

Table IV. Reaction Constants from Hammett LFER Correlations of Electron-Transfer Reactions of Pyridinium Ions and Metal-Pyridine Complexes

oxidizing agent	reducing agent	ρ	ref
Group A: Electron Transfer to Metal Known or Inferred			
(NH ₃) ₅ Co(NC ₅ H ₄ X) ³⁺	*C(CH ₃) ₂ OH	1.1	1
(H ₂ O) ₅ Cr(NC ₅ H ₄ X) ³⁺	Ru(bpy) ₃ ³⁺	1.1	11
(NH ₃) ₅ Co(NC ₅ H ₄ X) ³⁺	Ru(NH ₃) ₆ ²⁺	1.3	1
(NH ₃) ₅ Co(NC ₅ H ₄ X) ³⁺	V(H ₂ O) ₆ ²⁺	1.5	1
(NH ₃) ₅ Ru(NC ₅ H ₄ X) ³⁺	V(H ₂ O) ₆ ²⁺	1.8	29
(NH ₃) ₅ Co(NC ₅ H ₄ X) ³⁺	Cr(H ₂ O) ₆ ²⁺	1.9	30
Group B: Electron Transfer to Pyridine Known or Inferred			
(H ₂ O) ₅ Cr(NC ₅ H ₄ X) ³⁺	*C(CH ₃) ₂ OH	7.2	a
X-C ₅ H ₄ NH ⁺	*C(CH ₃) ₂ OH	8.5 (6.6 ± 1.9)	12, a
X-C ₅ H ₄ NCH ₃ ⁺	*C(CH ₃) ₂ OH	9.0	12
X-C ₅ H ₄ NCH ₃ ⁺	*[Ru(bpy) ₂ (CN) ₂]	10.2	27
X-2,6-Me ₂ C ₅ H ₂ NCH ₃ ⁺	*[Ir(COD)(μ-pz) ₂] ^b	10.3	28

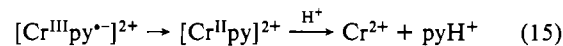
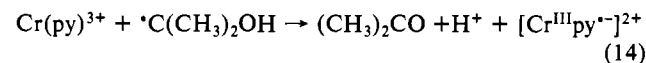
^aThis work. ^bCOD = 1,5-cyclooctadiene; pz = pyrazolyl.

earlier as to the site of electron attack. The new results along with values from several sources are summarized in Table IV. As noted elsewhere,^{1,11} all the data fall quite cleanly into one of two categories, those with "low" values of ρ (1.1-1.9) and those with "high" values (6.6-10.3). Each category contains some members where there is little doubt about the mechanism; all of those following a known mechanism fall in the expected group. On that basis we infer that reduction of Cr(py)³⁺ occurs by electron transfer to the pyridyl ring.

The same conclusion might have been reached from different logic. Other Cr(III) complexes, lacking a pyridine ligand, react with this radical very slowly; e.g. for Cr(H₂O)₆³⁺, $k = 5.6 \times 10^2$

M⁻¹ s⁻¹,¹⁹ and for (H₂O)₅CrCl²⁺, $k < 3 \times 10^4$ M⁻¹ s⁻¹.^{12b} Clearly, then, the donor ligand pyridine enhances the electron-transfer rate very substantially. This suggests that its effect is a consequence of its direct chemistry and is not an incidental feature.

The next step in the reaction sequence is suggested to be intramolecular electron transfer (as reported^{31,32} on the basis of a direct measurement for a Co(III)-pyridyl radical complex) yielding the observed products.



An alternative possibility is that the immediate metal-bound radical product would, like the free Hpy* radical, react by bimolecular disproportionation. We are inclined to discount that, however, in light of the products observed.

The LFER analysis of the reduction of the chromium and cobalt series by *C(CH₃)₂OH poses a challenging question:³³ Will the relative reactivity of the two series become identical ($\rho = 10$) beyond the intersection point at $\sigma \sim 0.6$, i.e., when the reducibility of the ligand apparently exceeds that of the cobalt center? The answer may be difficult to obtain experimentally, since the rate constants in this region are high ($>10^8$ M⁻¹ s⁻¹) and the limitation imposed by the diffusion control may reduce the effect.

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Registry No. (H₂O)₅Cr(NC₅H₅)³⁺, 34714-27-7; (H₂O)₅Cr(NC₅H₄-4-CN)³⁺, 102436-45-3; (H₂O)₅Cr(NC₅H₄-3-CN)³⁺, 42422-49-1; (H₂O)₅Cr(NC₅H₄-4-Cl)³⁺, 102436-46-4; (H₂O)₅Cr(NC₅H₄-3-Cl)³⁺, 42476-27-7; (H₂O)₅Cr(NC₅H₄-4-*t*-Bu)³⁺, 102436-47-5; HNC₅H₄-4-CN⁺, 37449-63-1; HNC₅H₄-3-CN⁺, 53760-43-3; *C(CH₃)₂OH, 5131-95-3.

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Kinetic Studies on the Perchlorate Oxidation of Aqua Mo³⁺ and Mo^{III}₂

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The pale yellow hexaqua Mo³⁺ ion and green aqua Mo^{III}₂ dimer [(H₂O)₄Mo(OH)₂Mo(H₂O)₄]⁴⁺ are both oxidized by ClO₄⁻ in acidic solutions [H⁺] = 0.2-0.7 M, I = 1.0 M, to the yellow Mo(V) aqua dimer, [Mo₂O₄(H₂O)₆]²⁺. In each case three reaction stages are observed here referred to as involving induction, propagation, and termination. The behavior is quite different from that observed in all previous studies of ClO₄⁻ oxidations.

All reactions of perchlorate that it has been possible to study in any detail involve metal ions.¹ Each of the labile hexaqua ions V²⁺ (-0.25 V), V³⁺ (0.36 V), and Ti³⁺ (~0.1 V) reduces ClO₄⁻ to Cl⁻ in an 8e⁻ process.^{2,3} In the case of Ti³⁺ the rate law is rate = (k₁ + k₂[H⁺])[Ti³⁺][ClO₄⁻], and typical half-lives are up to 2 h at 40 °C.³ With V²⁺, rate constants are in the range

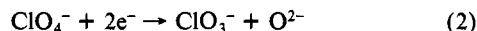
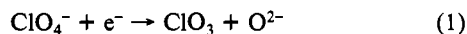
(5.3-7.6) × 10⁻⁷ M⁻¹ s⁻¹ at 25 °C,^{1,2,4} and with V³⁺, the rate constant is 3.0 × 10⁻⁶ M⁻¹ s⁻¹ at 50 °C.² Small contributions from [H⁺]-dependent terms are also observed. Results for hexaqua Ru²⁺ (0.23 V) with ClO₄⁻ are consistent with a substitution-controlled process (3.2 × 10⁻³ M⁻¹ s⁻¹), and ClO₃⁻ is the final product.⁵ Although Cr²⁺ (-0.41 V) and Eu²⁺ (-0.38 V) are stronger reducing agents, there is little or no reaction with ClO₄⁻,

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and rate constants are $<10^{-8} \text{ M}^{-1} \text{ s}^{-1}$.⁴

One- or two-equivalent reaction paths are believed to be relevant, (1)–(2). With Ti^{3+} (1) only can occur, but for V^{2+} and



V^{3+} (1) and (2) may contribute. An important question is whether the metal ion in its oxidized form has a sufficient affinity for the O^{2-} released in order to facilitate reaction. The existence of VO^{2+} , TiO^{2+} , and Ru^{IV} -oxo complexes, but no corresponding Cr or Eu products, is consistent with the behavior observed. In the case of Mo there have been a number of earlier studies,^{6–9} but no established pattern has emerged. Now that hexaqua Mo^{3+} has been prepared,^{10,11} a study of the reaction with ClO_4^- merited attention. Preliminary results have been reported.¹² The aqua ions of Mo(IV) and Mo(V) (possible reaction products) have been characterized.^{13–16} The structure factor being relevant, the aqua Mo^{III}_2 dimer $[(\text{H}_2\text{O})_4\text{Mo}(\text{OH})_2\text{Mo}(\text{H}_2\text{O})_4]^{4+}$ ^{17–19} was also studied.

Experimental Section

Reactants. Hexaquamolybdenum(III), Mo^{3+} , was obtained by aqution of $\text{K}_3[\text{MoCl}_6]$ under rigorous air-free conditions.²⁰ The Mo^{3+} ($\sim 0.06 \text{ M}$) was eluted from a Dowex 50W-X8 column with 2 M *p*-toluenesulfonic acid, HPTS (Sigma Chemicals), and has absorption peaks at 310 nm ($23.2 \text{ M}^{-1} \text{ cm}^{-1}$) and 380 nm ($14.1 \text{ M}^{-1} \text{ cm}^{-1}$).²¹

The aqua dimer, Mo^{III}_2 , was prepared by reduction of sodium molybdate (BDH, AnalaR) ($100 \text{ mL}, 10^{-2} \text{ M}$) in 1.0 M HPTS on a Zn/Hg column under rigorous O_2 -free conditions followed by Dowex 50W-X2 ion-exchange chromatography.¹⁸ Solutions of Mo^{III}_2 in 2.0 M HPTS were standardized by using previously determined peak positions λ/nm (absorption coefficient, $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$ for dimer): 360 (910), 572 (96), 624 (110). For studies in which Mo(III) was in methanesulfonic acid, HMS (BDH), the preparation was carried out in an identical manner with HMS substituted for HPTS.

A sample of the bis(μ -hydroxo)bis[aqua(1,4,7-triazacyclononane)molybdenum(III)] complex, $[(9\text{-aneN}_3)(\text{H}_2\text{O})\text{Mo}(\text{OH})_2\text{Mo}(\text{H}_2\text{O})(9\text{-aneN}_3)]^{4+}$, was prepared from the related μ -carbonato bis(μ -hydroxo) complex $[(9\text{-aneN}_3)\text{Mo}(\text{OH},\text{OH},\text{CO}_3)\text{Mo}(9\text{-aneN}_3)]\text{I}_2$ ²² by allowing 0.2 g to react with 0.10 M HPTS (20 mL) for 1 h under air-free conditions. The dark green solution was then loaded onto an ice-cooled Dowex 50W-X2 column ($8 \times 1 \text{ cm}$) previously washed with air-free H_2O (1 L). After the column was washed with 1 M HPTS, an emerald green band separated and was eluted ($3 \times 10^{-3} \text{ M}$) with 2 M HPTS. Peak positions were at 379, 490, 610, and 650 nm, compared to those reported for the iodide salt in H_2O at 379, 490, 643, and 715 (sh) nm.²² The dominant 379-nm peak ($\epsilon 1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ per dimer) was used for standardization purposes.

Lithium perchlorate (BDH, reagent grade) was recrystallized three times. Sodium perchlorate and perchloric acid (BDH, AnalaR) were

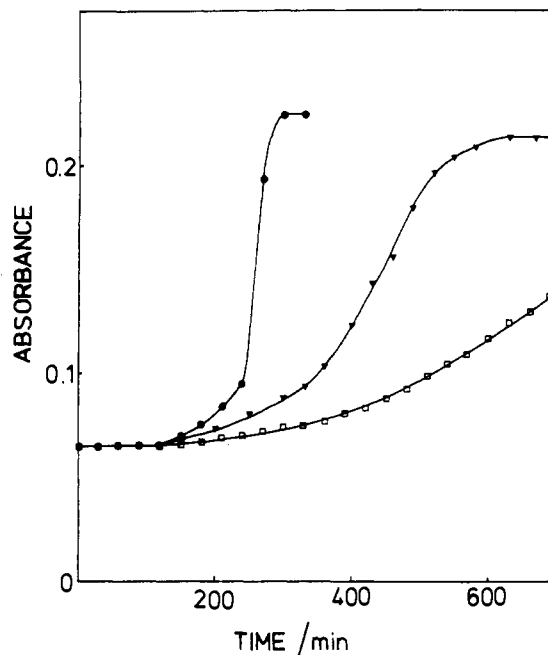


Figure 1. Effect of varying $[\text{ClO}_4^-]$ on the reaction of Mo^{3+} with ClO_4^- at 25 °C, where $[\text{Mo}^{3+}] = 4.3 \times 10^{-3} \text{ M}$ and $[\text{H}^+] = 0.7 \text{ M}$. Absorbance changes at 385 nm are shown for $[\text{ClO}_4^-] = 0.40 \text{ M}$ (●), 0.30 M (▼), and 0.20 M (□). $I = 1.0 \text{ M}$ (LiPTS).

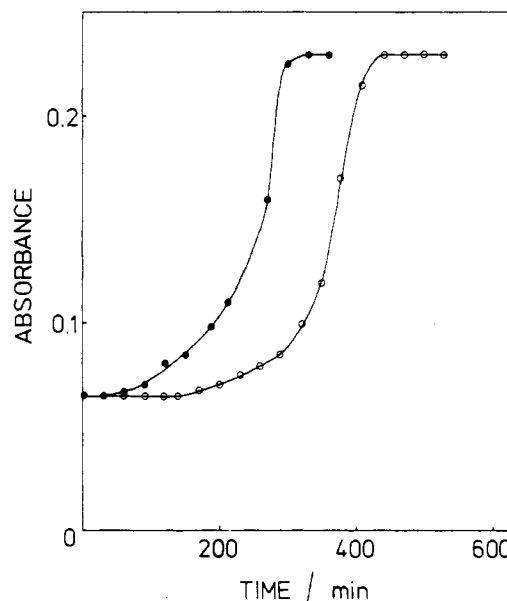
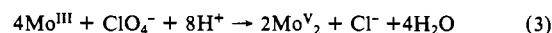


Figure 2. Effect of varying $[\text{H}^+]$ on the reaction of Mo^{3+} with ClO_4^- at 25 °C, where $[\text{Mo}^{3+}] = 4.3 \times 10^{-3} \text{ M}$ and $[\text{ClO}_4^-] = 0.30 \text{ M}$. Absorbance changes at 385 nm are shown for $[\text{H}^+] = 0.7 \text{ M}$ (●) and 0.3 M (○). $I = 1.0 \text{ M}$ (LiPTS).

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used without further purification. Lithium *p*-toluenesulfonate and lithium methanesulfonate were prepared by reacting lithium carbonate (Koch-Light) with HPTS and HMS and recrystallizing from H_2O .

Product Analyses. Both the Mo^{3+} and Mo^{III}_2 reactions yield the aqua MoV_2 ion $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$, peak at 384 nm ($\epsilon 103 \text{ M}^{-1} \text{ cm}^{-1}$ per dimer). Addition of AgNO_3 confirmed that Cl^- was produced, and the opalescence was estimated to be the same as for solutions containing a stoichiometric amount of Cl^- . Relevant equations are therefore as in (3) and (4).



Kinetics Studies. Reactions at 25 °C, $I = 1.0 \text{ M}$, were followed by conventional spectrophotometry. Formation of $\text{Mo}_2\text{O}_4^{2+}$ was monitored at 384 nm ($\epsilon 103 \text{ M}^{-1} \text{ cm}^{-1}$ per dimer) in the case of the Mo^{3+} reaction.

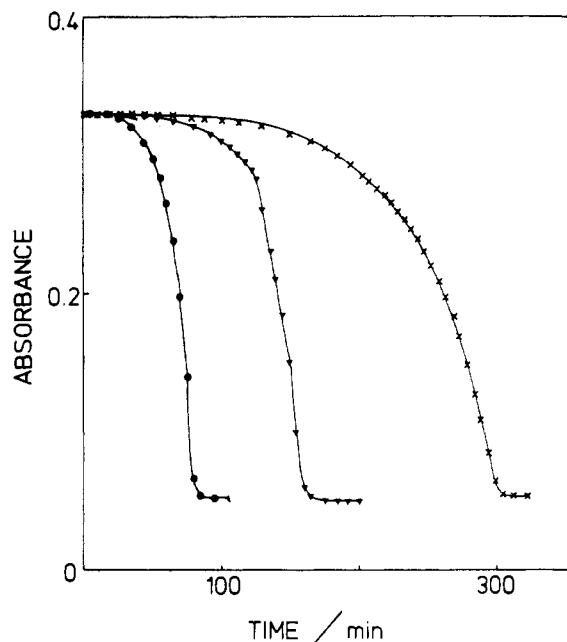


Figure 3. Effect of varying $[\text{ClO}_4^-]$ on the reaction of Mo^{III}_2 with ClO_4^- at 25 °C, where $[\text{Mo}^{\text{III}}_2] = 3.6 \times 10^{-4} \text{ M}$ and $[\text{H}^+] = 0.20 \text{ M}$. Absorbance changes at 360 nm are shown for $[\text{ClO}_4^-] = 0.80 \text{ M}$ (●), 0.40 M (▼), and 0.2 M (×). $l = 1.0 \text{ M}$ (LiMS).

For Mo^{III}_2 the decrease in absorbance at 360 nm (ϵ 910 $\text{M}^{-1} \text{ cm}^{-1}$ per dimer), or in some cases the increase at 320 nm where the Mo^{V}_2 absorption is dominant, was monitored. The reaction of the 9-ane N_3 Mo^{III}_2 complex with ClO_4^- was monitored at the 525-nm peak position of the purple *anti*- $[(9\text{-aneN}_3)_2\text{Mo}_2\text{O}_4]^{2+}$ product (ϵ 380 $\text{M}^{-1} \text{ cm}^{-1}$ per dimer).²³

None of the reactions was sufficiently rapid to study with the $\text{Mo}(\text{III})$ reactant in excess.

Results

Reactions of Mo^{3+} and Mo^{III}_2 are characterized by a slow initial phase followed by rapid propagation and termination. Solutions of Mo^{3+} with no ClO_4^- added could be kept for 4–5 h (the duration of many of the ClO_4^- runs), by using the same air-free procedures, without any increase in absorbance due to formation of $\text{Mo}_2\text{O}_4^{2+}$ from traces of O_2 . When the initial concentration of ClO_4^- is varied with $[\text{Mo}^{3+}]$ and $[\text{H}^+]$ fixed, the behavior, as illustrated in Figure 1 is observed, and it can be concluded that the time required for induction and the rate of propagation are both dependent on $[\text{ClO}_4^-]$. Dependences on $[\text{Mo}^{3+}]$ and $[\text{H}^+]$ (Figure 2) are also observed although in no case has the precise order been established. Runs were reproducible with the same ClO_4^- source. However, for otherwise identical runs the time for induction could be doubled by using different preparations of LiClO_4 to adjust the $[\text{ClO}_4^-]$ to 0.5 M. Also, the introduction of ClO_4^- (0.3 M) from HClO_4 instead of LiClO_4 to give solutions of identical compositions gave longer (by factor of ~ 2) times for induction. In both cases the propagation stage retained the same appearance. The presence of traces of intermediate chlorine oxidation states could explain these observations. For the same reactant solutions changing from a 1 cm to a 4 cm path length optical cell (surface area per milliliter of solution 4.3 and 2.8 cm^2 , respectively) had no effect on the rate. With ClO_3^- (0.3 M) instead of ClO_4^- , $[\text{Mo}^{3+}] = 3.9 \times 10^{-3} \text{ M}$, and $[\text{H}^+] = 0.6 \text{ M}$, rapid formation of Mo^{V}_2 is observed, which is oxidized over $\sim 20 \text{ h}$ to $\text{Mo}(\text{VI})$.

Similar behavior is observed for Mo^{III}_2 with ClO_4^- in PTS^- or MS^- solutions (Figure 3). Dependences on $[\text{Mo}^{\text{III}}_2]$ and $[\text{H}^+]$ were also obtained.

Discussion

In the case of the Mo^{3+} reactions at 25 °C with $[\text{Mo}^{3+}] = (2.2\text{--}8.6) \times 10^{-3} \text{ M}$, $[\text{H}^+] = 0.2\text{--}0.7 \text{ M}$, and $[\text{ClO}_4^-] = 0.2\text{--}0.7$

M, induction times of 50–200 min and propagation and termination times of 60 to ~ 700 min are observed. Dependences on the concentrations of $[\text{ClO}_4^-]$ and $[\text{Mo}^{\text{III}}_2]$, respectively, and $[\text{H}^+]$ are again noted.

Of some concern at the outset was whether the three-stage behavior was trivial in the sense of being due to impurities. Although ion-exchange procedures are generally presumed to give pure products, the possibility that some impurity was introduced (not necessarily a metal ion) was considered. To test this, we prepared the 9-ane N_3 Mo^{III}_2 complex $[(9\text{-aneN}_3)(\text{H}_2\text{O})\text{Mo}(\text{OH})_2\text{Mo}(\text{H}_2\text{O})(9\text{-aneN}_3)]^{4+}$ and introduced ion-exchange chromatography as the last stage in the isolation. With ClO_4^- a uniphase reaction was observed, as in the earlier study. The first-order rate constant with $[\text{Mo}^{\text{III}}_2] = 2.2 \times 10^{-4} \text{ M}$ and $[\text{ClO}_4^-] = 0.8 \text{ M}$ ($1.36 \times 10^{-3} \text{ s}^{-1}$ at 25 °C) is in satisfactory agreement with the literature value of ($1.81 \times 10^{-3} \text{ s}^{-1}$ at 21 °C),²⁴ bearing in mind that PTS^- and not MS^- was used to adjust the ionic strength to 1.0 M. Clearly the redox behavior of the 9-ane N_3 Mo^{III}_2 complex is quite different from that of Mo^{3+} and Mo^{III}_2 .

An induction stage generally implicates reactive intermediates in a process requiring high activation energy. It has been demonstrated that the oxidation of Mo^{3+} with ClO_3^- is rapid, and it is concluded that other steps through to Cl^- are rapid. An inner-sphere reaction is envisaged in (1) or (2), and the rate of substitution of ClO_4^- into $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ is relevant therefore. Present information suggests that substitution reactions of $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ are strongly associative,^{11,25} with rate constants ranging from $4.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for Cl^- to $180 \text{ M}^{-1} \text{ s}^{-1}$ for O_2 ,^{25,26} and it is likely that with ClO_4^- (a poor donor) substitution is slow.

The nature and identity of intermediate oxidation states of Mo are of considerable interest. In the first transition series V(IV) and Ti(IV) are known to exist as mononuclear ions with oxo attached.^{27,28} This same structure is not observed for early second- and third-row transition metals, and no ZrO^{2+} or MoO^{2+} ions have been identified.²⁹ The simplest stable aqua ion of Mo(IV) is in fact the triangular oxo-bridged trimer $\text{Mo}_3\text{O}_4^{4+}$.¹⁴ Moreover molybdenum(V) is present as the $\text{Mo}_2\text{O}_4^{2+}$ dimer, which gives monomer only under extreme conditions, e.g. 7 M HCl. Insofar as a monomeric form has been identified,³⁰ unlike Mo(IV), we are inclined to discuss the reaction as proceeding by this route. A 2-equiv process as in (3), with Mo(III) to Mo(V) conversion represented by the change Mo^{3+} to MoO^{3+} (or a related form), would incorporate O atom transfer. Rapid dimerization of Mo(V) will occur once there is a sufficient build-up of monomer. The following factors are believed to be relevant therefore in these studies: (a) the slow complexing of ClO_4^- to $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$, (b) the high activation energy required to generate monomeric Mo(V) (and/or mononuclear Mo(IV)), (c) the high activation energy required to reduce ClO_4^- to ClO_3^- (or ClO_2).

The observation that induction requires less time for Mo^{III}_2 , and that reaction proceeds at a comparable rate when the concentration of Mo^{III}_2 is one-tenth that of Mo^{3+} , suggests that relevant intermediates are formed more easily. This may be because the binuclear complex is more readily oxidized and/or that substitution of ClO_4^- into Mo^{III}_2 is more rapid. It is unlikely that the reaction of Mo^{3+} proceeds via Mo^{III}_2 since induction and propagation proceed more readily at higher $[\text{H}^+]$. The converse would have been expected if bis(μ -hydroxo) Mo^{III}_2 were generated in a rate-determining step.

Beneficial effects of $[\text{H}^+]$ on the V^{2+} , V^{3+} , and Ti^{3+} reductions of ClO_4^- ^{2,3} are seen to apply also in the case of the Mo^{3+} and Mo^{III}_2 reactions. The effect presumably originates from pro-

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tonation helping cleavage of the O atom being transferred from ClO_4^- to the Mo reactant in reaction 1 and/or 2.

Although we have no way at present of proceeding to a fuller interpretation with precise identification of the Mo ions involved as intermediates, distinctive features of the reactions have been indicated in this work.

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Registry No. ClO_4^- , 14797-73-0; $\text{Mo}(\text{H}_2\text{O})_6^{3+}$, 34054-31-4; $\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}$, 40804-49-7; $[(9\text{-aneN}_3)(\text{H}_2\text{O})\text{Mo}(\text{OH})_2\text{Mo}(\text{H}_2\text{O})(9\text{-aneN}_3)]^{4+}$, 92542-35-3.

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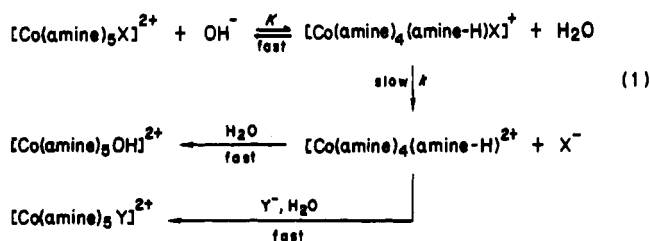
Alkaline Hydrolysis of $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{SCN}]^{2+}$ and Other $t\text{-}$ and $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{X}]^{2+}$ Complexes

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The synthesis of $t\text{-}$ and $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{NCS}]^{2+}$ and $t\text{-}$ and $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{SCN}]^{2+}$ is reported. Alkaline hydrolysis of $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{SCN}]^{2+}$ ($k_{\text{OH}} = 1.1 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) results in only $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)(\text{OH})]^{2+}$, but hydrolysis of $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{SCN}]^{2+}$ ($k_{\text{OH}} = 3.1 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) results in $t(\text{SCN})\text{-}[\text{Co}(\text{tren})(\text{OH})\text{SCN}]^+$ (35%), $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{NCS}]^{2+}$ (5%) as well as $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)(\text{OH})]^{2+}$ (50%) and $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)(\text{OH})]^{2+}$ (10%). In alkaline solution $t(\text{SCN})\text{-}[\text{Co}(\text{tren})(\text{OH})\text{SCN}]^+$ isomerizes to $t(\text{NCS})\text{-}[\text{Co}(\text{tren})(\text{OH})\text{NCS}]^+$ ($k = 3 \times 10^{-5} \text{ s}^{-1}$) while in aqueous acid isomerization of $t(\text{SCN})\text{-}[\text{Co}(\text{tren})(\text{OH}_2)\text{SCN}]^{2+}$ is slower ($k = 1.3 \times 10^{-6} \text{ s}^{-1}$). The alkaline hydrolysis of $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{X}]^{2+}$ ($\text{X} = \text{NCS}^-, \text{N}_3^-$) gives only $t(\text{X})\text{-}[\text{Co}(\text{tren})(\text{OH})\text{X}]^+$ products ($k_{\text{OH}}^{\text{NCS}} = 2.5 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, $k_{\text{OH}}^{\text{N}_3} = 1.2 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). All data are at $I = 1.0 \text{ mol dm}^{-3}$ (NaClO_4) and 25.0°C .

A major remaining question to be answered in the base hydrolysis of cobalt(III)-acido complexes concerns the lifetime of the five-coordinate intermediate formed following the loss of X^- (eq 1).¹ Is any molecular event possible within this intermediate

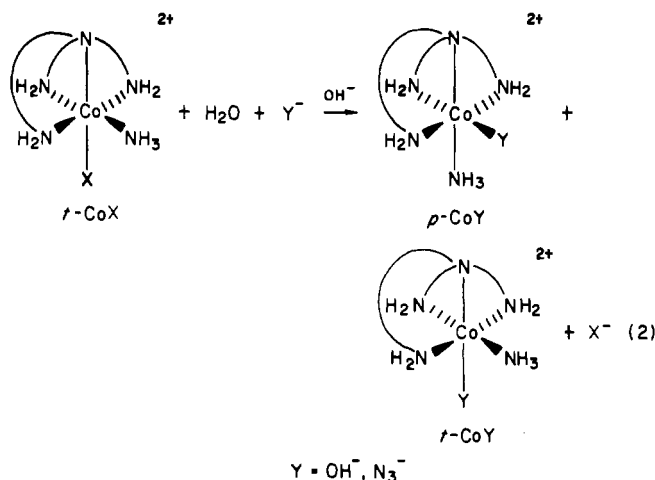


prior to the coordination of a H_2O molecule or other entering group Y^- ? It appears that capture from the immediate environment of the solvent cage occurs,² but it is unclear whether the intermediate moves toward equilibration with its solvent cage or whether it is more reactive than that. Possibly the best evidence concerning lifetimes comes from the mutarotation of deprotonated amine centers during the base hydrolysis of (R) - and (S) - α, β - $[\text{Co}(\text{tren})(\text{NO}_3)]^{2+}$ and β_2 - $(RR, SS)\text{-}[\text{Co}(\text{trien})(\text{glyOR})\text{Cl}]^{2+}$,⁴ which cannot be accounted for by mutarotation in the deprotonated reactant or in the hydroxo product. Mutarotation of deprotonated amine centers in Co(III) complexes occurs at a rate of $10^4\text{--}10^5 \text{ s}^{-1}$,⁵ which implies some stability for the intermediate. However, in base hydrolysis reactions coordination by H_2O and reprotonation may be concerted, forcing more rapid inversion in these cases.

Another possibility is to look for stereochemical change about the metal that cannot arise from preconditioned solvation or ion-pairing effects. Clear evidence of this is not easy to find, but a few years ago we reported a small amount ($\sim 0.5\%$) of isomerization and geometrical change of $\text{trans-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{SCN}]^{2+}$ to $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)\text{NCS}]^{2+}$ during the base hydrolysis of the former that could not be accounted for by exchange of coordinated SCN^- with solvent-labeled S^{14}CN^- .⁶ This suggests a definite

lifetime for the intermediate within the solvent cage sufficient to allow stereochemical reorganization within a tight $[\text{Co}(\text{en})(\text{en-H})(\text{NH}_3)]^{2+}\text{SCN}^-$ ion pair.

A significant feature of the base hydrolysis of $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{X}]^{2+}$ complexes is the large amount of stereochemical change to the p configuration (eq 2).⁷ Such stereochemical change



can be regarded as mutarotation about the metal, and it must occur in the five-coordinate intermediate or as part of the rate-determining loss of X^- , since it does not occur in the reactant, its conjugate base, or the $t\text{-CoY}$ products. For different X the amount of mutarotation varies, and for particular X it is dependent on the electrolyte and its concentration.⁷ However, the difficulty here is that the entering group Y is, or can be considered as, part of the solvent cage and its geometrical origin remains obscure. A more precisely located internal competitor in the reactant is required to test for mutarotation about the metal.

We therefore decided to investigate the base hydrolysis of $t\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{SCN}]^{2+}$ to see if mutarotation included $p\text{-}[\text{Co}(\text{tren})(\text{NH}_3)\text{NCS}]^{2+}$ as a product and if so study its isomerization within the solvent cage as a function of added external competitors. A positive answer would imply an intermediate with

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