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Decomposition of the Ethylenediaminetetraacetate Complex of Manganese(III)[1]

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The slow decomposition of manganese(III) ethylenediaminetetraacetate complex was studied by spectrophotometric methods. The observed kinetics were explained by assuming three parallel reactions all of which were first order in the complex concentration when above 2 mmoles/l. The rate law was found to be: decomposition rate = $k_1\alpha_3[\text{EDTA}_f]\cdot[\text{Mn}^{\text{III}}\text{Y}] + k_2[\text{Mn}^{\text{III}}\text{Y}] + k_3[\text{EDTA}_f][\text{Mn}^{\text{III}}\text{Y}]^2/(K_3 + [\text{Mn}^{\text{III}}\text{Y}])$, with rate constants $k_1 = 0.60$ sec.$^{-1}$ M^{-1}, $k_2 = 1.70 \times 10^{-5}$ sec.$^{-1}$, $k_3 = 2.62 \times 10^{-3}$ sec.$^{-1}$ M^{-1}, $K_3 = 0.51 \times 10^{-3}$ M. The products of all the steps were found to be carbon dioxide, formaldehyde, and manganese(II) complex. The previously reported inhibition due to manganese(II) was shown to be due to its effect in complexing free EDTA. The difference in the rates due to terms one and three of the rate law was explained by the protonation of the free EDTA. It was necessary to invoke a steady-state mechanism to explain the variation of the rate with the concentration of the manganese(III) complex.

In an investigation of the analytical applications of the ethylenediaminetetraacetate complex of manganese(III), Pribil and co-workers[5,6] found that the complex slowly decomposed. Yoshino and others[7] isolated the complex and found the decomposition was enhanced by heat, light, and traces of manganese(II) ion. Studies of the oxalato complexes of manganese(III) showed[8,9] that the decomposition was dependent on the concentrations of oxalate and hydrogen ions. Decomposition of the tartrate[10] and glycolate[11] complexes of manganese(III) was found to be first order in the complex concentration in the presence of excess complexing agent and to be inhibited by the addition of manganese(II) ion.

The investigation reported in this paper was started as a detailed study of the manganese(III) ethylenediaminetetraacetate complex as a function of the various solution variables with the view of trying to understand the effect of manganese(II) ion which appeared strange in the papers reported previously.

Experimental

Reagent grade potassium permanganate, manganese(II) perchlorate, and ethylenediaminetetraacetic acid disodium salt ($\text{Na}_2\text{H}_2\text{Y}$) were used to prepare the complex in solution. The pH was adjusted with perchloric acid or carbonate-free sodium hydroxide solution. The ionic strength was maintained at 0.10 with sodium perchlorate made by neutralizing perchloric acid with carbonate-free sodium hydroxide solution.

The decomposition rate was determined by observing the change in absorption at 490 mμ with a Beckman Model DU spectrophotometer. The molar absorbancy index was found to be 444 by titrating the iodine liberated when the complex reacted with excess potassium iodide. Sodium thiosulfate, standardized against the KMnO_4 solution used in preparing the complex, was used to titrate the iodine in a dead-stop titration. Stock solutions and samples were kept in a constant temperature bath and thermostated water was pumped through the cell compartment of the spectrophotometer with the temperature controlled at 20.00 ± 0.05°. No photochemical reaction was found to result from ordinary room light or from light absorbed when samples were left exposed to the light beam in the spectrophotometer between absorption readings.

Reaction vessels consisted of 250-ml. erlenmeyer flasks which were fitted with a pressure system for the purpose of taking samples into a cuvette without removing the flask from the thermostat.

The complex was prepared in solution at the start of each kinetic run. The manganese(II) ion, EDTA, acid or base, and sodium perchlorate were added to the flask and diluted to give a final volume of 200 ml. A measured volume of the standard permanganate solution was added to the mixture to prepare the complex and start the reaction.

In order to determine the rate of a reaction, eight to twelve absorbance readings were taken over a period of time involving about a loss of $^1/_4$ in absorbance. The observed pseudo-first-order rate constant was found by plotting $-\ln A$ against the time, using least squares to determine the slope of the line. This was possible because samples reacting for a long period of time reached zero absorbance at 490 mμ.

Ionic strengths were calculated assuming zero charge on the $\text{Mn}^{\text{III}}\text{Y}$ complex and a minus one charge on the $\text{Mn}^{\text{II}}\text{Y}$ complex. The concentrations of the various EDTA species (H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}) were calculated using dissociation constants reported by Schwarzenbach.[12] The concentration of free EDTA in solution was calculated by assuming one to one complexing of manganese and EDTA.

The decomposition of the complex was studied in the pH range from 2 to 5. Some difficulty was encountered with precipitation of H_4Y in the most acid of these solutions. All pH readings were taken with a Beckman Model G pH meter equipped with a calomel electrode filled with 4 M sodium chloride to avoid difficulty with precipitation of potassium perchlorate at the liquid junction.

With the exception of the three lowest points plotted in Fig. 2, the rate determinations reported in this paper were run under conditions of excess free EDTA (pseudo first order). In making calculations the assumption was made that the free EDTA concentration did not change. Within the accuracy obtainable in kinetic runs this was completely justified in all cases.

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[5] R. Pribil and J. Horacek, *Collection Czech. Chem. Commun.*, **14**, 454, 626 (1949).

[6] R. Pribil and E. Hornychova, *ibid.*, **15**, 456 (1950).

[7] Y. Yoshino, Y. Tsunodu, and A. Oushi, *Bull. Chem. Soc. Japan*, **34**, 1194 (1961).

[8] F. R. Duke, *J. Am. Chem. Soc.*, **69**, 2885 (1947).

[9] H. Taube, *ibid.*, **70**, 1216 (1948).

[10] T. N. Srivastava, *Z. physik. Chem.*, **209**, 22 (1958).

[11] T. N. Srivastava, *ibid.*, **211**, 251 (1959).

[12] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

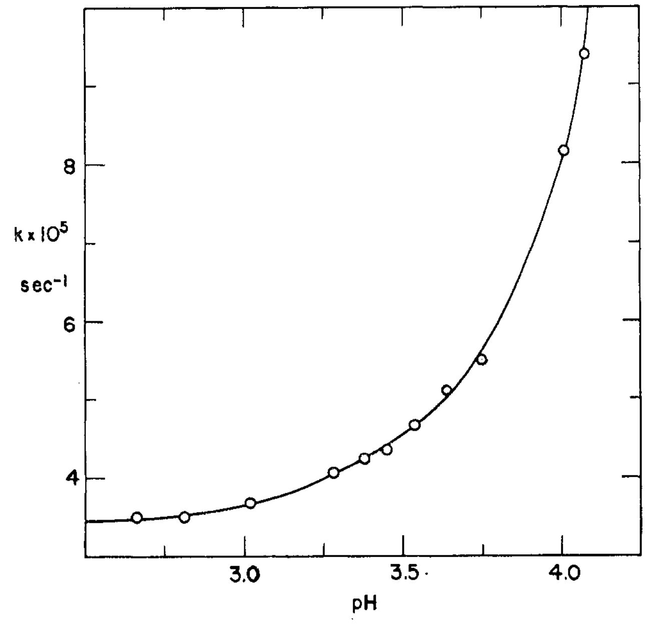

Fig. 1.—Pseudo-first-order rate constant for decomposition of ethylenediaminetetraacetate complex of Mn(III) as a function of pH: $[EDTA_f] = 1.0 \times 10^{-2}\ M$, $[Mn^{III}Y] = 1.0 \times 10^{-3}\ M$.

Results

Hydrogen Ion Dependence.—When samples were prepared so that the concentrations of $Mn^{II}Y$, $Mn^{III}Y$, and free EDTA in any one series were constant, the plot of pH *vs.* the observed first-order rate constant had the general shape shown in Fig. 1. The curve was fitted by assuming that the more protonated species of EDTA (H_4Y, H_3Y^-, and H_2Y^{2-}) reacted in such a way that the rate constant was the same for all and that HY^{3-} reacted with a rate constant approximately 200 times as great. The fraction of the HY^{3-} present in solution, α_3, was calculated using the ionization constants reported by Schwarzenbach[12] at 20° and an ionic strength of 0.10. In the pH range studied, HY^{3-} accounted for 2% or less of the total free EDTA, and the concentration of Y^{4-} was negligible.

The "cage structure" proposed by Chapman and co-workers[13] for EDTA can be used to explain the great increase in rate constant from the more protonated species to HY^{3-}. The HY^{3-} ion has two acetate ions at one end free to react, while the more protonated species have the acetate groups either protonated or tied up by the hydrogen bond to the hydrogen on the nitrogen, in the "cage structure."

EDTA Dependence.—The concentration of the free EDTA is represented in this paper by $[EDTA_f]$. When the concentrations of the manganese(II) and manganese(III) complexes were held constant and the concentration of free EDTA was increased, the reaction was found to be first order in free EDTA as is shown in Fig. 2. When the $[EDTA_f]$ was held constant and manganese(II) was added, the reaction became slower. However, when the added ion was zinc(II) instead of manganese(II) essentially the same inhibition occurred, indicating that the decrease in speed was due to the decrease in $[EDTA_f]$. When the $[EDTA_f]$ was held constant and excess $Mn^{II}Y$ was added the observed pseudo-first-order rate constant was not significantly altered. The intercept at the extrapolation of the graph in Fig. 2 to zero $[EDTA_f]$ indicates a reaction occurring that is not dependent upon EDTA.

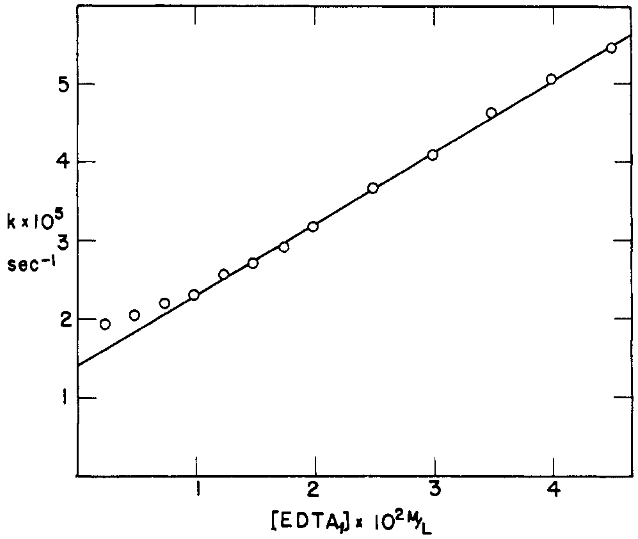

Fig. 2.—Pseudo-first-order rate constant for decomposition of ethylenediaminetetraacetate complex of Mn(III) as a function of free EDTA concentration: $[Mn^{III}Y] = 4.75 \times 10^{-4}\ M$, pH 3.0.

$Mn^{III}Y$ Dependence.—The decomposition of Mn^{III}-Y was found to be nearly first order at higher concentrations of the complex; however, when the initial concentration of the manganese(III) complex was decreased while keeping the other concentrations constant, the observed rate constant was found to decrease as shown in Fig. 3, where the observed rate constant is plotted as a function of the initial concentration of the complex, $Mn^{III}Y$. This dependence upon $Mn^{III}Y$ concentration can be explained by using a steady-state mechanism. If

$$Mn^{III}Y + EDTA_f \underset{k_{-3}}{\overset{k_3'}{\rightleftharpoons}} B$$

$$B + Mn^{III}Y \xrightarrow{k_4} 2Mn^{II}Y + \text{oxidation products}$$

where B is a reactive intermediate of negligible concentration. A steady-state approximation gives

$$\frac{d[B]}{dt} = k_3'[Mn^{III}Y][EDTA_f] - k_{-3}[B] - k_4[B][Mn^{III}Y] = 0 \quad (1)$$

$$[B] = \frac{k_3'[Mn^{III}Y][EDTA_f]}{k_{-3} + k_4[Mn^{III}Y]} \quad (2)$$

the disappearance of the complex can be expressed as

$$-\frac{d[Mn^{III}Y]}{dt} = 2k_4[B][Mn^{III}Y] \quad (3)$$

substitution of the value of [B] from (2) gives

$$-\frac{d[Mn^{III}Y]}{dt} = \frac{2k_3'k_4[Mn^{III}Y]^2[EDTA_f]}{k_{-3} + k_4[Mn^{III}Y]} \quad (4)$$

This expression would appear to become first order in

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(13) D. Chapman, D. R. Lloyd, and R. H. Prince, *Proc. Chem. Soc.*, 336 (1962); *J. Chem. Soc.*, 3645 (1963).

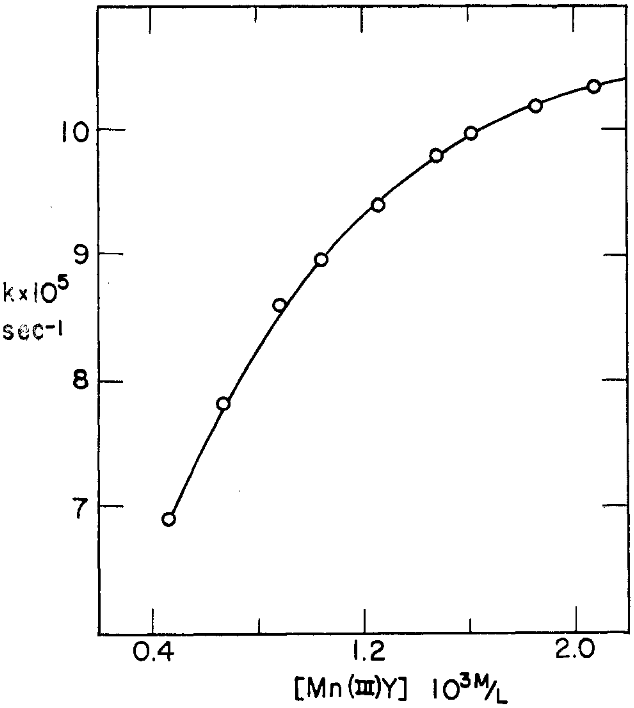

Fig. 3.—Pseudo-first-order rate constant for decomposition of ethylenediaminetetraacetate complex of Mn(III) as a function of beginning Mn(III) complex concentration: $[\mathrm{EDTA}_f] = 4.1 \times 10^{-2}\ M$, pH 3.0.

TABLE I

FIRST-ORDER RATE CONSTANTS EXPRESSED AS $k \times 10^5$ SEC.$^{-1}$

	Sample 1	Sample 2	Sample 3
$[\mathrm{EDTA}_f] \times 10^2$, M	1.20	1.70	2.20
pH	2.98	3.05	3.12
k (20.0°)	4.2	5.2	6.4
k (24.9°)	7.3	9.1	11.0
k (30.7°)	13.6	16.4	19.7
k (35.7°)	22.2	28.6	34.3
E_A, kcal./mole	19.0	19.1	18.9

$\mathrm{Mn^{III}Y}$ concentration at higher concentrations as observed experimentally.

Temperature Dependence.—Three different samples were studied at four different temperatures over a 15° range. The activation energies were calculated for each of these samples and are shown in Table I.

Ionic Strength Dependence.—As the ionic strength increased, the rate of decomposition increased. The ionic strength dependence was more pronounced at higher concentrations of free EDTA and higher values of pH. The literature[14] values of the ionization constants of EDTA at different ionic strengths indicate that the fraction of $\mathrm{HY^{3-}}$ increases as the ionic strength increases. It was felt that the entire increase in the observed rate with ionic strength could be attributed to this change in the fraction $\mathrm{HY^{3-}}$. Due to the difficulty of trying to get suitable kinetic data at various ionic strengths, the ionic strength of each experimental solution was adjusted so that it would be approximately 0.10 at 20° at the pH of the particular experimental solution.

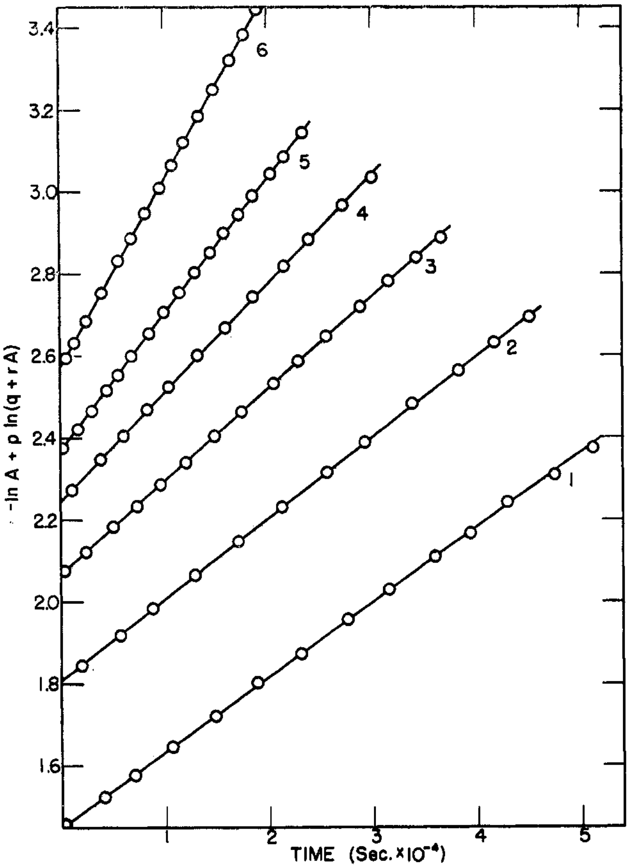

Fig. 4.—Plot of eq. 6 for experimental data.

Interpretation and Discussion

Rate Expression.—From the foregoing preliminary investigations it was apparent that three separate rate processes would need to be visualized to explain the kinetics; one dependent on the triply charged EDTA and first order in the complex, one independent of EDTA and first order in the complex, and one dependent on the more protonated species of EDTA and first order in the complex only at sufficiently high concentrations of the complex.

The total rate expression which results from these considerations and eq. 4 is

$$-\frac{\mathrm{d}[\mathrm{Mn^{III}Y}]}{\mathrm{d}t} = k_1\alpha_3[\mathrm{Mn^{III}Y}][\mathrm{EDTA}_f] + k_2[\mathrm{Mn^{III}Y}] + \frac{k_3[\mathrm{Mn^{III}Y}]^2[\mathrm{EDTA}_f]}{K_3 + [\mathrm{Mn^{III}Y}]} \quad (5)$$

where $k_3 = 2k_3'$ and $K_3 = k_{-3}/k_4$.

Assuming the $[\mathrm{EDTA}_f]$ is a constant, eq. 5 can be integrated to give

$$-\ln[\mathrm{Mn^{III}Y}] + p \ln\{q + r[\mathrm{Mn^{III}Y}]\} = st + C_1$$

or in terms of absorbance units

$$-\ln A + p \ln(q + rA) = st + C \quad (6)$$

where

$$p = k_3[\mathrm{EDTA}_f]/(k_1\alpha_3[\mathrm{EDTA}_f] + k_2 + k_3[\mathrm{EDTA}_f])$$
$$q = (k_1\alpha_3[\mathrm{EDTA}_f] + k_2)K_3$$
$$r = (k_1\alpha_3[\mathrm{EDTA}_f] + k_2 + k_3[\mathrm{EDTA}_f])$$
$$s = (k_1\alpha_3[\mathrm{EDTA}_f] + k_2)$$

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[14] F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5745 (1952).

Evaluation of Rate Constants.—Three series of runs were made in which each series was made under conditions where everything except the hydrogen ion concentration was held constant. When the observed rate constants for each series were plotted against the value of α_3, straight line plots were obtained in which the slopes were interpreted as $k_1[\text{EDTA}_f]$. The results of these series of runs are shown in Table II.

Table II

Results of Plotting k_{obsd} *vs.* α_3 at $[\text{Mn}^{\text{II}}\text{Y}] = 6.42\ \text{m}M$; $[\text{EDTA}_f] = 18.48\ \text{m}M$

Series	$[\text{Mn}^{\text{III}}\text{Y}]$, m$M$	k_1
1	4.14	0.60
2	2.05	0.59
3	1.04	0.61

The agreement among these values of k_1 indicates that no steady-state mechanism is involved in the high pH rate.

Table III

Sample	$[\text{EDTA}_f]$, $M \times 10^2$	pH	No. of points	$a \times 10^{10}$	$b \times 10^5$	c	μ
1	1.056	2.81	116	1.406	4.235	0.0043	0.099
2	1.584	2.93	107	2.363	5.433	0.0058	0.099
3	2.113	3.03	103	3.900	6.885	0.0063	0.099
4	2.64	3.13	98	5.784	8.344	0.0157	0.101
5	3.17	3.23	66	8.108	10.05	0.0357	0.103
6	4.22	3.32	62	15.30	13.77	0.0493	0.133

Because the observed rate changes as a function of the $\text{Mn}^{\text{III}}\text{Y}$ concentration as shown in Fig. 3, it was expected that kinetic runs which were observed over a long period of time should curve when $-\ln A$ was plotted against time. Experimentally six samples were observed for periods of from 3 to 4 half-lives. The plots showed the gentle curvature which was expected and the results were fitted by the equation

$$-\ln A = at^2 + bt + c \qquad (7)$$

Table III gives the results of this experiment with the constants determined by the method of least squares using an IBM 1620 computer.

Taking the derivative of eq. 7 with respect to time gives

$$-\frac{\mathrm{d}\ln[\text{Mn}^{\text{III}}\text{Y}]}{\mathrm{d}t} = 2at + b = k_{\text{i}} \qquad (8)$$

Eliminating t between eq. 7 and 8 gives

$$k_{\text{i}} = (b^2 - 4ac - 4a\ln A)^{1/2} \qquad (9)$$

Equations 8 and 5 when combined yield

$$k_{\text{i}} = k_1\alpha_3[\text{EDTA}_f] + k_2 + \frac{k_3[\text{Mn}^{\text{III}}\text{Y}][\text{EDTA}_f]}{K_3 + [\text{Mn}^{\text{III}}\text{Y}]} \qquad (10)$$

Equation 9 was used to calculate k_{i} for a number of concentrations of the complex for each sample; $k_1\alpha_3 \cdot [\text{EDTA}_f]$ was subtracted from each k_{i}. The remaining equation can be written

$$k_{\text{ii}} = k_2 + \frac{k_3[\text{Mn}^{\text{III}}\text{Y}][\text{EDTA}_f]}{K_3 + [\text{Mn}^{\text{III}}\text{Y}]} \qquad (11)$$

When k_{ii} was plotted against $[\text{EDTA}_f]$, the result was a straight line for each sample which gave k_2 as the intercept and a slope which can be defined as

$$k_{\text{iii}} = \frac{k_3[\text{Mn}^{\text{III}}\text{Y}]}{K_3 + [\text{Mn}^{\text{III}}\text{Y}]} \qquad (12)$$

Treating the data in this way gave a series of values of k_{iii} which were associated with particular values of $[\text{Mn}^{\text{III}}\text{Y}]$. When eq. 12 was rearranged the equation

$$\frac{1}{k_{\text{iii}}} = \frac{K_3}{k_3[\text{Mn}^{\text{III}}\text{Y}]} + \frac{1}{k_3} \qquad (13)$$

resulted so that a plot of $1/k_{\text{iii}}$ *vs.* $1/[\text{Mn}^{\text{III}}\text{Y}]$ gave a straight line with an intercept $1/k_3$ and a slope of K_3/k_3. The values of the rate constants determined by these procedures are $k_1 = 0.60\ \text{sec.}^{-1}\ M^{-1}$, $k_2 = 1.70 \times 10^{-5}\ \text{sec.}^{-1}$, $k_3 = 2.62 \times 10^{-3}\ \text{sec.}^{-1}\ M^{-1}$, and $K_3 = 0.51 \times 10^{-3}\ M$.

Integrated Rate Expression.—The values for the rate constants were checked against the experimental data by plotting the left side of eq. 6 *vs.* time. The plot gave straight lines with slopes very nearly equal to the expected value of s ($k_1\alpha_3[\text{EDTA}_f] + k_2$), as shown by Fig. 4 and Table IV.

Table IV

Values of $(k_1\alpha_3[\text{EDTA}_f] + k_2) \times 10^5$ Sec.$^{-1}$

Sample	Calculated	Experimental	% error
1	1.83	1.85	1.1
2	1.99	2.05	2.9
3	2.28	2.35	2.1
4	2.68	2.77	3.2
5	3.32	3.42	2.9
6	4.60	4.66	1.3

Mechanism.—The products of the decomposition were found to be carbon dioxide and formaldehyde. Experiments introducing formaldehyde to the reaction mixture indicated that formaldehyde was not oxidized by $\text{Mn}^{\text{III}}\text{Y}$. After complete decomposition of samples containing the complex the reaction mixture was distilled and the formaldehyde quantitatively titrated.[15] The concentration of formaldehyde was found to be from 47.5 to 49.5% of the initial concentration of the complex, independent of the concentration of excess EDTA or the pH of the solution. These results indicated a two-electron process where for every mole of

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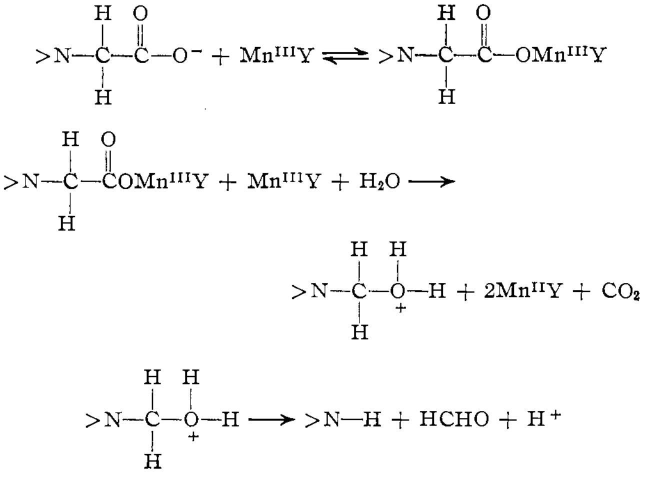
(15) F. Solymosi, *Chemist-Analyst*, **51**, 71 (1962).

formaldehyde produced two moles of complex had been consumed.

These results also indicated that the same products resulted from each of the three parallel parts of the rate expression. Terms one and three of eq. 5 involve only the difference in the ease with which $Mn^{III}Y$ can oxidize the free EDTA. Term two of eq. 5 must involve the possibility of intramolecular electron transfer from the chelated EDTA to the manganese(III). This process is much slower than either of the other processes, but becomes the rate-controlling process when the free EDTA concentration becomes very small.

A mechanism which is in agreement with the experimental data is shown.



$$>N-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O^- + Mn^{III}Y \rightleftharpoons >N-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OMn^{III}Y$$

$$>N-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}OMn^{III}Y + Mn^{III}Y + H_2O \longrightarrow >N-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{+}{O}}-H + 2Mn^{II}Y + CO_2$$

$$>N-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{+}{O}}-H \longrightarrow >N-H + HCHO + H^+$$

CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, CENTRAL RESEARCH DIVISION,
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Polyamine Complexes of Molybdenum Trioxide

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Diethylenetriamine (dien) forms a crystalline, monomeric complex with MoO_3 having the formula (dien)MoO_3. Ethylenediamine and triethylenetetramine dissolve MoO_3, but compounds of uniform composition could not be obtained. Partial neutralization of these solutions results in precipitation of photosensitive complex mixtures of amine salts of molybdates. The variation of precipitation and neutralization points with the amine used is employed to predict possible structures for these complexes in solution.

Introduction

No report of a true crystalline amine complex, as differentiated from a salt, of molybdenum(VI) has been found in the literature. Lower valence states of molybdenum have been studied, and molybdenum(V) chloride forms a 1:1 adduct with trimethyl- and triethylamine.[1] Molybdenum(0) also forms complexes with amines, a most interesting one with regard to this paper being (diethylenetriamine)$Mo(CO)_3$.[2]

The reactions between solid molybdenum trioxide, MoO_3, and several polyamines have now been investigated. We have found that MoO_3 forms a monomeric, crystalline, 1:1 compound with diethylenetriamine (dien) and that more complex materials are formed with ethylenediamine (en) and triethylenetetramine (trien).

Experimental

(dien)MoO_3.—Reagent grade molybdenum trioxide (7.2 g., 0.05 mole) was suspended in a solution of dien (10.3 g., 0.10 mole) in 200 ml. of H_2O, and the mixture was heated to boiling on a hot plate with stirring until the solids were all dissolved. The pale yellow solution was cooled, diluted to 250 ml., and a 50-ml. aliquot was added to 300 ml. of rapidly stirred ethanol. The resulting white solid was filtered, washed with ethanol, redissolved in 50 ml. of de-ionized water, and reprecipitated with ethanol. The product separated in small, white needles and weighed 2.3 g., a yield of 94%. Larger crystals can be obtained by dissolving about 2 g. of the complex in 30–40 ml. of water, adding ethanol until the solution is turbid, and cooling in an ice bath.

Anal. Calcd. for $C_4H_{13}N_3O_3Mo$: C, 19.4; H, 5.3; N, 17.0; mol. wt., 247. Found: C, 19.3; H, 5.6; N, 16.8; mol. wt. in H_2O, 290.

Titration Experiments.—Titrations were carried out using a Beckman Model G pH meter. The results were independent of the acids used (HCl, H_2SO_4, $HClO_4$), and the acid anions did not appear in the solid products isolated at the end points in the titrations.

Anal. From (dien)MoO_3 titration: C, 7.6; H, 2.9; N, 6.3; Mo, 54; N/Mo, 1.2. From (trien)MoO_3 titration: C, 8.5; H, 2.7; N, 7.2; Mo, 53; N/Mo, 1.1. From en-MoO_3 titration: C, 4.9; H, 2.8; N, 5.7; Mo, 56; N/Mo, 0.7.

Molybdenum was determined by digesting the sample with aqua regia for several hours, heating with hydrochloric acid to remove the nitric acid, diluting to volume, and estimating the molybdenum according to the colorimetric method of Busev and Fan[3] using thioglycolic acid.

Results and Discussion

Aqueous solutions of en, dien, and trien will dissolve considerable quantities of solid MoO_3 up to a ratio of nitrogen to molybdenum of 2.2 to 2.5. Concentrations of MoO_3 exceeding 25% by weight can be readily obtained free of other metal ions. Such solutions have a pH between 6 and 7. By contrast, solutions of am-

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(1) G. A. Edwards and G. W. A. Fowles, *J. Chem. Soc.*, 24 (1961).

(2) E. W. Abel, M. A. Bennett, and G. A. Wilkinson, *ibid.*, 2323 (1959).

(3) A. I. Busev and C. Fan, *Z. anal. Chem.*, **193**, 153 (1963).