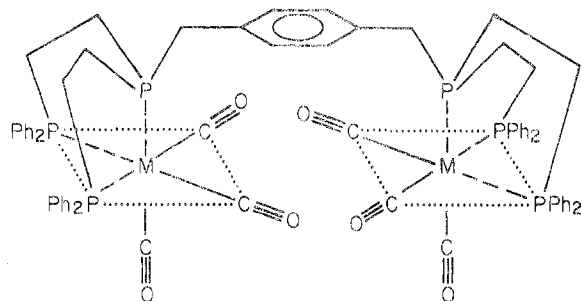$M_2(CO)_6(TDDX)$ is shown in formula 4.

4, $M_2(CO)_6(TDDX)$

In conclusion it may be mentioned that TDDX differs from hexaphos in forming binuclear complexes in most cases. This behavior may be expected on the basis of the stereochemistry of the ligand, which has two triphos moieties separated by six carbon atoms of the rigid *p*-xylene aromatic system.

Further studies on the reactions of the complexes of TDDX with small molecules such as dioxygen, dinitrogen, hydrogen, carbon monoxide, and nitric oxide are in progress.

Registry No. $Rh_2Cl_2(TDDX)$, 53862-63-8; $Ir_2Cl_2(TDDX)$, 53862-64-9; $Ru_2Cl_4(TDDX)(PPh_3)_2$, 53862-70-7; $Ru(TDDX)(PF_6)_2$, 53862-66-1; $Ru_2Cl_4(TDDX)(PF_6)_2$, 53862-72-9; $Rh_2Cl_4(TDDX)$-(PF_6)_2, 53862-74-1; $Rh_2Cl_6(TDDX)$, 53862-75-2; $Ir_3Cl_9(TDDX)$, 53906-80-2; $Ir_2Cl_4(TDDX)(PF_6)_2$, 53862-68-3; $Cr_2(CO)_6(TDDX)$, 53906-82-4; $Mo_2(CO)_6(TDDX)$, 53862-69-4; $Fe_2(CO)_6(TDDX)$, 53906-81-3; α,α'-dibromo-*p*-xylene, 623-24-5; triethyl phosphite, 122-52-1; $(C_2H_5O)_2P(O)CH_2C_6H_4CH_2P(O)(OC_2H_5)_2$, 4546-04-7; diphenylvinylphosphine, 2155-96-6; TDDX, 53850-32-1; Rh(CO)-Cl(PPh_3)_2, 13938-94-8; Ir(CO)Cl(PPh_3)_2, 14871-41-1; RhCl(PPh_3)_3, 14694-95-2; $RuCl_2(PPh_3)_3$, 15529-49-4.

References and Notes

(1) (a) R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **93**, 4158 (1971); (b) R. B. King and H. S. Saran, *Inorg. Chem.*, **10**, 1861 (1971).
(2) G. A. Barclay, C. M. Harris, and J. V. Kingston, *Chem. Commun.*, 965 (1968).
(3) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syn.*, **2**, 99 (1968).
(4) J. P. Collman, C. T. Sears, Jr., and M. Kubota, *Inorg. Syn.*, **2**, 102 (1968).
(5) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(6) P. S. Hallman, T. A. Stephenson, and G. Wilkinson, *Inorg. Syn.*, **12**, 238 (1970).
(7) K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **26**, 2537 (1961).
(8) K. Issleib and H. Weichmann, *Chem. Ber.*, **101**, 2197 (1968).
(9) A. H. Ford-Moore and J. W. Williams, *J. Chem. Soc.*, 1465 (1947).
(10) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).
(11) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).
(12) W. O. Siegl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **10**, 2158 (1971).
(13) W. J. Greary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(14) M. M. Taqui Khan and A. E. Martell, *Inorg. Chem.*, **13**, 2961 (1974).
(15) W. O. Siegl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **12**, 674 (1973).

Contribution from the Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455

Induced and Spontaneous Aquation of (Dimethyl sulfoxide)pentaaminecobalt(III) Perchlorate

WARREN L. REYNOLDS

The reaction between permanganate ion and (dimethyl sulfoxide)pentaamminecobalt(III) in aqueous solutions containing hydrochloric and perchloric acids gave approximately the same ratios of chloro- to aquopentaamminecobalt(III) products as reactions between nitrous acid and the azido- or carbamatopentaamminecobalt(III) complexes and hence supplied further evidence for the formation and existence of the five-coordinate pentaamminecobalt(III) complex. Effects of variation of the composition of the reaction medium on the competition reactions of this five-coordinate complex were studied and an effect by so-called "inert" cations was found. Since the aquation of (dimethyl sulfoxide)pentaamminecobalt(III) may possibly proceed through the five-coordinate intermediate, the rate of aquation of the dimethyl sulfoxide complex was studied in $HClO_4$ and in $NaClO_4$ solutions to determine whether this effect also occurred in the aquation reaction; it did not.

Introduction

It has been postulated[1,2] that the five-coordinate intermediate $Co(NH_3)_5{}^{3+}$ (here symbolized by M^{3+}) was formed in the induced aquations of $MN_3{}^{2+}$ and of $M(CO_2NH_2)^{2+}$ upon reaction with NO^+. Because these two complexes are of the same charge type and involve a common reactant, it is desirable to obtain, if possible, further evidence for the occurrence of M^{3+} by generating it from other reactions. Such evidence has been obtained by oxidizing (dimethyl sulfoxide)penta-amminecobalt(III), represented by $M(DMSO)^{3+}$, with permanganate ion in the presence of competing ligands and is reported here. The oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone by $KMnO_4$ is rapid and quantitative.[3] The dimethyl sulfone is a poor ligand and apparently leaves the first coordination shell of Co(III) generating M^{3+}. Also reported here are studies supporting an earlier conclusion[4] that

spontaneous aquation of $M(DMSO)^{3+}$ in various aqueous media and mixed solvents proceeded by an I_d mechanism. Pearson and Moore[5] have already shown that the aquation of $Co(NH_3)_5NO_3{}^{2+}$ involved a different intermediate than the one formed in the induced aquations.

Experimental Section

Chemicals. (Dimethyl sulfoxide)pentaamminecobalt(III) per-chlorate was prepared by the method of Mac-Coll and Beyer.[6] (Acetonitrile)pentaamminecobalt(III) perchlorate was prepared by heating the corresponding aquo complex with liquid acetonitrile containing just enough water to dissolve the aquo complex at 70° until a golden yellow precipitate began to form and the supernatant liquid was a clear yellow. Liquid acetonitrile was added from time to time to replace that lost by evaporation. The mixture was cooled to 0° and filtered, and the precipitate dissolved in a minimum amount of water with slight warming. The solution was cooled to 0° and 1:3 by volume of $HClO_4-H_2O$ was added dropwise with continuous

Table I. Values of the Ratio R^a = ([MCl^{2+}]/[MOH$_2{}^{3+}$][Cl$^-$]) for HCl + HClO$_4$ Media [0.150 mmol of [M(DMSO)](ClO$_4$)$_3$·2H$_2$O, 25°]

[HCl], M	[HClO$_4$], M	I,^{b} M	mmol of MCl^{2+}	mmol of MOH$_2{}^{3+}$	R, M^{-1}
1.00		1.0	0.022	0.125	0.18
2.00		2.0	0.038	0.110	0.17
1.50	0.50	2.0	0.029	0.122	0.16
1.00	1.00	2.0	0.019	0.128	0.15
0.50	1.50	2.0	0.0094	0.137	0.14

^{a} Defined in ref 1. ^{b} Ionic strength calculated on the basis of the predominant electrolytes present.

stirring and cooling. The precipitate was filtered, washed with cold water, then ethanol, and then ether, and oven-dried at 50°. *Anal.* Calcd for [Co(NH3)5(CH3CN)](ClO4)3: C, 5.07; H, 3.84; N, 17.76. Found: C, 5.02; H, 3.93; N, 17.10. The spectrum showed absorption maxima at 332 and 465 nm with molar extinction coefficients of 53.7 and 61.0 M^{-1} cm^{-1} in satisfactory agreement with literature values for the product obtained by a different synthetic method.[7] [Co(NH3)5SO4]HSO4·2H2O was prepared as described.[8]

Determination of Product Ratios. A 0.0835-g (0.150-mmol) sample of [Co(NH3)5(DMSO)](ClO4)3·2H2O was dissolved in an aqueous solution containing the competing ligand and HClO4 or NaClO4 to maintain a given ionic strength. The dissolution of the solid occurred rapidly and negligible aquation of the DMSO complex occurred at 25°. The solution was stirred magnetically and 3.50 ml of 0.039 M KMnO4 was injected rapidly by syringe at zero time. After 10 min the precipitate of MnO2 was filtered and washed until washings were colorless. The filtrate and washings were poured onto about 3 ml of wet AG5OW-X4 200–400 mesh resin and transferred in small portions, while being kept cold, to a 25 cm × 1 cm column of the same resin. Negligible interconversion of the product complexes occurred under these conditions.

The MnO2 precipitate always retained about 4–8% of the product cobalt(III) complexes. These complexes were apparently occluded in the precipitate so they could not be removed by washing with water. Their recovery was effected by dissolving the MnO2 precipitate in concentrated HCl and diluting to 50.00 ml so as to yield a 4 M HCl solution. After several hours in a 45° bath the manganese was completely reduced to nonabsorbing manganese(II) and the total concentration of the aquo- and chloropentaammine complexes resulting could be determined spectrophotometrically at the isosbestic point, 508.5 nm; the absorbance of this solution did not change over periods up to 2 days. After elution of the product complexes from the resin column the total recovery of cobalt(III) was (100 ± 1.5)%.

The MSO4+ complex was eluted with 1 M HClO4. The 2+ complexes were separated from the 3+ complexes with 2 M HClO4. After the two charge types were well separated, 3 M HClO4 was usually used to elute the 2+ complex. The eluent was collected in a container cooled in an ice–water bath and diluted to a known volume with the acid used for the elution. The spectrum of the eluent was taken to confirm the product obtained and the amount of product therein was determined spectrophotometrically.

Co(NH3)5(CH3CN)$^{3+}$ was separated from Co(NH3)5OH2^{3+} and eluted with 3 M HClO4. Co(NH3)5OH2^{3+} was usually eluted with 4 M HCl; negligible conversion to the chloro complex occurred because a duplicate experiment using 3 M HClO4 for elution gave a very similar spectrum for the product aquo complex and the same analysis for the amount of aquo complex formed when spectrophotometrically determined at λ_{max} 490 nm. However, as a precaution the amount of aquo complex formed was always determined at the isosbestic point as well as at 490 nm; the two values were always in agreement. The wavelengths (in nm) and molar extinction coefficients (in M^{-1} cm^{-1}), respectively, used for the determination of the amounts of complexes formed were as follows: Co(NH3)5OH2^{3+}, 490 (48.0), 508.5 (45.0); Co(NH3)5Cl^{2+}, 532 (50.4), 508.5 (45.0); Co(NH3)5N3^{2+}, 518 (266), 302 (7810); Co(NH3)5Br^{2+}, 550 (57.7); Co(NH3)5NO3^{2+}, 500 (57.4); Co(NH3)5SO4$^+$, 514 (61.6); Co(NH3)5(CH3CN)$^{3+}$, 465 (61.0).

The error in the number of millimoles of a product formed was not more than ±3% when more than 0.01 mmol of product was formed and did not exceed ±5% for any of the results given.

Aquation Rate of Co(NH3)5(DMSO)$^{3+}$. Sufficient solid [Co(NH3)5(DMSO)](ClO4)3·2H2O was weighed out to give a 1 × 10^{-3} M solution and dissolved in the reaction medium thermostated at 45.0 ± 0.1° in a water bath. Aliquots of reaction mixture were removed
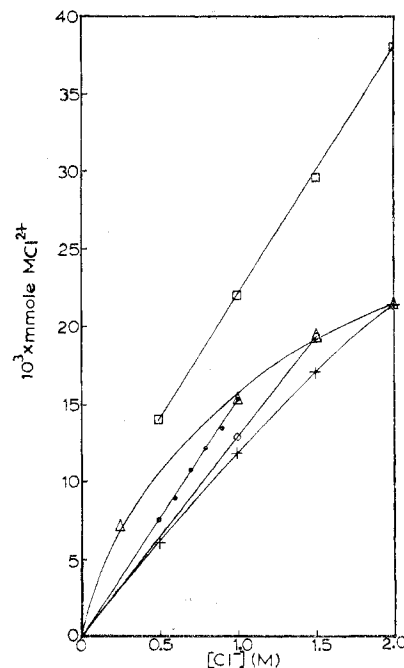

Figure 1. Chloride ion–water competition in the induced aquation of M(DMSO)$^{3+}$ by MnO4$^-$, using 0.150 mmol of [M(DMSO)](ClO4)3·2H2O and 0.02 M HClO4 (except when HCl was used), at 25°: solid circles, I = [NaCl] + [NaClO4] = 1.00 M; open circles, I = [NaCl] + [NaClO4] = 1.50 M; crosses, I = [NaCl] + [NaClO4] = 2.00 M; squares, I = [HCl]; triangles, I = [NaCl].

at time t, the absorbance A determined at 290 nm, and the aliquot discarded. Plots of log $(A - A\infty)$ *vs.* time gave straight lines for at least 3 half-lives and $A\infty$ was obtained after 10 half-lives.

Results and Discussion

Chloride Ion–Water Competition. In Table I are listed values of the ratio, R, defined by Haim and Taube.[1] It is seen that the values are in the range 0.14 ≤ R ≤ 0.18 as compared to 0.18 ≤ R ≤ 0.24 for the azido complex[2] and 0.20 ≤ R ≤ 0.27 for the carbamato complex.[2] The similarity of the R values despite the difference in the nature of the reactants strongly indicates that a common intermediate is formed. Part of the small difference in the R ranges may be due to the rather large correction of 20% which had to be applied[2] for carbon–oxygen bond fission in the carbamato complex. Furthermore, equal amounts of MX^{2+} (X$^-$ = Cl$^-$, Br$^-$) were formed in 1 M HX solutions[2] and equal amounts of the same two products were also formed in equimolar NaX solutions in the induced aquation of the dimethyl sulfoxide complex (see the following section on bromide ion–water competition).[9]

Further results for Cl$^-$–water competition are shown in Figure 1. It is seen that the amount of MCl^{2+} formed at 1.0 and 1.5 M ionic strength, I, in NaCl + NaClO4 media is strictly proportional to NaCl concentration; the anation reaction between the Co(NH3)5^{3+} intermediate and Cl$^-$ does not show the saturation effect shown by the anation reaction between MOH2^{3+} and Cl$^-$ for similar media.[10,11] The plot for I = 2.0 M shows a very small saturation effect above 1.0 M NaCl. The curves for NaCl and HCl in the absence of ClO4$^-$ to maintain I constant show the saturation effect with simultaneously increasing Cl$^-$ concentration and ionic strength. Increasing ionic strength stabilizes the separated reactants, M^{3+} and Cl$^-$, as compared to the activated complex or to a precursor complex formed between the two ions.

Figure 1 also shows that more MCl^{2+} is formed in HCl solutions than in NaCl solutions of equal concentration; *i.e.*, the nature of the "inert" cation affects the amount of MCl^{2+} produced. More results on the effect of the "inert" cation are shown in Table II. The increase in the values of (mmol of

Table II. Dependence of Amount of MCl^{2+} on Nature of "Inert" Cation Present [0.150 mmol of $[M(DMSO)](ClO_4)_3 \cdot 2H_2O$, 25°]

Salt	[Salt], M	[NaClO₄], M	[HCl], M	[HClO₄], M	$I,^a M$	(mmol of MCl²⁺)/[Cl⁻]
			1.00	1.00	2.00	0.0192
		1.00	1.00		2.00	0.0176
NaCl	1.00	1.00		0.02	2.02	0.0119
			2.00		2.00	0.0191
AlCl₃	0.333			0.02	2.02	0.0146
LiCl	2.00			0.02	2.02	0.0111
NaCl	2.00			0.02	2.02	0.0107
KCl	2.00			0.02	2.02	0.00925
NH₄Cl	2.00			0.02	2.02	0.0105
			1.50		1.50	0.0197
NaCl	1.50			0.02	1.52	0.0129
MgCl₂	0.500			0.02	1.52	0.0296
CaCl₂	0.500			0.02	1.52	0.0288

^{a} Calculated on the basis of the salts and acids listed.

MCl^{2+})/[Cl⁻] for a given ionic strength for a series of cations can be explained in terms of decreasing water activity and/or increasing Cl⁻ activity as an accompanying result. The cations which are most strongly hydrated, or which are structure forming in water, allow the largest amounts of MCl^{2+} to be formed. Hence, the water–water and water–Cl⁻ interactions in the bulk solvent phase are an important factor in determining the relative amounts of products formed.

Bromide Ion–Water Competition. The amount of MBr^{2+} formed from 0.150 mmol of $M(DMSO)^{3+}$ at 2.0 M constant ionic strength was proportional to NaBr concentration: 0.011 mmol of MBr^{2+} for 1.00 M NaBr + 1.00 M NaClO₄ and 0.021 mmol of MBr^{2+} for 2.00 M NaBr. The amount of MBr^{2+} produced was essentially equal to the amount of MCl^{2+} produced (0.012 and 0.021 mmol, respectively) for the same media with NaBr in place of NaCl. Therefore equimolar Br⁻ and Cl⁻ compete equally well for the present intermediate, when other conditions are the same, as Buckingham, *et al.*,[2] found. The fact that Br⁻ and Cl⁻ show essentially identical behavior toward the intermediate formed in the induced aquations but have different rate laws for the anation of MOH_2^{3+} supports the argument[5,12] that the spontaneous anations of MOH_2^{3+} by Cl⁻ and Br⁻ proceed through a different intermediate than do the induced reactions. The values of k_X/k_w (to use the notation of Haim and Taube[1]), obtained from the halide ion–water competition products and from the relation $k_X/k_w = Kk_a/k_e$, are equal within experimental error when improved values[11,12,13] of K, k_a, and k_e are used for 1 M ionic strength and 25°, and hence they cannot be used to show that the spontaneous and induced anations by Cl⁻ and Br⁻ do not involve the same intermediate.

Azide Ion–Water Competition. In a 2.00 M NaN₃ solution with I = 2.0 M, 0.0385 mmol of MN_3^{2+} and 0.0736 mmol of MOH_2^{3+} were produced giving k_X/k_w = 0.261 compared to 0.263 calculated from the available data[14–17] for K, k_a, and k_e. Because of differing ionic strengths at which different parameters were determined the excellent agreement is fortuitous, but it is doubtful that comparison of the two values can be used to determine whether or not the spontaneous and induced reactions have different intermediates.

Nitrate Ion–Water Competition. The results are listed in Table I of the supplementary material and are also in fair agreement with those found previously.[2] At constant ionic strength the amount of MNO_3^{2+} formed was not strictly proportional to NO₃⁻ concentration but the effects of increasing ionic strength and of replacement of H⁺ by Na⁺ were smaller in NO₃⁻ media than in Cl⁻ media.

Sulfate Ion–Water Competition. The results are listed in Table II of the supplementary material for aqueous sulfate media. The amount of MSO_4^+ formed was not proportional to the concentration of the sulfate compound used. Partly this result was due to the effect of increasing ionic strength and partly it was probably due to the saturation effect resulting from ion-pair formation. There was a small increase in the amount of MSO_4^+ formed when H⁺ replaced Na⁺.

Some results for simultaneous SO_4^{2-} + NO_3^- + H_2O competition are listed in Table III of the supplementary material. The small change in the number of millimoles of MSO_4^+ formed between the most dilute and the most concentrated solutions suggests that the M^{3+} intermediate exists mainly in the form of M^{3+},SO_4^{2-} ion pairs at all SO_4^{2-} concentrations listed. The NO₃⁻ ion is not expected to saturate the solution with M^{3+},NO_3^- ion pairs and the change in the number of millimoles of MNO_3^{2+} produced for the same change in concentration is much larger. If, indeed, near-saturation of M^{3+},SO_4^{2-} ion-pair formation is the explanation of the results in Table III, then it would seem that the ion pairs live long enough to establish equilibrium with the M^{3+} and SO_4^{2-} ions so that the M^{3+} ions can seek out NO₃⁻ ions or that some ion pairs live long enough to meet and react with NO₃⁻ ions while others collapse to give an essentially constant ratio of aquo and sulfato complexes.

Acetonitrile–Water Competition. In 0.667 mol fraction water + 0.333 mol fraction acetonitrile (calculated on the basis of the solvents only), 0.100 mmol of $M(DMSO)^{3+}$ in two experiments gave a value of 0.26 for the ratio of the acetonitrile to the aquo complex.

Relative Rates of $M(DMSO)^{3+}$ Aquation in NaClO₄ and HClO₄ Media. The first-order rate constants for aquation of $M(DMSO)^{3+}$ at 45° for various perchlorate salt concentrations and various ionic strengths up to 2.0 M have been reported[4] but the rate constants for various perchloric acid concentrations have not been. Since substitution of HClO₄ for NaClO₄ affected the relative amounts of MCl^{2+} and MOH_2^{3+} formed in the competition studies, it was of interest to determine whether or not there was also an effect on the aquation rate constant because it is not known with certainty whether this aquation involves a D or Iₐ mechanism.[18] There was no effect at 0.0100, 0.100, 0.250, 0.500, 1.00, or 2.00 M HClO₄ and so the aquation rate constants will not be repeated here. The rate constants for 3.00 M HClO₄ and 3.00 M NaClO₄ were in the range (1.32–1.37) $\times$ 10⁻⁴ sec⁻¹ at 45° and fell on an extension of the previously established[4] curve relating rate constant to perchlorate concentration.

References and Notes

(1) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).
(2) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).
(3) T. B. Douglas, *J. Amer. Chem. Soc.*, **68**, 1972 (1946); K. H. Krull and M. Friedman, *J. Chromatogr.*, **26**, 336 (1967).
(4) W. L. Reynolds, M. Biruš, and S. Ašperger, *J. Chem. Soc., Chem. Commun.*, 822 (1973); *J. Chem. Soc., Dalton Trans.*, 716 (1974).
(5) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).
(6) C. R. P. Mac-Coll and L. Beyer, *Inorg. Chem.*, **12**, 7 (1973).

(7) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

(8) S. M. Jorgensen, *J. Prakt. Chem.*, [2] **31**, 264 (1885).

(9) One molar HBr solutions reacted with KMnO$_4$ and could not be used. Consequently equimolar NaCl and NaBr solutions were used to show that equal quantities of MCl^{2+} and MBr^{2+} were formed from equal halide ion concentrations.

(10) C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, **89**, 3141 (1967).

(11) E. S. Barber and W. L. Reynolds, *Inorg. Chem.*, **12**, 951 (1973).

(12) W. L. Reynolds, I. Murati, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 719 (1974).

(13) S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, 724 (1965).

(14) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8**, 1604 (1969).

(15) G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963).

(16) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

(17) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

(18) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N.Y., 1965.

Kinetics of the Oxidation of Tin(II) by Cobalt(III) in Aqueous Perchlorate Solutions

N. A. DAUGHERTY* and J. K. ERBACHER

The rate law for the oxidation of tin(II) by cobalt(III) in perchlorate acid solutions is given by $-d[Co(III)]/dt = k' \cdot [Co(III)][Sn(II)]$, where $k' = k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$. The activation parameters associated with k_{-1} and k_{-2} are $\Delta H_{-1}^* = 13.2 \pm 0.3$ kcal/mol, $\Delta S_{-1}^* = 5.2 \pm 1$ cal/(mol deg), $\Delta H_{-2}^* = 17.4 \pm 0.8$ kcal/mol, and $\Delta S_{-2}^* = 17 \pm 3$ cal/(mol deg).

Introduction

Alternate mechanisms, involving either a sequence of one-electron steps or a single, two-electron step, are possible for the oxidation of Sn(II). Therefore, the reactions of Sn(II) with one-electron oxidants such as Co(III) are of mechanistic interest. Many[1-7] of the previous studies involving the reaction of Sn(II) with a variety of oxidants were carried out in hydrochloric or sulfuric acid solutions in order to prevent formation of insoluble stannic oxide. These complexing acids often affect the reaction rate and may even have an effect on the stoichiometry. Complex formation and its problems may be avoided by using perchloric acid as the solvent. Although the oxidation of Sn(II) in perchloric acid eventually produces colloidal stannic oxide, the rate of oxide formation is slow[8] compared to the rate of oxidation of Sn(II). As a result, oxide formation does not interfere with rate measurements made in perchloric acid solution.

Experimental Section

Materials. Solutions of tin(II) perchlorate were prepared, stored, and handled as described previously.[9] Most of the rate runs were made using solutions of cobalt(III) perchlorate prepared by the electrolytic oxidation of cobalt(II) perchlorate solutions. The electrolysis was carried out in a two-compartment cell employing a platinum gauze anode through which a current of 0.5 A was passed for 6-7 hr. During the electrolysis, the cell contents were stirred and were maintained at 0-5° with an ice bath. A few runs were made using Co(III) solutions prepared by a slight modification of the method of Hofmann-Bang and Wulff.[10] In this method, Co(II) is oxidized by hydrogen peroxide in the presence of potassium bicarbonate to yield solutions of tris(carbonato)cobaltate(III) ion. Acidification of the solutions produces solutions of the aquo ion. Solutions of iron(III) perchlorate were prepared from G. F. Smith iron(III) perchlorate which had been recrystallized three times. Lithium perchlorate was prepared by neutralizing the carbonate with perchloric acid. The salt was recrystallized twice from water before being used to prepare stock solutions.

Analyses. Stock cobalt(III) perchlorate solutions were analyzed for Co(III) by delivering an aliquot of the deaerated solution into a known excess of iron(II) sulfate solution followed by back-titration of the Fe(II) left after the Co(III)–Fe(II) reaction was complete. The Co(III) content of solutions used in kinetic experiments was determined spectrophotometrically at 250 nm. Total cobalt concentrations of stock solutions were determined spectrophotometrically[11] after reduction of the Co(III) with sodium sulfite. Cobalt(II) concentrations were determined from the difference in total cobalt and Co(III) concentrations.

Table I. Apparent Second-Order Rate Constants at Different Reactant Concentrations[a]

$10^4[Co\text{-}$ $(III)]_0, M$	$10^4[Sn\text{-}$ $(II)]_0, M$	$10^{-3}k',$ M^{-1} $\sec^{-1}$	$10^4[Co\text{-}$ $(III)]_0, M$	$10^4[Sn\text{-}$ $(II)]_0, M$	$10^{-3}k',$ M^{-1} $\sec^{-1}$
21.3	10.4	16.0	2.83	2.04	14.2
14.5	10.4	16.1	6.15	5.20	15.9
9.56	10.4	15.6[b]	14.2	18.0	15.3
5.74	10.4	15.7	14.0	31.0	14.4
1.25	10.4	15.3			

[a] Conditions: 20°, 1.0 M HClO$_4$, $\mu = 2.0$ (LiClO$_4$). [b] Co(III) prepared by bicarbonate method.

The Sn(II) content of the tin(II) perchlorate solutions was either determined iodometrically[12] or determined by addition of an aliquot to a known excess of vanadium(V) perchlorate solution followed by titration of the excess vanadium(V) with Fe(II) in 6 M sulfuric acid. In a few stoichiometry experiments Sn(II) was determined spectrophotometrically at 252.5 nm.

The acid concentration of metal ion solutions was calculated from a knowledge of the metal ion concentration and the total perchlorate concentration as determined by passage of an aliquot through a cation-exchange resin and titration of the hydrogen ion in the eluent.

Rate Measurements. The rate of the reaction was followed by measuring the decrease of the absorbance of Co(III) at either 402 nm or 604 nm as a function of time using a Durrum-Gibson D-110 stopped-flow spectrophotometer. Apparent second-order rate constants were calculated from the absorbance *vs.* time data.

Calculations. Apparent second-order rate constants and activation parameters were calculated using a nonlinear least-squares computer program.

Induction Experiments. Attempts were made to induce the slow[13] reaction between Sn(II) and Fe(III) by the addition of Co(III). In a typical experiment 0.034 mequiv of Co(III) was added to a stirred solution containing 0.359 mequiv of Sn(II) and 0.105 mequiv of Fe(III). In other experiments, the order of addition was Fe(III)–Co(III)–Sn(II). The reaction medium was 1.2–2.9 M HClO$_4$ at 22–24°. The amount of Fe(III) consumed was determined spectrophotometrically at 310 nm.

Results

Stoichiometry. The expected stoichiometry is given by

$$Sn(II) + 2Co(III) \rightarrow Sn(IV) + 2Co(II) \qquad (1)$$

The stoichiometry was checked by mixing Sn(II) and Co(III) in mole ratios ranging from 10:1 to 1:10, allowing the reaction to take place, and determining the amount of excess reactant left after the reaction was complete. Agreement between the