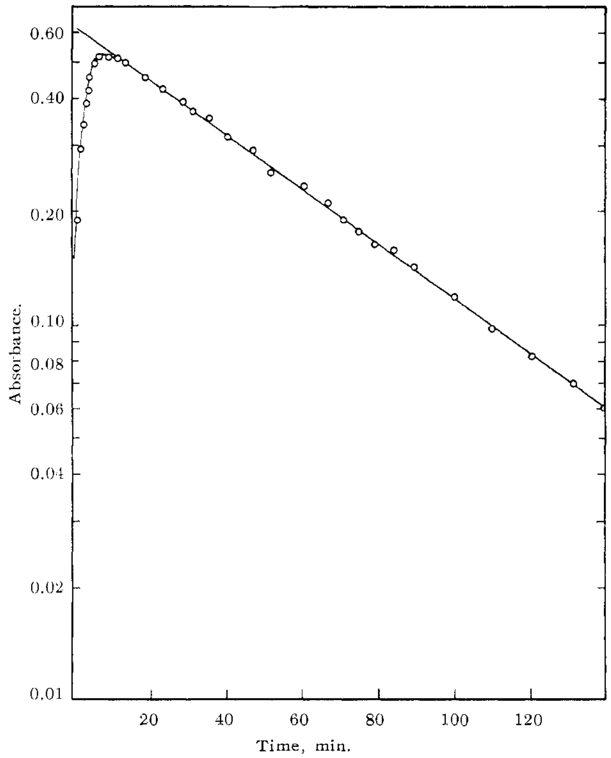

Figure 2.—Absorbance at 440 mμ (on a logarithmic scale) plotted against time for the reaction of 4.35 × 10^{-4} *M* [Mn^{III}-EDTA(OH$_2$)$^-$] with 0.4 *M* NaN$_3$ at 25° and pH 4.5.

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[12] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 457 (1953).

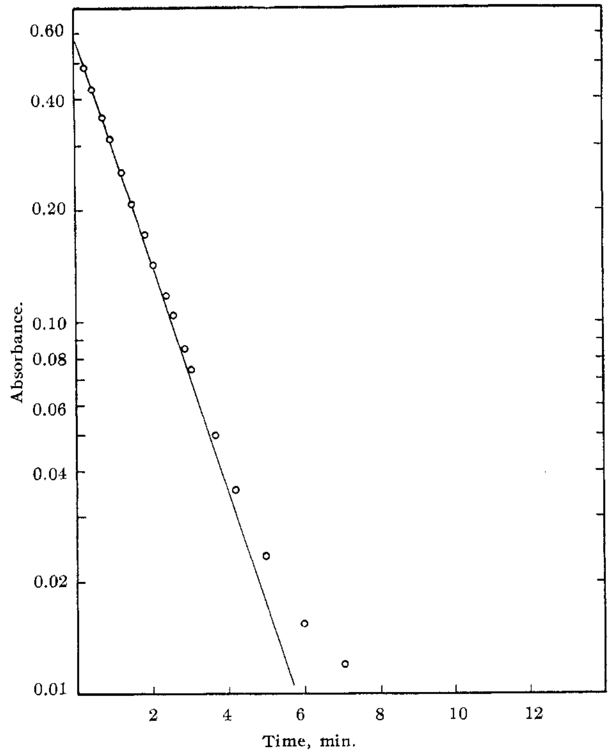

Figure 3.—Difference in absorbance at 440 mμ (on a logarithmic scale) plotted against time for the early points in the reaction of 4.35 × 10^{-4} *M* [$Mn^{III}EDTA(OH_2)^-$] with 0.4 *M* NaN_3 at 25° and pH 4.5.

the slow portion of such plots were within experimental error of each other.

Under the conditions of large excess of N_3^- ion, the slope of the straight line in Figure 3 would be equal to $(k_1[N_3^-] + k_{-1})/2.3$. It was found experimentally that the slope of this line increased with increasing azide ion concentration which would support this equation. Since the ratio k_1/k_{-1} should be equal to the equilibrium constant defined by

$$K_{eq} = \frac{[Mn^{III}EDTA(N_3)^{2-}]}{[Mn^{III}EDTA(OH_2)^-][N_3^-]}$$

we have a set of equations we can use to solve for k_1 and k_{-1} if we evaluate K_{eq}

$$k_1/k_{-1} = K_{eq}$$

$$k_1[N_3^-] + k_{-1} = k_{obsd}$$

The equilibrium constant was evaluated by dissolving weighed amounts of $K_2[Mn^{III}EDTA(N_3)]\cdot H_2O$ in solutions of varying concentrations of stock azide solution and recording the absorbance at 440 and 497 mμ at a time when the system has reached equilibrium as evidenced by the fact that the log (absorbance) plots had become straight. The pH was also determined to permit calculation of the azide ion concentration. From the absorbances at the two wavelengths and the molar absorptivities of the two complexes at these two wavelengths, the concentration of each species can be calculated. From these concentrations and the azide ion concentration, the equilibrium constant can be evaluated. The constant was evaluated over the temperature range 6.5–30.0°. Fifteen different azide concentrations over the range 0.05–0.50 *M* were run at each temperature. The values determined are given in Table II.

TABLE II

VALUES OF K_{eq} CALCULATED AT DIFFERENT TEMPERATURES

Temp, °C	K_{eq}	Std dev
6.5	28.3	0.23
10.0	28.9	0.22
15.0	30.0	0.21
20.0	31.2	0.29
25.0	32.1	0.33
30.0	33.5	0.23

The following differential equations can be written to describe the mechanism proposed in eq 1–3 assuming that k_r is very large

$$\frac{d[Mn^{III}EDTA(OH_2)^-]}{dt} = -k_1[Mn^{III}EDTA(OH_2)^-]\,[N_3^-] + k_{-1}[Mn^{III}EDTA(N_3)^{2-}]$$

$$\frac{d[Mn^{III}EDTA(N_3)^{2-}]}{dt} = -k_{-1}[Mn^{III}EDTA(N_3)^{2-}] + k_1[Mn^{III}EDTA(OH_2)^-][N_3^-] - k_2[Mn^{III}EDTA(N_3)^{2-}]$$

$$\frac{d[Mn^{II}EDTA(OH_2)^{2-}]}{dt} = k_2[Mn^{III}EDTA(N_3)^{2-}]$$

Numerical approximation methods can be used to solve these linear differential equations. One such method is commonly called the Runge–Kutta[13] method. A computer program was set up to take the estimated values of the rate constants, k_1, k_{-1}, k_2, and the starting concentrations of $Mn^{III}EDTA(OH_2)^-$ and N_3^- and solve for the concentrations of $Mn^{III}EDTA(OH_2)^-$, $Mn^{III}EDTA(N_3)^{2-}$, and $Mn^{II}EDTA(OH_2)^{2-}$ as a function of time. Using the molar absorptivities of the three species, the program then computed the absorbance as a function of time. These values were compared with the experimental values and the rate constants adjusted until the best fit was obtained between the computed absorbance values and the experimental values. Since k_2 was evaluated directly from the log (absorbance) plots, k_1 and k_{-1} were the constants which needed to be varied the most. They were adjusted with no further reference to the relationship $K_{eq} = k_1/k_{-1}$ once the first estimate was made. The purpose of this was to see how well the ratio would agree with the independently measured equilibrium constant.

In general, at each temperature that the reaction was studied, 20 experimental runs with varying concentration of azide, pH, and starting concentration of the $Mn^{III}EDTA(OH_2)^-$ complex were run and the values of k_1 and k_{-1} were adjusted until one set of values gave the best fit for all 20 experiments. The value for k_2 was taken as the average value obtained for all 20 experiments. It was found that the calculated curve was quite sensitive to the values of k_1 and k_{-1} used. Figure 4 shows a plot of absorbance *vs.* time for an experimental run, the calculated values, and the calculated values using a value for k_1 which was 10% greater than

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[13] H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1956, p 486.

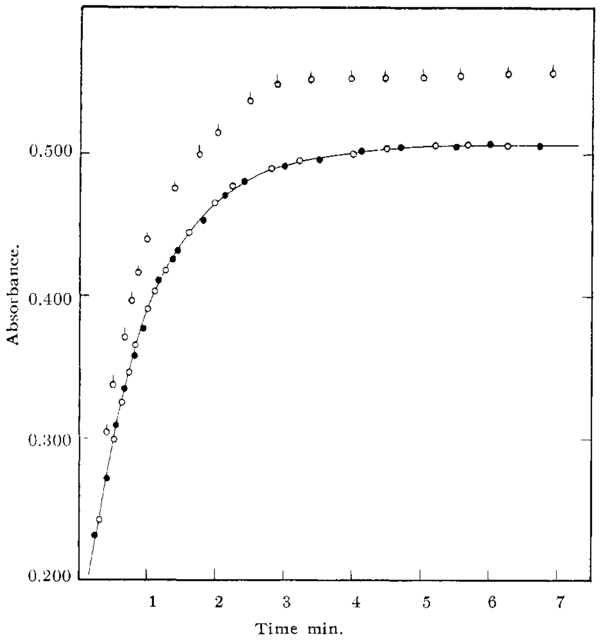

Figure 4.—Absorbance at 440 mμ plotted against time for the reaction of 3.9×10^{-4} *M* $[Mn^{III}EDTA(OH_2)^-]$ with 0.4 *M* NaN_3 at 20°: ○, observed; ●, calculated; ȯ, calculated with $k_1' = 1.1k_1$.

the final value for k_1. It can be seen that changing k_1 by 10% had a fairly large effect on the calculated curve.

The values of the rate constants were calculated over the temperature range 6.5–30.0° and are shown in Table III. A comparison between the ratio of k_1 to k_{-1} and the values found for the equilibrium constant reported in Table II shows them to be fairly close. The data were plotted according to the method of absolute reaction rates and the slopes and intercepts were determined by the method of least squares. Table IV shows the activation parameters and their standard deviations that were calculated.

TABLE III

RATE CONSTANTS AT VARIOUS TEMPERATURES

	Temp, °C					
	6.5	10.0	15.0	20.0	25.0	30.0
k_1, M^{-1} sec^{-1} × 10	0.22	0.29	0.45	0.71	1.03	1.57
k_{-1}, sec^{-1} × 10^3	0.73	0.94	1.46	2.23	3.18	4.74
k_2, sec^{-1} × 10^4	0.86	1.20	2.15	3.63	5.99	9.80
k_1/k_{-1}	30.1	30.4	31.1	31.8	32.4	33.1

The thermodynamic values for reaction 1 can be calculated in two ways. First from the equilibrium constants of the reactions at various temperatures, and second from the activation parameters of the forward and backward reactions as given in Table IV. The results of these calculations are shown in Table V. The agreement between the two sets of values is considered to be excellent considering the uncertainty in the rate constants. This in no way casts any doubt on the proposed mechanism.

TABLE IV

ACTIVATION PARAMETERS OF REACTIONS AND THEIR STANDARD DEVIATIONS

	ΔH^*, kcal mole^{-1}	ΔS^*, cal deg^{-1} mole^{-1}
k_1	13.7 ± 0.86	−17.1 ± 0.92
k_{-1}	13.0 ± 0.53	−26.3 ± 0.76
k_2	17.1 ± 0.97	−20.6 ± 1.08

TABLE V

THERMODYNAMIC VALUES FOR REACTION 1

	Calcd from equilibrium constant	Calcd from activation parameters
$\Delta G°$, kcal mole^{-1}	2.01 ± 0.3	2.0 ± 0.6
$\Delta H°$, kcal mole^{-1}	1.28 ± 0.5	0.7 ± 1.0
$\Delta S°$, cal deg^{-1} mole^{-1}	11.2 ± 0.5	9.2 ± 1.2

A mechanism might be written which involved the unimolecular decomposition of $Mn^{III}EDTA(OH_2)^-$ rather than the azido complex. However, this reaction has been studied[3] and the activation parameters and rate constants are such that the data cannot be fitted using them. Also, the products of that reaction were found to be CO_2 and formaldehyde which were not detected as products in this investigation. One other possible product of the azide oxidation could be hydroxylamine but this too was not found as a product. The N_3^0 radical has been detected spectroscopically by Thrush.[14] It has been proposed as the initial product in the reactions of the type $MN_3 \rightarrow M^0 + N_3^0$, where M^+ is a metal ion such as Ag^+ or Cu^+.[15] In the study of the electrolysis of potassium azide using $N^{14}N^{15}N^{14}$, it was found that no N_2^{15} was formed[16] but rather N^{14}_2 + $2N^{15}N^{14}$, which is consistent with a reaction such as that given in eq 3.

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(15) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959).

(16) K. Clusis and H. Schumacher, *Helv. Chim. Acta*, **41**, 972 (1958).