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The Kinetics and Stoichiometry of the Reaction between Manganese(III) and Hydrazoic Acid in Acid Perchlorate Solution

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Received June 5, 1968

The stoichiometry of the reaction $\mathrm{Mn(III)} + \mathrm{NH_3} \rightarrow \mathrm{Mn(II)} + {}^3/_2\mathrm{N_2} + \mathrm{H^+}$ has been studied by standard chemical analysis under conditions of excess Mn(III) and by direct measurement of the nitrogen evolved for large excesses of hydrazoic acid. The kinetics of the reaction has been followed spectrophotometrically with a stopped-flow apparatus at 25° in 1.00–2.87 M $\mathrm{HClO_4}$ and ionic strength of 3.8 M. A pink color produced upon mixing the reactants has been assigned to the formation of a monoazidomanganese(III) complex. The formation constant $K = [\mathrm{MnN_3}^{2+}][\mathrm{H^+}]/[\mathrm{Mn^{3+}}][\mathrm{HN_3}]$ has been determined from initial optical densities which give the value $K = 89 \pm 18$; evaluation of the rate data leads to a value of about 70 ($\pm 20\%$). The spectrum of the complex has been determined from 440 to 570 nm. The observed rate is second order in [Mn(III)] and is consistent with the mechanism

$$2\mathrm{MnN_3}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mn^{2+}} + \mathrm{Mn(N_3)_2}^{2+} \qquad \text{(I)}$$

$$\mathrm{Mn(N_3)_2}^{2+} \xrightarrow{k_2} \mathrm{Mn^{2+}} + 3\mathrm{N_2} \qquad \text{(II)}$$

$$\mathrm{Mn(N_3)_2}^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{MnN_3}^{+} + \mathrm{N_3}^{+} \qquad \text{(III)}$$

$$\mathrm{HN_3} + \mathrm{N_3}^{+} \xrightarrow{k_4} 3\mathrm{N_2} + \mathrm{H^+} \qquad \text{(IV)}$$

Steps III and IV provide the predominant path to nitrogen production. The chief features of this mechanism are the reaction of two monoazidomanganese(III) complexes *via* a bridged intermediate and the formation of $\mathrm{N_3}^+$. The values of the kinetic parameters calculated from the mechanism with the additional assumption that k_1 and k_{-1} limited by water exchange in $\mathrm{MnN_3}^{2+}$ and $\mathrm{Mn^{2+}}$, respectively, are $10^6 \leq k_1 \leq 10^7$ M^{-1} sec^{-1}, $k_{-1} \leq 3 \times 10^8$ M^{-1} sec^{-1}, $k_3 \gg 6k_2$, and $k_4 \approx 0.15$ $k_{-3}K'$, where K' is the formation constant for $\mathrm{MnN_3}^+$.

Introduction

Although information is available on the thermal and photochemical decomposition of solid azide salts[1] and on the equilibrium properties[2] and exchange rates[3] of aqueous solutions of metal–azide complexes, kinetic studies of the oxidation of hydrazoic acid by transition metal ions have, until recently, been lacking.

In this paper we report a study of the stoichiometry and kinetics of the oxidation of hydrazoic acid by manganese(III). Measurements of the quantity of reactants consumed and of nitrogen produced have confirmed the stoichiometry indicated by eq 1. The kinetics of the reaction have been followed spectrophotometrically in a stopped-flow apparatus at 25° in aqueous perchlorate media under conditions of excess hydrazoic acid.

$$\mathrm{Mn(III)} + \mathrm{HN_3} \longrightarrow \mathrm{Mn(II)} + {}^3/_2\mathrm{N_2} + \mathrm{H^+} \qquad (1)$$

A summary of pertinent data on the uncomplexed manganese(III) species has recently been given.[4] Hydrazoic acid is a weak acid (its acid dissociation constant[5] is $K_a = 1.8 \times 10^{-5}$ M) and thus exists entirely in the protonated form at the large hydrogen ion concentrations necessary for the stabilization of Mn(III).

The reactions of azide species ($\mathrm{HN_3}$ and/or $\mathrm{N_3}^-$) with metal ions have been found to produce stoichiometric quantities of molecular nitrogen only for the cases of Ce(IV) (in $\mathrm{H_2SO_4}$),[6] $\mathrm{Mn^{III}EDTA(OH_2)^-}$ (pH 3.0–5.0),[7] and Co(III) (in $\mathrm{HClO_4}$).[8] Kinetic studies of the latter two reactions have led to the postulation of the unimolecular decomposition of coordinated metal–azide species to give a neutral $\mathrm{N_3}$ radical intermediate. The radical species $\mathrm{H_2N_6}^+$ has been postulated as an intermediate in the oxidation of $\mathrm{HN_3}$ by Mn(III) at low excesses of hydrazoic acid.[9] Although the free energy decrease for the oxidation of azide to nitrogen by ferric ion is quite large (96 kcal/mol),[10] this reaction does not occur spontaneously. However, photolysis of ferric–azide solutions has been shown to initiate polymeriza-

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tion of acrylonitrile, giving evidence for the oxidation of the complexed azide *via* a free-radical mechanism.[11]

Azide ion forms reasonably stable complexes with metal ions.[2,12] The azide group, being a highly conjugated, symmetrical system, is an excellent bridging ligand and participates as such in inner-sphere electron-transfer reactions in which the formation of the bridged intermediate (rather than the actual electron transfer) is the rate-determining step.[13,14]

Experimental Section

Reagents.—Preparation and standardization procedures for perchloric acid, manganese(III) solutions, and the perchlorates of manganese(II), iron(II), sodium, and barium were as previously described.[4] Acrylonitrile (Eastman, practical) was purified by distillation in a nitrogen atmosphere.

Sodium azide stock solutions were prepared from solid NaN_3 (purified, Fisher Scientific Co.), which had been twice recrystallized from water. Azide concentration was determined by the addition of an excess of standard ceric solution followed by back-titration with standard iron(II) to a ferroin end point.[15] Reactant hydrazoic acid solutions were made by pipetting the stock NaN_3 solution into volumetric flasks containing the appropriate quantities of $HClO_4$, $Mn(ClO_4)_2$, and $NaClO_4$.

Stoichiometry.—Stoichiometric measurements were made by spectrophotometric analysis of manganese(III) for moderate excesses of [Mn(III)] over $[HN_3]$ and by gaseous analysis of product nitrogen for conditions of excess hydrazoic acid. The general experimental procedures have already been described for the reaction between Mn(III) and hydrogen peroxide.[4] Because of the high volatility of hydrazoic acid (pure HN_3 boils at 37°[16]), a gas-line stoichiometry vessel was designed which would isolate the two reactant solutions during the initial degassing period, thus eliminating the possibility of prereaction due to hydrazoic acid distillation.[17] Since HN_3 solutions are stable in the absence of strong ultraviolet light or catalytic agents such as platinum foil,[18] no errors due to production of gases from the spontaneous decomposition of HN_3 were introduced. Collection and measurement of the gaseous product was as previously described.[4] The sample was analyzed using a Varian 90-P-3 gas chromatograph, and, from the ratio of the integrated peaks for nitrogen and oxygen, the volume was corrected for contaminating air. The stoichiometry was calculated as $\Delta[\mathrm{Mn(III)}]/\Delta[N_2]$.

Kinetics.—Since the reaction between manganese(III) and excess hydrazoic acid in perchlorate media is too rapid to be studied by more conventional techniques, an all-glass stopped-flow apparatus[4,17] was employed for kinetic measurements. All runs reported here were at 25° and at constant ionic strength of $\mu = 3.8$ *M*, adjusted with sodium perchlorate. In each case a solution of freshly prepared Mn(III) was mixed with a series of four hydrazoic acid solutions all having [Mn(II)], $[HClO_4]$, and $[NaClO_4]$ identical with those in the Mn(III) solution. The increase in absorbance upon mixing was presumed to be due to the rapid formation of the monoazido complex of Mn(III).

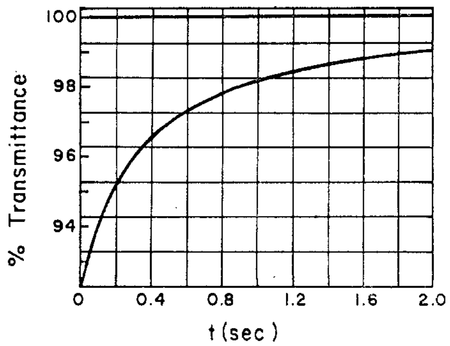

Figure 1.—Oscillograph of a stopped-flow experiment at 25° and $\mu = 3.8$ *M*. Concentrations are $[\mathrm{Mn(III)}]_{T,0} = 4.30 \times 10^{-4}$ *M*, $[HN_3]_0 = 1.0 \times 10^{-2}$ *M*, $[\mathrm{Mn(II)}] = 1.5 \times 10^{-1}$ *M*, $[HClO_4] = 1.98$ *M*, and $[NaClO_4] = 1.35$ *M*.

The disappearance of total manganese(III) concentration, $[\mathrm{Mn(III)}]_T$, given by eq 2 was followed either at 470 nm, where

$$[\mathrm{Mn(III)}]_T = [\mathrm{Mn}^{3+}] + [\mathrm{MnOH}^{2+}] + [\mathrm{MnN_3}^{2+}] \tag{2}$$

Mn^{3+} and $MnOH^{2+}$ have absorption maxima, or at 510 nm, where the total optical density is greatest in the presence of HN_3. To verify the assumption that the measured rates are independent of wavelength, one set of experiments was repeated at increments of 10 nm in the range 440–570 nm. At least three reaction traces were recorded for each set of concentrations. Results of duplicate runs generally agreed to within ±5%. An example of a kinetic run is shown in Figure 1.

For all cases, the excess of $[HN_3]_0$ over $[\mathrm{Mn(III)}]_{T,0}$ (concentrations at zero time) was such that the concentration of HN_3 did not change appreciably during the course of the reaction. Thus the concentrations of uncomplexed Mn(III), complexed Mn(III), and total Mn(III) were in the same proportions at all times. Consequently, the observed optical density at any time *t* was related to total Mn(III) concentration by

$$A_t = \epsilon_a l[\mathrm{Mn(III)}]_{T,t} \tag{3}$$

where *l* is the path length of the apparatus (6.9 mm) and the apparent extinction coefficient, ϵ_a, is a constant for each run but varies with initial concentrations. Reaction traces were found to be second-order in $[\mathrm{Mn(III)}]_T$, plots of $(A_0 - A_t)/A_t$ *vs.* time being linear throughout at least 2 half-lives. The observed pseudo-second-order rate constants for $[\mathrm{Mn(III)}]_T$ disappearance, k_{obsd}, were calculated from the slopes of these plots using the relation $k_{obsd} = 1/[\mathrm{Mn(III)}]_{T,0}$ (slope).

Complexation Studies.—When solutions of manganese(III) and hydrazoic acid are mixed, a pink color forms which disappears as the manganese(III) is reduced to Mn(II). We are able to attribute this pink color to the presence of a monoazidomanganese(III) species. The fact that second-order kinetic plots are linear even in the earliest portion of a reaction trace indicates that equilibrium is established within the first few milliseconds after mixing and that the optical density of the solution at zero time is equal to that for an equilibrium solution of Mn(III), HN_3, and the complex, where $[HN_3] = [HN_3]_0$ and $[\mathrm{Mn(III)}]_0 + [\mathrm{MnN_3}^{2+}]_0 = [\mathrm{Mn(III)}]_{T,0}$. We define an equilibrium quotient, *Q*, by

$$Q = [\mathrm{MnN_3}^{2+}][\mathrm{H}^+]/[\mathrm{Mn(III)}][\mathrm{HN_3}] \tag{4}$$

where *Q* is acid-dependent because of the manganese(III) hydrolysis relation

$$[\mathrm{Mn(III)}] = [\mathrm{Mn}^{3+}] + [\mathrm{MnOH}^{2+}] = [\mathrm{Mn}^{3+}](1 + (K_H/[\mathrm{H}^+])) \tag{5}$$

with $K_H = 0.93$ *M* at 25°.[19]

The following procedure was used in the determination of *Q*.

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Before each series of kinetic runs, the Mn(III) solution, of concentration (after mixing) $[\mathrm{Mn(III)}]_T$, was mixed in the stopped-flow apparatus, with a solution of equal [Mn(II)], $[H^+]$, and μ. The absorbance of this solution was $A_T = \epsilon_1 l[\mathrm{Mn(III)}]_{T,0}$, where ϵ_1 is the extinction coefficient for Mn(III) at the particular wavelength and acidity. For a given reaction mixture at time $t = 0$, the absorbance is given by

$$A_0 = \epsilon_1 l[\mathrm{Mn(III)}]_0 + \epsilon_2 l[\mathrm{MnN_3}^{2+}]_0 \qquad (6)$$

where ϵ_2 is the extinction coefficient for the complex. Using eq 2, 4, and 5 we obtain

$$A_0(1 + (Q[\mathrm{HN_3}]_0/[\mathrm{H^+}])) = A_T + (Q\epsilon_2 l[\mathrm{Mn(III)}]_T \times [\mathrm{HN_3}]_0/[\mathrm{H^+}]) \qquad (7)$$

The best value of Q was taken to be the estimate Q_{estd} which resulted in a linear plot of $A_0(1 + (Q_{\mathrm{estd}}[\mathrm{HN_3}]_0/[\mathrm{H^+}]))$ *vs.* $[\mathrm{HN_3}]_0$ for a given series of hydrazoic acid concentrations. Using eq 5, the formation constant, $K = [\mathrm{MnN_3}^{2+}][\mathrm{H^+}]/[\mathrm{Mn^{3+}}][\mathrm{HN_3}]$, for the complexation of $\mathrm{Mn^{3+}}$ with $\mathrm{HN_3}$, was calculated from the relation $K = Q(1 + (K_H/[\mathrm{H^+}]))$. The analogous quantity $K_{\mathrm{OH}} = [\mathrm{MnN_3}^{2+}]/[\mathrm{MnOH^{2+}}][\mathrm{HN_3}]$ is given by $K_{\mathrm{OH}} = Q(1 + ([\mathrm{H^+}]/K_H))/[\mathrm{H^+}]$. A spectrum of the complex was determined in 1.98 M $\mathrm{HClO_4}$ in the range 440–570 nm by comparing the initial optical density of a reaction mixture with the absorbance of a solution in the absence of $\mathrm{HN_3}$ under the same conditions. The spectrum is presented in Figure 2.

Polymerization.—A series of reactions between Mn(III) and $\mathrm{HN_3}$ were carried out in stoppered vessels at 25° in the presence of 6% v/v acrylonitrile. Initial conditions were $[\mathrm{Mn(III)}] = 9.4 \times 10^{-4}$ M, $[\mathrm{HClO_4}] = 2.00$ M, and $[\mathrm{Mn(II)}] = 0.60$ M. Hydrazoic acid concentrations were 0.005, 0.01, and 0.02 M. A cloudy suspension formed in all of the reaction mixtures within a few minutes after addition of hydrazoic acid. After several hours, a large amount of polymer had precipitated. Blank experiments in which either manganese(III) or hydrazoic acid was absent yielded no signs of polymer formation in this time. These experiments show that the reaction between manganese(III) and hydrazoic acid produces species which are capable of initiating polymerization but cannot be used to identify the initiator.

Results and Treatment of Data

Stoichiometry.—Results of four independent sets of experiments by the spectrophotometric method[4] gave a value of $\Delta[\mathrm{Mn(III)}]/\Delta[\mathrm{HN_3}] = 1.02 \pm 0.05$. For these experiments, all at $[\mathrm{H^+}] = 2.00$ M and $[\mathrm{Mn(II)}] = 0.60$ M, the initial concentration of Mn(III) was 1.1×10^{-3} M with initial $\mathrm{HN_3}$ concentrations between 3.0×10^{-4} and 8.0×10^{-4} M. Three direct determinations of the amount of nitrogen produced in the reaction by the gas-line method using solutions with high hydrazoic acid concentrations ($[\mathrm{HN_3}]_0 = 0.10$ M, $[\mathrm{Mn(III)}]_{T,0} = 4.7 \times 10^{-4}$–$7.0 \times 10^{-4}$ M, $[\mathrm{H^+}] = 2.00$ M, $[\mathrm{Mn(II)}] = 0.60$ M) yielded a stoichiometry of $\Delta[\mathrm{Mn(III)}]/\Delta[\mathrm{N_2}] = 0.69 \pm 0.02$. Thus, over a range of $[\mathrm{HN_3}]_0/[\mathrm{Mn(III)}]_{T,0}$ from 0.3 to 210, the reaction follows the stoichiometry indicated by eq 1.

Kinetics.—Values for apparent pseudo-second-order rate constants for $[\mathrm{Mn(III)}]_T$ disappearance from experiments at $\mu = 3.8$ M are given in Table I. The following qualitative dependences exist throughout the data. The value of k_{obsd} increases with increasing hydrazoic acid concentration and decreases with increasing [Mn(II)]. At constant Mn(II) concentration, the effect of perchloric acid on k_{obsd} is not large, the direction of the variation being a somewhat irregular function of

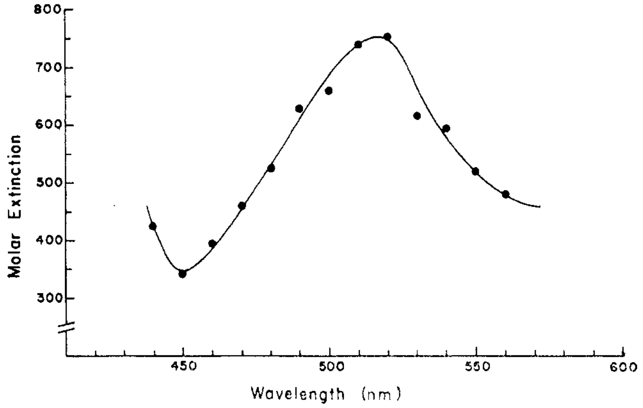

Figure 2.—Visible spectrum of $\mathrm{MnN_3}^{2+}$. The experimental points were obtained as follows. A point by point spectrum of Mn(III) in 1.98 M $\mathrm{HClO_4}$ and 0.60 M $\mathrm{Mn(ClO_4)_2}$ was determined in the stopped-flow apparatus. Then, from initial points on stopped-flow traces for a particular set of concentrations, the absorbance was determined at each wavelength. Using the experimental value of $Q = 30$ (see Results) the concentrations of $[\mathrm{Mn(III)}]_0$ and $[\mathrm{MnN_3}^{2+}]_0$ were calculated and eq 6 was solved for the extinction coefficient of the complex.

TABLE I

KINETIC RESULTS AT 25° AND $\mu = 3.8$ M[a]

$[\mathrm{HClO_4}]$	[Mn(II)]	10^4 $[\mathrm{Mn(III)}]_{T,0}$	10^2 $[\mathrm{HN_3}]_0$	10^{-4} k_{obsd}[b]	10^{-4} k_{calcd}[b,c]
2.87	0.30	4.91	5.00	4.20	2.97
			2.50	2.04	1.26
			1.00	0.491	0.304
			0.50	0.140	0.0888
1.98	0.60	4.17	10.0	1.93	1.79
			5.00	1.05	1.05
			2.50	0.428	0.491
			1.00	0.118	0.129
	0.45	4.36	5.00	1.74	1.70
			2.50	0.694	0.793
			1.00	0.167	0.208
			0.50	0.0623	0.633
	0.30	3.31	5.00	3.15	3.23
			2.50	1.55	1.51
			1.00	0.388	0.395
			0.50	0.129	0.120
	0.15	4.30	5.00	5.19	8.77
			2.50	2.65	4.09
			1.00	0.728	1.07
			0.50	0.209	0.326
	0.075	2.73	5.00	21.3	21.2
			2.50	10.9	9.87
			1.00	4.12	2.59
			0.50	1.65	0.788
1.50	0.30	2.90	5.00	4.88	3.24
			2.50	1.96	1.60
			1.00	0.694	0.450
			0.50	0.156	0.141
1.00	0.93	3.40	5.00	0.449	0.391
			2.50	0.238	0.210
			1.00	0.0582	0.0646
			0.50	0.0210	0.0213
	0.60	2.76	5.00	0.949	0.880
			2.50	0.437	0.472
			1.00	0.159	0.145
			0.50	0.0427	0.0478
	0.30	3.09	5.00	2.79	2.98
			2.50	1.56	1.60
			1.00	0.578	0.492
			0.50	0.173	0.162
	0.10	1.15	5.00	20.1	16.5
			2.50	11.9	8.85
			1.00	2.94	2.72
			0.50	1.50	0.897

[a] All concentrations in M. [b] Units: M^{-1} sec^{-1}. [c] Calculated from eq 11 with $K = 67$, $D/C = 0$, $k_1 = 3 \times 10^6$ M^{-1} sec^{-1}, $B = 0.131$, and $k_1C = 9.7 \times 10^3$ sec^{-1}.

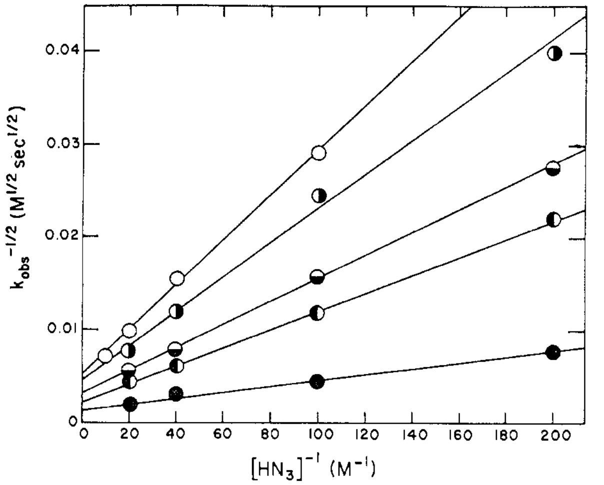

Figure 3.—Plot of $(1/k_{obsd})^{1/2}$ *vs.* $1/[HN_3]_0$ for different [Mn(II)] at $[HClO_4]$ = 1.98 *M* and μ = 3.8 *M*. [Mn(II)] concentrations: ○, 0.60; ◑, 0.45; ◓, 0.30; ◐, 0.15 ●, 0.075.

$[HClO_4]$. In the presence of a large excess of Mn(II), Mn(III) disproportionates to a negligible extent at high acidity, and there is no evidence for Mn(III) dimerization under these conditions.[19]

A fraction-weighted least-squares treatment was used to fit all 11 sets of data at constant $[Mn^{2+}]$ and $[H^+]$ to straight lines of the form

$$\frac{1}{\sqrt{k_{obsd}}} = (S/[HN_3]) + I \tag{8}$$

where the slopes, *S*, and intercepts, *I*, are different for each set of data. The deviations of the observed points from the best straight line is within ±5% for all cases. Figure 3 gives the results of this analysis for five sets (*i.e.*, five different $[Mn^{2+}]$) at 1.98 *M* $HClO_4$. The linearity of plots of $1/\sqrt{k_{obsd}}$ *vs.* $1/[HN_3]$ indicates that the rate law is of the form

$$\begin{aligned} \text{rate} &= [Mn(III)]^2[HN_3]^2 f([H^+],[Mn^{2+}]) \\ &= [MnN_3^{2+}]^2 f'([H^+],[Mn^{2+}]) \end{aligned} \tag{9}$$

where the functions f and f′ are related by the equilibrium condition given by eq 4. A mechanism which is consistent with eq 9 and explains the variation in rate with $[Mn^{2+}]$ and $[H^+]$ is

$$Mn^{3+} + HN_3 \rightleftarrows MnN_3^{2+} + H^+ \quad (K)$$

$$MnOH^{2+} + HN_3 \rightleftarrows MnN_3^{2+} \quad (K_{OH})$$

$$Mn^{2+} + HN_3 \rightleftarrows MnN_3^{+} + H^+ \ . (K')$$

$$Mn^{3+} \rightleftarrows MnOH^{2+} + H^+ \quad (K_H)$$

$$2MnN_3^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Mn^{2+} + Mn(N_3)_2^{2+} \tag{I}$$

$$Mn(N_3)_2^{2+} \xrightarrow{k_2} Mn^{2+} + 3N_2 \tag{II}$$

$$Mn(N_3)_2^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} MnN_3^{+} + N_3^{+} \tag{III}$$

$$HN_3 + N_3^{+} \xrightarrow{k_4} 3N_2 + H^+ \tag{IV}$$

All equilibria are assumed to be maintained throughout the course of the reaction.

Application of the steady-state approximation to N_3^+ and $Mn(N_3)_2^{2+}$ yields the rate law

$$\text{rate} = k_{obsd}[Mn(III)]_T^2 \tag{10}$$

where

$$k_{obsd} = k_1\left\{\frac{K[HN_3]}{[H^+] + K_H}\Big/\left(1 + \frac{K[HN_3]}{[H^+] + K_H}\right)\right\}^2 \times \left\{\frac{C[H^+] + D[Mn^{2+}]}{[Mn^{2+}]^2 + B[Mn^{2+}][H^+] + C[H^+] + D[Mn^{2+}]}\right\} \tag{11}$$

with $B = k_4/k_{-3}K'$, $C = k_4(k_2 + k_3)/k_{-1}k_{-3}K'$, and $D = k_2/k_{-1}$.

Equation 11 predicts that the slopes and intercepts of eq 8 should obey the relationship $I/S = Q/[H^+] = K/([H^+] + K_H)$, from which we may obtain values of *K*. These kinetically determined values can be compared with the values of *K* from the analysis of initial optical densities (see Table II and Complexation Studies section).

Table II

Kinetic and Equilibrium Parameters[a]

$[HClO_4]$	[Mn(II)]	K^b	$K_{kin}{}^c$	$10^5 I^{2\,d}$
2.87	0.30	124	76	0.574
1.98	0.60	73	55	2.28
	0.45	59	60	1.57
	0.30	59	71	0.952
	0.15	118	74	0.592
	0.075	118	151	0.246
1.50	0.30	84	47	0.514
1.00	0.93	74	50	6.90
	0.60	91	59	3.70
	0.30	84	79	1.61
	0.10	91	79	0.224
	Av	89 ± 18	73 ± 14	

[a] All concentrations in *M*. [b] Determined from initial optical densities. [c] $K_{kin} = (I/S)([H^+] + K_H)$. [d] Units: *M* sec.

From eq 8 and 11 we have

$$I^2 = \frac{1}{k_1} + \frac{[Mn^{2+}]^2 + B[Mn^{2+}][H^+]}{k_1C([H^+] + [Mn^{2+}](D/C))} \tag{12}$$

Inspection of eq 12 and the values of I^2 given in Table II indicate that (i) k_1 is significantly greater than 4 × 10^5 M^{-1} sec^{-1} (see the point for $[HClO_4]$ = 1.00 *M*, $[Mn^{2+}]$ = 0.10 *M*) and hence (ii) the first term in eq 12 is small with respect to the fraction for all $[Mn^{2+}]$ and $[H^+]$ studied, with the possible exception of those at the lowest $[Mn^{2+}]$. This latter observation explains the formulation of eq 12 in terms of the parameters *B*, k_1, k_1C, and *C*/*D* rather than *B*, k_1, *C*, and *D*. Because of the small number of points used in the determination of each value of I^2 and the relatively large deviation in K_{kin} (Table II), attempts to solve eq 12 using values of I^2 from Table II and the experimental concentrations of Mn^{2+} and $HClO_4$ gave results which did not yield satisfactory agreement when used with *K* = 73 to recalculate k_{obsd} from eq 11.

The approach which was finally adopted was to apply a fraction-weighted, nonlinear, least-squares treatment to eq 11 in terms of the independent variables $[HN_3]$, $[H^+]$, and $[Mn^{2+}]$ using all 44 data points from Table

I.[20] The minimum sum of squares of fractional deviations $\{\Sigma[(k_{\text{obsd}} - k_{\text{calcd}})/k_{\text{obsd}}]^2 = 2.90\}$ occurred for $K = 67$, $D/C = 0$, $B = 0.162$, and $k_1C = 1.02 \times 10^4$ sec^{-1}. Values of k_1 of 3×10^7 M^{-1} sec^{-1} or higher gave identical values for k_{calcd}. However solutions for which $\Sigma[(k_{\text{obsd}} - k_{\text{calcd}})/k_{\text{obsd}}]^2$ are only very slightly different from the "best" fit were found using $K = 67$, $D/C \approx 0$, $k_1C \approx 1 \times 10^4$ sec^{-1}, and much smaller values of k_1. For example $\Sigma[(k_{\text{obsd}} - k_{\text{calcd}})/k_{\text{obsd}}]^2 = 3.04$ for the set of parameters $k_1 = 3 \times 10^6$ M^{-1} sec^{-1}, $K = 67$, $k_1C = 9.7 \times 10^3$ sec^{-1}, $B = 0.131$, and $D/C = 0$. Similar solutions exist for intermediate values of k_1. Below $k_1 = 3 \times 10^6$ M^{-1} sec^{-1} the weighted sum of squares increases quite rapidly. Thus, from the treatment of data alone, we are unable to determine a unique value for k_1. It appears, however, that k_1 is greater than 10^6 M^{-1} sec^{-1}. Because of the inner-sphere nature of step I, k_1 should be significantly less than the diffusion-controlled limit of $\sim 2 \times 10^8$ M^{-1} sec^{-1} [21] for encounter between two dipositive ions. The nature of this step will be discussed more fully in the next section.

The result that $D/C \approx 0$ indicates that $D/C \ll [H^+]/[Mn^{2+}]$ for all experimental conditions. Thus, using $[Mn^{2+}] = 0.93$ M and $[H^+] = 1.00$ M, we have $D/C \ll 1$. The conclusions to be drawn from the analysis of the kinetic data are summarized in Table III. Table I contains values of k_{calcd} calculated from the solution mentioned above with $k_1 = 3 \times 10^6$ M^{-1} sec^{-1}.

TABLE III

KINETIC PARAMETERS AT 25°

$k_1 \geq 10^6$ M^{-1} sec^{-1}

$k_1C = 10^4$ sec^{-1}

$D/C = k_2k_{-3}K'k_4(k_2 + k_3) \ll 1$

$C = k_4(k_2 + k_3)/k_{-1}k_{-3}K' \leq 10^{-2}$ M

$D = k_2/k_{-1} \ll 10^{-2}$ M

$B = k_4/k_{-3}K' \approx 1.5 \times 10^{-1}$

$B(D/C) = k_2/(k_2 + k_3) \ll 1.5 \times 10^{-1}$

It should be noted that mechanisms other than the one given in steps I–IV can be written which are consistent with eq 9 and have $[Mn^{2+}]$ and $[H^+]$ dependences which are similar to those given in eq 11. Other mechanisms have been considered but lead to rate laws which do not fit the observed data as well. In addition, these schemes necessitate the inclusion of azide radicals in equilibrium and of radical–radical reactions as rate-determining steps.[22]

Complexation Studies.—The value of K for complexation between Mn^{3+} and HN_3 calculated from initial absorbancies is $K = 89 \pm 18$, while the values determined from kinetic arguments average 70 (relative error $\sim$20%). A possible explanation (other than experimental error) for any differences is that the former value contains contributions from higher order complexes. In a recent study of the iron(III)–HN_3 complexation reaction, for example, Carlyle and Espenson[12] were able to correct their data for the concentration of $Fe(N_3)_2^+$ and determine a refined value of Q_1 which is almost 20% lower than previous determinations. Because of the difficulty in accurately determining the optical density at $t = 0$ for our stopped-flow experiments, the data for the manganese(III)–hydrazoic acid complexation do not lend themselves to similar refinement.

No spectrophotometric evidence for the formation of complexes between manganese(II) and hydrazoic acid could be obtained in the range 10^{-2}–6 M $HClO_4$, even at very high [Mn(II)] and $[HN_3]$. At higher pH, hydrolyzed manganese(II) species are formed, preventing experiments at very low $[H^+]$. Thus, the complex MnN_3^+, postulated in step III of the mechanism, must be present in low concentrations or have a visible spectrum which is nearly identical with that of Mn(II).[23] As has been prevously mentioned, the fact that plots of $(k_{\text{obsd}})^{-1/2}$ *vs.* $1/[HN_3]_0$ are linear suggests that the amount of hydrazoic acid removed by complexation is small. We will now discuss the results in detail.

Discussion

The spectrum of MnN_3^{2+} is similar to that of other complexed Mn(III) species.[24] Its high extinction coefficient can be attributed to the large reduction in symmetry in going from Mn^{3+} (distorted from O_h by the Jahn–Teller effect) or $MnOH^{2+}$ (C_{4v}) to the complex which, because of the nonlinear MnNN bond angle, has C_s symmetry. The stability constant that we have determined for complexation between Mn^{3+} and HN_3 is two orders of magnitude greater than that found in the ferric–azide system.[12] However, it is substantially less than the value found by Fackler and Chawla[24b] for complexation with HF. As already mentioned, we are not able to treat our data for the presence of higher order complexes. In a study of the oxidation of bromide ion by Mn(III) Wells and Mays[23] were able to rule out the presence of the hydrolyzed complex, $MnOHBr^+$. The protonated species MnN_3H^{3+} might also exist in the present system but would not be expected to participate in the redox reaction, which requires a symmetrical bridging ligand.

Failure to account for protonated and/or hydroxylated complexes as well as higher order complexes may be responsible for the deviations encountered in the fit of the kinetic data.

The mechanism proposed in this study involves, as

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(20) We acknowledge Dr. T. W. Newton for adapting and applying a nonlinear, least-squares program to the data. The original program was written by R. H. Moore and R. K. Zeigler and is described in Los Alamos Report LA-2367 + addenda.

(21) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, **3**, 239 (1964).

(22) *E.g.*, one such mechanism involves, in addition to the formation of MnN_3^{2+}, the rapid equilibria $Mn^{3+} + HN_3 \rightleftarrows Mn^{2+} + HN_3^+$ and $HN_3^+ \rightleftarrows H^+ + N_3$ followed by the rate-determining steps $MnN_3^{2+} + N_3 \rightarrow Mn^{2+} + 3N_2$ and $HN_3^+ + N_3 \rightarrow H^+ + 3N_2$. An additional objection to this mechanism is that, because of the high value of $\Delta H_f(HN_3^+) = 308 \pm 5$ kcal mol^{-1}, the production of HN_3^+ in a single step appears less likely than the two-step formation of N_3^+ (see Discussion). A similar scheme, which leads to a slightly different $[H^+]$ dependence, contains the rapid preequilibrium $MnN_3^{2+} \rightleftarrows Mn^{2+} + N_3$ followed by $MnN_3^{2+} + N_3 \rightarrow Mn^{2+} + 3N_2$ and $2N_3 \rightarrow 3N_2$. *Cf.* ref 8.

(23) C. F. Wells and D. H. J. Mays, *J. Chem. Soc., A*, 577 (1968).

(24) (a) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967); (b) J. P. Fackler, Jr., and I. D. Chawla, *ibid.*, **3**, 1130 (1964); (c) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).

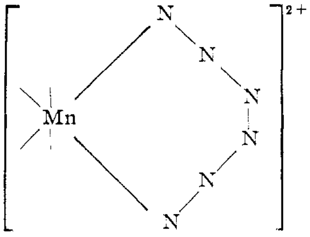
the initial step, the bimolecular reaction between two complexed species, while for the oxidation of HN_3 by Co(III)[8] and of N_3^- by $Mn^{III}EDTA(OH_2)^-$ [7] unimolecular decomposition of the metal–azide species to give the neutral N_3 radical has been postulated. Step I of our mechanism can be visualized as the transfer of an electron across an inner-sphere azide bridge with the formation of Mn^{2+} and a species which is *formally* a diazido complex of manganese(IV). The analogous reaction would not be expected to occur for the Co(III) reaction because of the unattainability of the formal +4 oxidation state nor for the reaction of seven-coordinated $Mn^{III}EDTA(N_3)^{2-}$ which cannot accommodate an additional azide group in the inner sphere.

The upper limit for the forward rate constant, k_1, should therefore be determined by the rate of water exchange in the monoazidomanganese(III) complex, assuming that subsequent electron- or group-transfer reactions are more rapid. One may infer, from temperature-jump measurements by Diebler and Eigen on the reaction of fluoride with aqueous Mn(III),[25] that the first-order rate constant, k_{ex}, for water exchange in uncomplexed Mn(III) is $k_{ex} \gtrsim 10^4$ sec^{-1}. A large increase in water exchange rate would be expected to result upon formation of MnN_3^{2+},[26] but because of a low ion-pair formation constant for ($N_3^-Mn^{III}$, $N_3^-Mn^{III}$), it is unlikely that the value of k_1 would be more than a factor of 10 larger than the lower limit of $k_1 \gtrsim 10^6\ M^{-1}$ sec^{-1}.

The magnitude of the reverse rate constant, k_{-1}, should be limited by the rate of water exchange in manganese(II). The first-order rate constant for water exchange in Mn(II) is 3×10^7 sec^{-1} [27] which, if we take 10 M^{-1} as the upper limit for the ion-pair formation constant for ($N_3^-Mn^{IV}N_3^-$, Mn^{2+}), leads to an upper limit of 3×10^8 M^{-1} sec^{-1} for k_{-1}. The disproportionation constants for Mn(III) in perchloric[24c] and sulfuric[28] acids are $<10^{-2}$ and $\sim 10^{-3}$, respectively. Although a direct comparison cannot be made, these values suggest that k_{-1} is indeed greater than k_1 and that, here too, the rate may be determined by water exchange.

The unimolecular rate constants, k_2 and k_3, for the decomposition of $Mn(N_3)_2^{2+}$ are, in fact, composite quantities involving the fractions of intermediates, f_c and f_t, in the *cis* and *trans* forms, respectively. Since step II can proceed only from the *cis* complex, $k_2 = f_ck_2^c$. Similarly, for step III, $k_3 = f_ck_3^c + f_tk_3^t$. The new parameters, k_2^c, k_3^c, and k_3^t are true first-order rate constants. From Table III we have $k_3 \gg 6k_2$; indeed, inclusion of step II is not strictly necessary for interpretation of the kinetic data. It is instructive to consider this pathway, however.

Although the azide group is linear, covalent bonds involving the azide group are asymmetrical; *e.g.*, the HNN bond angle is 110° in HN_3 while the CNN bond is 135° in methyl azide.[29] CrNN bonds of approximately 135° are necessary for the formation of the double-bridged intermediate in the electron-exchange reaction between Cr^{2+} and *cis*-diazidotetraaquochromium(III) ion.[30] The direct production of nitrogen from *cis*-$Mn(N_3)_2^{2+}$ *via* step II would require the formation of the cyclic intermediate Y. The fact that there is no detectable contribution from step II indicates either that Y does not form to an appreciable extent or that the cyclic structure is stable with respect to the direct formation of nitrogen.



Y

Using the upper limit for C (Table III) gives $k_3/k_{-1} = (C/B) - D \leq 7 \times 10^{-2}\ M$. Assuming $C \geq 10^{-3}$ (*i.e.*, assuming $k_1 \leq 10^7\ M^{-1}$ sec^{-1}) we get $k_3/k_{-1} \geq 7 \times 10^{-3}\ M$. Thus for all concentrations studied, the specific rate of the reverse of step I is greater than the rate of formation of nitrogen, and the over-all reaction is only moderately rapid in spite of the high values of k_1 and K.

The production of N_3^+ in step III of the proposed mechanism as opposed to a path involving neutral N_3 radicals[7,8] appears to take place in spite of a higher heat of formation for the N_3^+ species. The gas-phase heats of formation are $\Delta H_f(N_3^+) \leq 388$ kcal mol^{-1} [31] and $\Delta H_f(N_3) = 105 \pm 3$ kcal mol^{-1}.[1] The predominance of the N_3^+ path in the present system may be due to the lower free energy of the resulting manganese(II) complex over the +3 or +4 oxidation states, together with a high solution enthalpy for the positive intermediate and the possibility of solvent-assisted dissociation.[32] It has already been mentioned that for both of the azide oxidations previously investigated,[7,8] the formation of a diazido intermediate from which the N_3^+ species can arise is unlikely. Both of these reactions are much slower than the present one which has no detectable contribution that is first order in $[Mn(III)]_T$ as would be required if an analogous path were important. The absence of a first-order contribution under our conditions also precludes the mechanism proposed by Wells and Mays[9] for the reaction at low azide concentrations.

By analogy with other ligands, the monoazido complex of manganese(II) would be expected to be weaker than monoazidomanganese(III), but since the difference between formation constants could be less than an order of magnitude (as in the case of the monochloro

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[25] H. Diebler and M. Eigen, Abstracts, 9th International Conference on Coordination Chemistry, St. Moritz, Switzerland, 1966, p 360.

[26] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley, & Sons, Inc., New York, N. Y., 1967, Chapters 1 and 5.

[27] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[28] R. G. Selim and J. J. Lingane, *Anal. Chim. Acta*, **21**, 536 (1959); A. J. Fenton and N. H. Furman, *Anal. Chem.*, **32**, 748 (1960).

[29] See ref 5, p 63.

[30] R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).

[31] J. L. Franklin, V. H. Dibler, R. M. Reese, and M. Krauss, *ibid.*, **80**, 298 (1958).

[32] See ref 25, p 134.

complexes[2]) or several orders of magnitude, we are unable to determine the relative values of k_{-3} and k_4 from the experimental value of B.

Although step IV is very highly exothermic, the ground-state reaction[33]

$$N_3^+(^3\Sigma_g^-) + HN_3(^1A') \longrightarrow 3N_2(^1\Sigma_g^+) + H^+ \qquad -\Delta H \leq 420 \text{ kcal mol}^{-1}$$

is forbidden by spin-correlation rules. Step IV thus proceeds either (a) from the lowest singlet of N_3^+ or (b) *via* the sequence

$$N_3^+(^3\Sigma_g) + HN_3(^1A') \longrightarrow 2N_3(^2\Pi_g) + H^+$$

$$2N_3(^2\Pi_g) \longrightarrow 3N_2(^1\Sigma_g^+)$$

with the second process involving azide radicals of opposite spin. Either the N_3^+ triplet state or the neutral N_3 radical would be expected to be responsible for initiating the polymerization of acrylonitrile. Finally, it should be noted that the isotopic distribution of the nitrogen formed in the present system would be expected to be the same as that found in studies involving $^{15}N–N–^{15}N$ azide radical species.[7,34]

Acknowledgment.—This investigation was supported in part by Public Health Service Research Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service, and in part by National Science Foundation Grant GP-4277. L. J. K. acknowledges, with gratitude, the receipt of an NSF cooperative fellowship and a NASA traineeship.

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[33] (a) The term state for N_3^+ is given in ref 30. From electron impact data, these authors give ΔH_f as $\leq$388 kcal mol^{-1}, but in solution ΔH_f should be substantially smaller. (b) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959), gave 61.9 kcal mol^{-1} as the heat of formation of undissociated HN_3 at infinite dilution. Dissociation into $H^+ + N_3^-$ requires 3.6 kcal mol^{-1}. $\Delta H_f(N_3^-) = 35 \pm 1$ kcal mol^{-1}.

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

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Redox Reactions of Cobalt–Cyanide Complexes. III.[1] Reaction of $Co(CN)_5H^{3-}$ with *p*-Benzoquinone

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Received July 23, 1968

p-Benzoquinone reacts in alkaline solutions with $Co(CN)_5H^{3-}$ *via* two paths: a slow, pH-independent, direct reaction with the hydride species ($k_1 = 13.5\ M^{-1}\ \text{sec}^{-1}$) and a fast reaction with the univalent cobalt complex $Co(CN)_5^{4-}$, formed by the deprotonation of the hydride. The rate constant for the reaction with $Co(CN)_5^{4-}$ is of the order $10^9\ M^{-1}\ \text{sec}^{-1}$. In both cases $(CN)_5CoOC_6H_4OH^{3-}$ is the only primary product of the reaction. The formal rate constant of the process at pH >9.2 and 0° is $k = 13.5 + 8.7 \times 10^4[OH^-]$. An addition mechanism is proposed for both reaction paths, the direct hydride transfer or an insertion process being excluded. At pH <9, *p*-benzoquinone is partly reduced in two one-electron steps, $(CN)_5Co(\mu\text{-}OC_6H_4O)Co(CN)_5$ being the primary product of this reaction path.

In the preceding paper of this series[1] the reaction of pentacyanocobaltate(II) with *p*-benzoquinone was shown to proceed *via* the redox addition mechanism under the formation of a bridge species, $(CN)_5Co(\mu\text{-}OC_6H_4O)CO(CN)_5^{6-}$ (I). I decomposes giving in the first step $(CN)_5CoOC_6H_4OH^{3-}$ (II) and $Co(CN)_5H_2O^{2-}$.

p-Benzoquinone is known to react also with the hydrogenated solutions of pencyanocobaltate;[2] the reaction shows, however, several peculiar features, most probably due to the rather complicated system in which the reaction was studied. In the present paper we wish to report our results on the kinetics and mechanism of the reaction of *p*-benzoquinone with $Co(CN)_5H^{3-}$ in the absence of hydrogen.[3] As $Co(CN)_5H^{3-}$, unlike $Co(CN)_5^{3-}$, is not able to react by an ordinary redox addition mechanism, it was of importance to compare the mechanism of the redox reaction of these two complexes with the same substrate and to compare the intermediates and products of the reactions in order to find out what species represents the reactant proper in the reduced pentacyanocobaltate(II) solutions. Furthermore, as $Co(CN)_5H^{3-}$ is formally a two-electron agent, it was hoped that its reaction with *p*-benzoquinone might result in the direct formation of II which could thus have been prepared in the pure form.

Experimental Section

Most of the experimental details were the same as described in our earlier paper.[1] The spectrophotometric measurements were carried out using a Unicam SP 800 spectrophotometer.

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[1] Part II: A. A. Vlček and J. Hanzlík, *Inorg. Chem.*, **6**, 2053 (1967).

[2] J. Kwiatek, I. L. Mador, and J. K. Seyler, *J. Am. Chem. Soc.*, **84**, 304 (1962); Advances in Chemistry Series, No. 87, American Chemical Society, Washington, D. C., 1963, p 201.

[3] No molecular hydrogen was introduced into the system. There might, however, have been hydrogen present owing to the partial decomposition of the hydride species; see Experimental Section.