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Induced Aquation of Ligandopentaamminecobalt(III) Complexes

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The rate law for the reaction between nitrous acid and azidopentaamminecobalt(III) (designated MN_3^{2+}) in aqueous perchlorate solutions containing Hg(II) was found to be $-d \ln [Mn_3^{2+}]/dt = A[H^+]^2\sum[NO_2^-]/([H^+] + B[Hg^{II}])$ and although Hg(II) inhibited the reaction, it did not change the nature of the previously established rate-determining step. In acetonitrile–water media the formation of the $HgNO_2^+$ complex was more complete and the rate law was $-d \ln [Mn_3^{2+}]/dt = k_{obsd}\cdot[H^+]^2\sum[NO_2^-]/[Hg^{II}]$ with Hg(II) again inhibiting the reaction without changing the nature of the rate-determining step. Consequently competition reactions occurring after the induced decomposition of MN_3^{2+} by NO^+ can be studied in the presence of Hg(II) without Hg(II) preventing the presumed formation of the five-coordinate intermediate $Co(NH_3)_5^{3+}$ (i.e., M^{3+}). The rate law for the reaction between MCl^{2+} and Hg(II) in aqueous media containing NO_3^- was found to be $-d \ln [MCl^{2+}]/dt = \{k_0 + k_1[NO_3^-]\}[Hg^{II}]$. Determination of the percentages of MNO_3^{2+} formed under the same conditions as used for the rate law determination showed that if M^{3+} is generated in the $MN_3^{2+} + NO^+$ reaction, it is not generated in either path of the MCl^{2+} + Hg(II) reaction.

Introduction

Studies of the assisted aquation reactions of MN_3^{2+} and MCl^{2+} (where $M^{3+} = Co(NH_3)_5^{3+}$) in aqueous nitrate and sulfate media have shown[1] that the product ratios $[MNO_3^{2+}]/[MOH_2^{3+}]$ formed in the two reactions were very nearly equal as were the product ratios $[MSO_4^+]/[MOH_2^{3+}]$. It has been pointed out[2] that a constant product ratio for different leaving groups and a given pair of competing entering groups implies a common intermediate, most probably M^{3+} in this case.[3] However, the product ratios obtained from MN_3^{2+} were obtained in the absence of Hg^{2+} whereas those from MCl^{2+} were obtained in the presence of rather high concentrations of Hg^{2+}. Consequently the reaction media from which the two product ratios were obtained were not the same. Likewise, product ratios from these two assisted reactions in acetonitrile–water media have been compared[4] although Hg^{2+} was absent from the MN_3^{2+} reaction mixtures. When we added Hg^{2+} to the MN_3^{2+} reaction media, the reaction between MN_3^{2+} and nitrous acid was retarded both in purely aqueous and in acetonitrile–water media. A possible cause of the retardation was formation of a binuclear, azide-bridged cobalt(III)–mercury(II) complex similar to that proposed by Loeliger and Taube.[5] Consequently the question arose: Can the product ratios from MN_3^{2+} in the presence of Hg^{2+} be used to compare with those presumably arising from M^{3+} (however it may be generated) or does the presence of Hg^{2+} change the nature of the intermediate so as to invalidate the comparison? Here we report studies on the mechanism of Hg^{2+} retardation which show that production of M^{3+} from the reaction between MN_3^{2+} and NO^+ is consistent with all experimental data in the presence of Hg^{2+}.

Since the product ratio $[MNO_3^{2+}]/[MOH_2^{3+}]$ from the assisted MN_3^{2+} reaction in aqueous media is very nearly equal to that from the assisted MCl^{2+} reaction and since the former reaction presumably produces the M^{3+} intermediate in the presence and absence of Hg(II), it was of interest to ascertain whether or not the product ratio from MCl^{2+} also arose from the same intermediate. To achieve this objective kinetic studies of the $MCl^{2+} + Hg^{2+}$ reaction in aqueous nitrate media were made and are also reported here.

Experimental Section

Chemicals. The complexes $[Co(NH_3)_5Cl](ClO_4)_2$ and $[Co(NH_3)_5N_3](ClO_4)_2$ were prepared by standard literature methods.[6,7] Both complexes were converted to their perchlorate salts by repeated recrystallizations, first from perchloric acid solutions and then from water. Spectrophotometric analyses of the former compound before and after acid and base hydrolyses gave 100 ± 2% purity. The latter compound gave a molar extinction coefficient of 272 M^{-1} cm^{-1} at 516 nm as compared to a literature value of 266 M^{-1} cm^{-1} at the same wavelength.[8]

$Hg(ClO_4)_2$ solutions were prepared by weighing out the theoretical weight of 70.49 ± 0.14% perchloric acid to dissolve 1.00 M mercury(II) oxide and give 0.0500 M perchloric acid excess to prevent mercury(II) hydrolysis.

All other solutions were prepared by standard methods from reagent grade chemicals.

Kinetic Studies. Rate measurements for the reactions between $Co(NH_3)_5N_3^{2+}$ and $NaNO_2$ and between $Co(NH_3)_5Cl^{2+}$ and Hg(II) in acidic media were made spectrophotometrically at 516 nm and at 550 nm, respectively, with a Beckman Model 25 spectrophotometer. Each reaction was started by injecting a small volume of sodium nitrite or of mercury(II) perchlorate solution into a vigorously stirred solution of the cobalt(III) complex to give predetermined concentrations of reactants and supporting electrolyte at a temperature near that of the cell compartment. The reaction mixtures were injected into a thick-walled, small-volume optical cell already at a preset temperature, and absorbance time data were recorded. Infinite-time absorbances were recorded after 10 half-lives or calculated from known concentrations and absorbancies; both values were equal within experimental error.

Competition Reactions. The amounts of the products MNO_3^{2+} and MOH_2^{3+} formed in the reactions between MCl^{2+} and Hg(II) and between MN_3^{2+} and nitrous acid in acidic aqueous NO_3^- media were determined by previously described chromatographic techniques[1,9] employing AG50W-X4 resin, 200–400 mesh, keeping the column at approximately 8 °C with circulated ice water. The later precaution effectively prevents any aquation of MNO_3^{2+} in the column. The separated products were determined spectrophotometrically using λ 500 nm (ε 57.4 M^{-1} cm^{-1}) for MNO_3^{2+} and λ 490 nm (ε 48.0 M^{-1} cm^{-1}) and λ 509 nm (ε 45.9 M^{-1} cm^{-1}) for MOH_2^{3+}.

Results and Discussion

MN_3^{2+} + HNO_2 Reaction. It has previously been shown[10] that in aqueous perchlorate media at constant H^+ concentration the rate law is

$$-d[MN_3^{2+}]/dt = k_{p2}[HNO_2][MN_3^{2+}]$$

where $k_{p2} = k_3[H^+]$ and is a pseudo-second-order rate constant. In the presence of $Hg(ClO_4)_2$ the reaction obeyed eq 1 when the initial concentrations of azido complex and total nitrite were equal; in this equation the D's are the indicated

$$\frac{1}{D_t - D_\infty} = \frac{1}{D_0 - D_\infty} + \frac{k_{p2}}{\epsilon_N - \epsilon_0}t \qquad (1)$$

optical densities, and ϵ_N and ϵ_0 are the molar extinction coefficients of MN_3^{2+} and MOH_2^{3+}, respectively. The concentrations of H^+ and Hg(II) were essentially constant throughout a reaction because $[H^+] >> [NaNO_2]$ and Hg(II) was not used up in the oxidation of N_3^-. A typical plot of (D_t

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Table I. Observed Rate Constants for the $MN_3^{2+} + HNO_2 + H^+$ Reaction in 0.25 Mole Fraction[a] CH_3CN + 0.75 Mole Fraction H_2O at 29.5 °C and 0.7 M Ionic Strength

$[MN_3^{2+}]$/mM	$\Sigma[NO_2^-]$/mM	$[H^+]$/M	$[Hg^{II}]$/M	salt added[b]	$k_{obsd}/M^{-2}\ s^{-1}$	n[c]
3.00	3.00	0.085		$Mg(ClO_4)_2$	250	1
3.00	3.00	0.050		$Mg(ClO_4)_2$	221	4
3.00	3.00	0.030		$Mg(ClO_4)_2$	210	1
2.00	2.00	0.050		$Mg(ClO_4)_2$	249	3
1.50	1.50	0.100		$Mg(ClO_4)_2$	217	3
1.50	1.50	0.050		$Mg(ClO_4)_2$	206	2
1.50	3.00	0.030		$Mg(ClO_4)_2$	222	2
			$k_{obsd}(av) = 225 \pm 25\ M^{-2}\ s^{-1}$			
3.00	3.00	0.110	0.200		4.4	2
3.00	3.00	0.065	0.200		5.6	2
3.00	3.00	0.110	0.150	$Mg(ClO_4)_2$	4.4	2
3.00	3.00	0.220	0.100	$LiClO_4$	4.9	2
3.00	3.00	0.110	0.100	$Mg(ClO_4)_2$	4.6	1
3.00	3.00	0.110	0.100	$LiClO_4$	5.4	1
3.00	3.00	0.065	0.100	$Mg(ClO_4)_2$	5.2	2
1.50	1.50	0.050	0.100	$Mg(ClO_4)_2$	5.1	2
3.00	3.00	0.100	0.050	$LiClO_4$	5.6	2
3.00	3.00	0.073	0.025	$Mg(ClO_4)_2$	5.9	1
			$k_{obsd}(av) = 5.1 \pm 0.5\ M^{-2}\ s^{-1}$			

[a] Mole fractions calculated on the basis of solvents only. [b] The salt was added to keep ionic strength constant. [c] Number of measurements made.

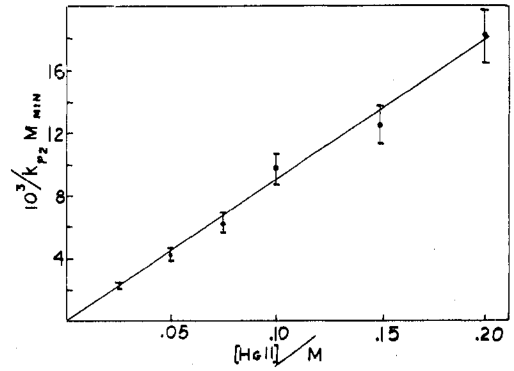

Figure 1. Plot of the reciprocal of k_{p2} vs. Hg(II) concentration for the assisted MN_3^{2+} substitution.

$- D_\infty)^{-1}$ against t was linear to at least 85% reaction. When the reciprocals of the k_{p2} rate constants were plotted against the Hg(II) concentration as in Figure 1, a straight line was obtained. This result is consistent with the mechanism given in eq 2–5. The rate law for this mechanism is given by eq

$$HNO_2 \rightleftarrows H^+ + NO_2^- \qquad K_a \tag{2}$$

$$Hg^{2+} + NO_2^- \rightleftarrows HgNO_2^+ \qquad K_{NO_2} \tag{3}$$

$$H^+ + HNO_2 \rightleftarrows NO^+ + H_2O \qquad K'' \tag{4}$$

$$MN_3^{2+} + NO^+ + H_2O \xrightarrow{k''} MOH_2^{3+} + N_2 + N_2O \tag{5}$$

6. Since $[Hg^{II}] >> \sum[NO_2^-]$, $[Hg^{2+}]$ is approximately equal

$$R = \frac{-d[MN_3^{2+}]}{dt} = \frac{k''K''[H^+]^2}{[H^+] + K_aK_{NO_2}[Hg^{2+}]} \times \sum[NO_2^-][MN_3^{2+}] = k_{p2}\sum[NO_2^-][MN_3^{2+}] \tag{6}$$

to $[Hg^{II}]$ and a plot of $(1000/k_{p2})$ against $[Hg^{II}]$ can be linear as shown in Figure 1. The value of the product $k''K''$ in the absence of Hg(II) has been found[10] to be approximately $9.5 \times 10^4\ M^{-2}\ min^{-1}$. Consequently the intercept of the plot in Figure 1 is very small as observed. When this value of $k''K''$ and the values of K_a and $[H^+]$ are combined with the observed value of the slope, an order-of-magnitude value of $K_{NO_2} \approx 10^5\ M^{-1}$ is obtained. No previous determinations of K_{NO_2} have been reported with which to compare this estimate.

It can be concluded that Hg(II) can be present in $MN_3^{2+} + HNO_2 + H^+$ aqueous reaction media without changing the nature of the rate-determining step (5) which presumably produces the five-coordinate intermediate M^{3+}. Consequently, product ratios obtained for competition reactions in the presence of Hg^{2+} will be those resulting from the competition reactions of M^{3+}.

The results for the assisted aquation of MN_3^{2+} in acetonitrile–water–perchlorate media are given in Table I. In the absence of Hg(II) the rate law was

$$R = -d[MN_3^{2+}]/dt = k_{obsd}[H^+][HNO_2][MN_3^{2+}]$$

since the total nitrite concentration, $\sum[NO_2^-]$, was very nearly equal to the HNO_2 concentration at the high H^+ concentrations used. The third-order rate constants k_{obsd} are given in the top half of Table I; their average value was 225 $M^{-2}\ s^{-1}$ with a standard deviation for a single measurement of ±25 $M^{-2}\ s^{-1}$ compared to $1.6 \times 10^3\ M^{-2}\ s^{-1}$ in purely aqueous media.[10] Apparently only the rate, and not the mechanism, of the assisted aquation was affected by the presence of acetonitrile.

In the presence of Hg(II) in acetonitrile–water media the rate law was

$$R = -d[MN_3^{2+}]/dt = k_{obsd}[H^+]^2(\sum[NO_2^-])[MN_3^{2+}]/[Hg^{II}] \tag{7}$$

as is readily deduced from eq 6 when $K_aK_{NO_2}[Hg^{II}] >> [H^+]$. Apparently the addition of acetonitrile to the reaction mixture displaced equilibrium 3 in favor of formation of the complex $HgNO_2^+$ so that the rate became second order in H^+ concentration and strictly inverse first order in Hg(II) concentration. The observed values of k_{obsd} defined by eq 7 are given in the lower half of Table I; they are constant within an error of approximately 10%. It may be concluded that although the presence of acetonitrile may alter the rate of the assisted aquation of MN_3^{2+} in the presence or absence of Hg(II), it does not alter the nature of the rate-determining step, namely, reaction 5. Consequently, the product ratios obtained in the presence and absence of Hg^{2+} in acetonitrile–water media will be those resulting from the competition reactions of M^{3+}.

MCl^{2+} + Hg(II) Reaction in NO_3^- Media. The rate of this reaction has been determined in sulfate media[11] where three reaction paths were found. In the first, second, and third paths the activated complexes were $[MClHg^{4+}]^\ddagger$, $[MClHgSO_4^{2+}]^\ddagger$,

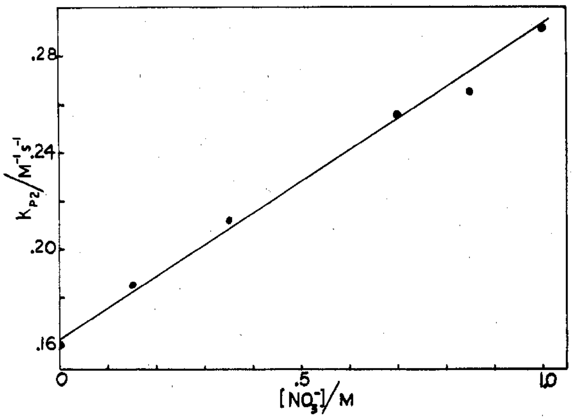

Figure 2. Plot of k_{p2} vs. NO_3^- concentration for the assisted MCl^{2+} substitution (0.050 M Hg(II), 1.00 M H^+, 1.2 M ionic strength, 26 °C).

and $[MClHg(SO_4)_2]^{\ddagger}$, respectively, and the rate constant for the first path was 0.057 M^{-1} s^{-1} at 0.30 M ionic strength and 25 °C. With NO_3^- we found that the integrated rate law for the conversion of MCl^{2+} to products

$$\log (D_t - D_\infty) = \log (D_0 - D_\infty) - k_{p1}t/2.303$$

was obeyed for 4 half-lives showing that the rate law was first order in MCl^{2+} concentration in nitrate media as it was in sulfate media. The pseudo-first-order rate constants k_{p1} were strictly proportional to the Hg(II) concentration; thus

$$k_{p2} = k_{p1}/[Hg^{II}]$$

A plot of k_{p2} against NO_3^- concentration, shown in Figure 2, yielded a straight line; apparently k_{p2} is given by

$$k_{p2} = k_0 + k_1[NO_3^-] \qquad (8)$$

The value of $k_0 = 0.16$ $M^- s^{-1}$ found here as compared to the value previously found[11] is qualitatively understood if the rate constant for the reaction between MCl^{2+} and Hg^{2+} increases with increasing ionic strength. Attempts to obtain K_1, the formation constant of $HgNO_3^+$, β_2, the overall formation constant of $Hg(NO_3)_2$, or k_2, the rate constant for the $[NO_3^-]^2$ term in k_{p2} failed because these constants appeared to be too small. Therefore, at concentrations of NO_3^- up to 1.00 M there are only two important kinetic paths leading to disappearance of MCl^{2+}; these are paths 1 and 2:

path 1 $MCl^{2+} + Hg^{2+} \rightleftarrows [MClHg^{4+}]^{\ddagger} \rightarrow$ products

path 2 $MCl^{2+} + Hg^{2+} + NO_3^- \rightleftarrows [MClHgNO_3^{3+}]^{\ddagger} \rightarrow$ products

Competition Reaction Products. The percentages MNO_3^{2+} formed from the assisted MCl^{2+} and MN_3^{2+} dissociations are reported in Table II. The recovery of MNO_3^{2+} and MOH_2^{3+} from the column was 100 ± 2%. The relative errors in the percentages of MNO_3^{2+} are no more than ±2%. The last line in Table II shows the percentage MNO_3^{2+} given by MN_3^{2+} in 1.00 M HNO_3 in the presence of Hg^{2+}, and this presumably is formed from the five-coordinate intermediate M^{3+}. This percentage is somewhat larger than the value (33.2%) previously reported[1] for 1.00 M HNO_3 in the absence of Hg^{2+} and gives better agreement with the percentage MNO_3^{2+} found for MCl^{2+}.

Also listed in Table II are the fractions f_1 and f_2 of the reaction proceeding by paths 1 and 2, respectively, which are given by

$$f_1 = k_0/k_{p2} \qquad (9a)$$

$$f_2 = 1 - f_1 \qquad (9b)$$

Table II. Percentage MNO_3^{2+} Formed in the Assisted Aquations of MCl^{2+} and MN_3^{2+} in Acidic Aqueous Nitrate Solution (1.2 M Ionic Strength, 26 °C, 0.050 M $Hg(ClO_4)_2$)

complex	$[NO_3^-]$/M	% MN_3^{2+}	f_1	f_2
MCl^{2+}	0.15	12.6	0.890	0.110
	0.35	25.4	0.776	0.224
	0.70	37.8	0.635	0.365
	0.85	40.8	0.589	0.411
	1.00	45.25	0.549	0.451
MN_3^{2+}	1.00	38.1		

where the k_{p2} values were obtained from the straight line through the data points of Figure 2. The first and second-to-last lines of Table II may be used to calculate the percentage x_1 of path 1 giving MNO_3^{2+} and the percentage x_2 of path 2 giving MNO_3^{2+} because in these two cases the former and latter contribute most heavily. Solution of the two simultaneous equations

$$0.890x_1 + 0.110x_2 = 12.6$$

$$0.549x_1 + 0.451x_2 = 45.25$$

yields $x_1 = 2.07\%$ and $x_2 = 97.8\%$. When these values of x_1 and x_2 are used with the f_1 and f_2 values for the three remaining experiments with MCl^{2+}, the calculated percentges of MNO_3^{2+} are 23.5, 37.0, and 41.4% in excellent agreement with the observed percentages of 25.4, 37.8, and 40.8%. Therefore, the results show that the intermediate of path 1 leads to only a very small percentage MNO_3^{2+} whereas the intermediate of path 2 leads to nearly quantitative production of MNO_3^{2+}. If the assisted MN_3^{2+} dissociation proceeds only through the intermediate M^{3+}, then the percentage of M^{3+} converted to MNO_3^{2+} varies with NO_3^- (because the percentage yield of MNO_3^{2+} varies with NO_3^- concentration) and is approximately 38% in 1.00 M HNO_3. This is very different behavior from that observed for the assisted MCl^{2+} dissociation. In the latter the percentage of the path 1 intermediate converted to MNO_3^{2+} is 2% at all NO_3^- concentrations and does not vary with the NO_3^- concentration although the contribution of path 1 to the total reaction varies with the NO_3^- concentration. Likewise the percentage of the path 2 intermediate converted to MNO_3^{2+} is 98% at all NO_3^- concentrations and does not vary with the NO_3^- concentration although the contribution of path 2 to the total reaction varies with the NO_3^- concentration. Therefore the two paths of the assisted MCl^{2+} substitution do not have the same intermediate as the assisted MN_3^{2+} substitution although the near-equality of the percentage MNO_3^{2+} formed at a given NO_3^- concentration for the two assisted substitution reactions might suggest that they do; it is concluded that M^{3+} is not formed in either path 1 or path 2.

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