on a more empirical basis with the rate constants[16,31,32] for outer-sphere electron transfer from $Cr^{II}(bpy)_3^{2+}$ to the same family of cobalt(III) complexes (eq 18). The quantities referred to are listed in Table VI.

$$Cr(bpy)_3^{2+} + Co(NH_3)_6^{3+} \xrightarrow{k_{18}} Cr(bpy)_3^{3+} + Co(NH_3)_6^{2+} \quad (18)$$

The rate constants for eq 18 decrease, as one might expect, with the excitation energy from the t_{2g}^6 ground state ($^1A_{1g}$) to the $t_{2g}^5e_g^*$ excited state ($^1T_{1g}$), as measured by λ_{max}. The standard reduction potentials of the different cobalt(III) complexes[28-30] are also consistent with the observed reactivity order, although the value for $Co(tn)_3^{3+}$ has not been measured.

One might expect a parallel between the values of k_2 and k_{18} if the same outer-sphere mechanism applies to both. Indeed, that is what is seen except for $Co(chxn)_3^{3+}$, whose reduction is >20 times slower than expected from the relationship followed by the other complexes, $\log k_2 = 4.30 + 0.55 \log k_{18}$. The success of the correlation lends support to our formulation of the free radical reductions as proceeding by an outer-sphere mechanism. We would suggest that the failure of $Co(chxn)_3^{3+}$ to react with $\cdot C(CH_3)_2OH$ may signal a conformational (λ, δ) change of the chelate ligands are required to facilitate approach of the planar radical to a trigonal face sufficient to permit facile electron transfer. Such conformational changes are readily experienced by all of the cobalt(III) complexes other than $Co(chxn)_3^{3+}$ whose cyclohexyl ring systems preclude similar steric adaptation. The character of the required conformational change is not, however, clear at this time.

The relative rate constants for the deuterated complex $Co(ND_3)_6^{3+}$ as compared to $Co(NH_3)_6^{3+}$ are not greatly different for $\cdot C(CH_3)_2OH$ ($k_D/k_H = 0.73$) than for $Cr(bpy)_3^{2+}$ (0.74). This supports our contentiopn that, in the strongly acidic medium, both reactions proceed by outer-sphere electron transfer. The failure of the Cr(III) complexes to react with $\cdot C(CH_3)_2OH$, on the other hand, probably arises from the much less favorable reduction potential for Cr(III) → Cr(II).

The substantial deuterium isotope effect in acidolysis of $CrC(CH_3)_2OH^{2+}$ corresponds to $k_{1A}(H)/k_{1A}(D) = 6.3$. It is similar to the corresponding rate constant ratios for $CrCH_2OH^{2+}$ (8.4),[33] $CrCH_3^{2+}$ (6.3),[34] and CrH^{2+} (4.8).[34] The reasons have already been given: the activation process along this pathway contains dominant contributions from the effect of O–H bond breaking, possibly from a water molecule coordinated to Cr(III), cis to the chromium–carbon bond.[34] The contrast between the isotope effect on acidolysis (6.3) and homolysis (1.01) is striking. The latter is consistent with our conclusion that homolytic cleavage is a genuine unimolecular process unassisted by solvent participation.[2]

As reactions of $\cdot C(CH_3)_2OH$ and $\cdot CH_2OH$ go, the reductions of the cobalt(III)–amine complexes are much slower than the reductions of most other metal complexes. On the other hand, these Co(III) complexes are notorious for their high kinetic barriers. The present reactions are, in fact, some of the most rapid reductions of these complexes which have been found. Reduction of $Co(NH_3)_6^{3+}$ by $\cdot C(CH_3)_2OH$ ($E° \approx -1.2$ V)[1] and $\cdot CH_2OH$ ($E° \approx -0.92$ V) are both highly exoergic processes. The former is much faster, $k_2 = 4.1 \times 10^5$ M^{-1} s^{-1} vs. $<1 \times 10^3$ M^{-1} s^{-1}. Observation of only a small extent of reduction of $Co(NH_3)_6^{3+}$ by $\cdot CH_2OH$ in acidic solution is not to be taken to indicate complete failure of reaction 12c but simply that another reaction, radical self-reaction eq 12b, is dominant under the conditions employed.

The effect of Cl^- most deserving of comment is the twofold increase of the k_{-1}/k_2 ratio, at the same time leaving k_1 unaltered. Since Cl^- does not interact appreciably with $Cr(H_2O)_6^{2+}$, and most likely not with $\cdot C(CH_3)_2OH$ either, it is tempting to argue from microscopic reversibility that k_{-1}, like k_1, is Cl^- independent. The consequence of that argument is then that k_2 is *decreased* by a factor of 2.0 for $Co(NH_3)_6^{3+}$ at 0.060 M Cl^- and by the same factor for $Co(en)_3^{3+}$ at 0.60 M Cl^-, each compared to the value in perchlorate medium. Although ion pairing between the cobalt(III) complexes and chloride ions does occur, its extent is inappreciable under these conditions.[35] Thus partial conversion of the reactive Co(III) ions to nonreactive Cl^- ion pairs cannot be invoked to account for this phenomenon, although other plausible explanations are not apparent.

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Registry No. $\cdot C(CH_3)_2OH$, 5131-95-3; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(tn)_3^{3+}$, 16786-53-1; $Co(ND_3)_6^{3+}$, 23945-61-1; $Co(chxn)_3^{3+}$, 41970-05-2; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3.

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S to O and O to S Linkage Isomerization in Sulfoxide Complexes of Pentaammineruthenium

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When $Ru(NH_3)_5Me_2SO^{2+}$ is oxidized to the 3+ state, S → O isomerization takes place at a specific rate of $(7.0 \pm 0.5) \times 10^{-2}$ s^{-1} (24×10^{-2} s^{-1} for the methioninesulfonate complex). Aquation is quite slow, k_{aq} being 7.7×10^{-5} s^{-1} (6.2×10^{-5} s^{-1}). On reduction to the 2+ state, O → S isomerization takes place, the values of k_{ism} being 30 ± 7 s^{-1} (99 ± 7 s^{-1}). Aquation accompanies isomerization in the 2+ species and $k_{aq} \approx 10$ s^{-1} (30 s^{-1}). The shift from the S- to the O-bound form changes the 3+/2+ reduction potential from 1.0 to 0.01 V.

Though a value of E_f for the couple $Ru(NH_3)_5Me_2SO^{3+/2+}$ as obtained by cyclic voltammetry has been reported (E_f = 1.0 V in 0.10 M HCl),[1] it has frequently been observed in our laboratories, and probably also by others, that complications

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are encountered when the sweep rate is varied. These complications seemed to imply that the changes in oxidation state are accompanied by structural changes. The studies that we now describe were undertaken to define the nature of these structural changes and to determine their rates. We were motivated to undertake the studies not only because they are intrinsically interesting but also because they are a necessary preparation for the investigation of the oxidation of $Ru(NH_3)_5S(CH_3)_2^{2+}$ which is in progress. As will be described in greater detail in a later section of this paper, certain oxidizing agents produce $Ru(NH_3)_5Me_2SO^{2+}$ as well as the expected product $Ru(NH_3)_5S(CH_3)_2^{3+}$, even when only 1 equiv of oxidizing agent/equiv of Ru(II) is used.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared according to the method of Vogt et al.[2] and was purified by recrystallization from 0.1 M HCl. Dimethyl sulfoxide (Aldrich Chemical Co.) and DL-methionine sulfoxide (Sigma Chemical Co.) were used without purification. Cerium(IV) perchlorate, 0.5 M in 6 M $HClO_4$, was purchased from G. Frederick Smith. The solution was restandardized with ferrous sulfate before use. A solution of Cr^{2+} was prepared by reducing $CrCl_3$ solution[3] in 0.1 M HCl with zinc amalgam under argon for 30 min. 4-Cyanopyridine (Aldrich Chemical Co.) was recrystallized once from ethanol containing activated carbon black as a decolorizing agent. All solutions were prepared from deionized house-distilled water, which was further purified by passing it through a Barnstead NANO water purification system. All other chemicals were reagent grade and were used as received.

Preparations. Pentaammine(dimethyl sulfide)ruthenium(II) hexafluorophosphate and pentaammine(dimethyl sulfoxide)ruthenium(II) tetrafluoroborate were prepared according to literature methods.[1] Pentaammine(methionine sulfoxide)ruthenium(II) tetrafluoroborate, $[(NH_3)_5RuSO(CH_3)(CH_2CH_2CH(NH_2)COOH)](BF_4)_2$, was prepared by the following procedure. Silver oxide (0.24 g) was dissolved in 5 mL of hot 3 M trifluoroacetic acid, and 0.30 g of $[RuA_5Cl]Cl_2$ was then introduced. The resulting solution was heated and stirred vigorously for a few minutes to ensure complete precipitation of AgCl. After the solution had cooled, AgCl was filtered off and the pH of the filtrate was adjusted to 3.5 with 3 M NaOH. The solution was reduced over zinc amalgam under argon for 30 min. DL-Methionine sulfoxide (1.0 g) was then added to the reduced solution, and the reaction was allowed to proceed for 50 min. The product solution was transferred to 3 mL of degassed 48% HBF_4 solution, and precipitation was brought about by adding 100 mL of degassed ethanol, cooling the solution on ice. The solid (pale yellow hygroscopic) was collected and washed with ethanol and ether. Anal. Calcd: C, 11.44; H, 4.99; N, 16.01; S, 6.11. Found: C, 10.8; H, 4.53; N, 14.92; S, 5.81. Attempts at recrystallization did not improve the quality of the product. No evidence of a second Ru-containing product was found in the cyclic voltammograms of dissolved samples. The similarity of behavior to that of the well-characterized Me_2SO complex gives us confidence that the impurity present in our samples does not seriously affect our results.

Electrochemical Measurements. All electrochemical studies were done with PAR Model 173 and 175 instruments and a Houston Instrument X-Y recorder. For fast cyclic voltammetry scan rates (0.5–200 V s^{-1}), a Tektronix single-beam storage oscilloscope was used. A conventional electrochemical cell was used for the experiments. The saturated calomel reference electrode (SCE) was isolated from the test solution by a glass frit of medium porosity. The working electrode in the cyclic voltammetry experiments was either carbon paste or a platinum wire. No difference in the response for the two types of electrodes was noted. Where two peaks are observed, the peak to peak separation was ca. 60 mV.

Kinetic Measurements. The rates were followed by using the cyclic voltammetry, stopped-flow method or orthodox spectrophotometry. The stopped-flow apparatus consists of a thermostated Aminco-Morrow flow system adapted to fit on a Beckman DU spectrophotometer, and the absorbance was monitored by a storage oscilloscope trace (Tektronix Model D11 oscilloscope). The rate constants were obtained from the slope of a least-squares fit of $\ln (A_\infty - A_t)$ vs. time plot. Nicholson and Shain's method[4] was used to estimate the rate constants from the cyclic voltammetric results.

Results

Absorption Spectra of Ruthenium Complexes. $Ru(NH_3)_5S(CH_3)_2^{3+}$ and $Ru(NH_3)_5Me_2SO^{2+}$ were found to have absorption maxima at 453 nm ($\epsilon = 280\ M^{-1}\ cm^{-1}$) and 315 nm ($\epsilon = 235\ M^{-1}\ cm^{-1}$), respectively, in agreement with the literature values.[1,5] The absorption spectrum of pentaammine(methionine sulfoxide)ruthenium(II) is very similar to that of the dimethyl sulfoxide complex with $\lambda_{max} = 315$ nm ($\epsilon = 270\ M^{-1}\ cm^{-1}$).

Oxidation of $Ru(NH_3)_5S(CH_3)_2^{2+}$. As oxidizing agents $Fe(SO_3CF_3)_3$, $Ce(ClO_4)_4$, and $Na_2S_2O_8$ were used. With either Fe^{3+} or Ce(IV), only the metal center is oxidized, but when persulfate ion is used as oxidizing agent, application of cyclic voltammetry showed that both $Ru(NH_3)_5S(CH_3)_2^{3+}$ and $Ru(NH_3)_5Me_2SO^{2+}$ are formed. Persulfate ion does not oxidize $Ru(NH_3)_5S(CH_3)_2^{3+}$ on the time scale of the experiments, and we conclude that in the case of this oxidant, parallel processes are taking place. The rate of reaction was measured[6] under pseudo-first-order conditions ($[Ru(II)] \approx 10^{-4}$ M, $[S_2O_8^{2-}] \approx 10^{-3}$ M) in (0.01 M HCl –0.09 M LiCl) and $-d \ln [Ru(II)]/dt[S_2O_8^{2-}]$ was found to be $4.9 \times 10^3\ M^{-1}\ s^{-1}$ at 25 °C. By use of spectrophotometry, $Ru(NH_3)_5S(CH_3)_2^{3+}$ was shown to constitute 75% of the product, when 1 equiv of $S_2O_8^{2-}$ was used for each 1 equiv of Ru(II), and thus the specific rates for the rate-determining steps governing the formation of the $(CH_3)_2SRu^{III}$ and Me_2SORu^{II} products are $2.9 \times 10^3\ M^{-1}\ s^{-1}$ and $2.0 \times 10^3\ M^{-1}\ s^{-1}$, respectively. (Note that a stoichiometric factor of 2 must be allowed for in resolving the composite specific rate into the components.)

Rates of Substitution by Sulfoxides. The rates of formation of the sulfoxide complexes were measured at 25.0 °C with ligand in excess, by monitoring the absorbance increase at $\lambda = 315$ nm. With Me_2SO as entering ligand ($[Ru(II)]_0 = 9 \times 10^{-4}$ M, [HCl] = 0.01 M, $\mu = 0.10$ M (LiCl)), k_f was determined as 8.86×10^{-2} and $8.35 \times 10^{-2}\ M^{-1}\ s^{-1}$ at $[Me_2SO] = 8.75 \times 10^{-3}$ and 14.6×10^{-3}, M, respectively. Three experiments were done with methionine sulfoxide as the entering ligand at concentrations of 5.2×10^{-2}, 7.8×10^{-2}, 10.4×10^{-2} M, leading to values of $k_f \times 10^2\ (M^{-1}\ s^{-1})$ of 3.00, 3.15, and 3.0 ($[Ru(II)]_0 = 4.5 \times 10^{-3}$ M, $[NaO_2CCF_3] = 0.09$ M, $[HO_2CCF_3] = 0.010$ M).

Aquation of $Ru(NH_3)_5Me_2SO^{2+}$. A solution of the dimethyl sulfoxide complex at 1.3×10^{-3} M in (0.01 HCl –0.09 M LiCl) at 25.0 °C was made up to 0.10 M in 4-cyanopyridine, this reagent being used to scavenge the aquo complex as it forms. The cyanopyridine complex of pentaammineruthenium(II), which has an absorption maximum at 525 nm, is not formed, but instead, a species with a maximum at 513 nm forms, and we conclude that NH_3 is being lost rather than dimethyl sulfoxide. The specific rate for aquation of ammonia in this experiment was found to be $1.1 \times 10^{-6}\ s^{-1}$. It is not known whether the loss of NH_3 is proton assisted as it is in the case of $Ru(NH_3)_6^{2+}$,[7] but in any event, aquation of NH_3 is slower than for the latter complex. ($t_{1/2}$ for loss of NH_3 from $Ru(NH_3)_6^{2+}$ in 0.01 M HCl is 5.8×10^4 s at 25 °C). The

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Table I. Rate Constants for S → O Conversion of $Ru(NH_3)_5Me_2SO^{3+}$ [a]

T, °C	10^2k_{ism}, s^{-1}	T, °C	10^2k_{ism}, s^{-1}
10.8	2.04	20.3	5.57
15.7	3.56	25.5	7.42

[a] $[Ru]_0 = (1\text{-}2) \times 10^{-3}$ M; $\mu = 0.1$ M (LiCl); [HCl] = 0.01 M.

experiment sets an upper limit on the specific rate of aquation of dimethyl sulfoxide as 0.2×10^{-6} s^{-1}. With introduction of the known rate of complex formation, a lower limit on the equilibrium quotient governing the reaction

$$Ru(NH_3)_5OH_2^{2+} + (CH_3)_2SO = Ru(NH_3)_5SO(CH_3)_2^{2+} + H_2O$$

of 4×10^5 is calculated.

Oxidation of the Sulfoxide Complexes of Ru(II). Both the dimethyl sulfoxide and methionine sulfoxide complexes of pentaammineruthenium gave values of $E_{1/2} = 1.0$ V vs. NHE in agreement with the value reported in the literature[1] (conditions $\mu = 0.10$, $[H^+] = 0.010$, 25 °C).

When a solution of the Ru(II) complex of either ligand is oxidized with a stoichiometric amount of Ce(IV), the wave characteristic of the S-bound complex disappears in less than 2 min and a new wave appears near 0 V on the reduction scan. At low scan rates, there is no corresponding oxidation wave, but one begins to appear at scan rates in excess of 10 V s^{-1}. The value of $E_{1/2}$ as defined by the complete wave is 0.01 V for each of the two complexes. When and only when the scan is extended to 0.01 V and below, does the wave characteristic of the S-bound complex reappear—that is, a solution oxidized by 1 equiv of Ce(IV) shows no voltammetric response in the range <1.0 V and >0.01 V. On repetitive scanning, the wave at 0.01 V decreases in amplitude and that at 1.0 V increases; at the steady state, waves are observed at 0.07 and 1.0 V, the former indicating the formation of the pentaammine–aquo complex.

These results suggest that S to O linkage isomerization takes place when oxidation to the 3+ state occurs and further that the O-bound species is kinetically rather stable in the 3+ state. It is reduced to the O-bound Ru(II) state at 0.01 V, and this species isomerizes rapidly to the S-bound form. Since it is known that the O-bound 3+ species does not aquate rapidly—note that no response at 0.07 V is observed for the solution prepared by oxidizing the S-bound Ru(II) to the 3+ state—we must conclude that $Ru(NH_3)_5H_2O^{2+}$ is formed from the O-bound form $Ru(NH_3)_5OS(CH_3)_2^{2+}$. These conclusions are borne out by the kinetic studies that will be described in the next sections.

It should be mentioned that, while $S_2O_8^{2-}$ is frequently a useful oxidizing agent in work with ruthenium(II) ammines, it is not suitable for the studies being described. The reaction of $S_2O_8^{2-}$ with $Ru(NH_3)_5Me_2SO^{2+}$ is slow, presumably because of the high redox potential for the 3+/2+ couple.

Rate of Isomerization. The rate of S → O linkage isomerization for $Ru(NH_3)_5SOR_2^{3+}$ was followed by both cyclic voltammetry and by stopped-flow techniques. When the rates were determined electrochemically by applying the method of Nicholson and Shain,[4] the ratios i_{cp}/i_{ap} were measured by the method of Nicholson.[8] The rate constant for the Me_2SO complex was obtained by making use of data at three different scan rates, 50, 20, and 10 mV/s, and the resulting rate constant is $k_{ism} = (7.0 \pm 0.5) \times 10^{-2}$ s^{-1} at $\mu = 0.1$ M (LiCl), [HCl] = 0.01 M, and 25 °C. For the methionine sulfoxide complex, the rate constant was found to be $k_{ism} = 0.24$ s^{-1} at $[NaO_2CCF_3] = 0.09$ M, $[HCO_2CF_3] = 0.01$ M, and 25.0 °C.

Table II. Rate Constants for S → O Conversion of the Methionine Sulfoxide Complex of Ru(III) as a Function of Temperature[a]

T, °C	k_{ism}, s^{-1}	T, °C	k_{ism}, s^{-1}
12.6	0.14	20.2	0.25
16.5	0.17	24.7	0.30

[a] $[Ru(II)] \approx 10^{-3}$ M; $[HCO_2CF_3] = 0.09$ M; $[HCO_2CF_3] = 0.01$ M.

Table III. Aquation of $Ru(NH_3)_5OS(CH_3)_2^{3+}$ [a]

t, min	% aqn	t, min	% aqn
0	24	117	58
30	36	182	67
73	44		

[a] $[Ru]_0 = (1\text{-}3) \times 10^{-4}$ M; [4-cyp] = 0.1 M; [LiCl] = 0.09 M; [HCl] = 0.01 M; 25 °C.

Table IV. Aquation of $Ru(NH_3)_5OS(CH_3)(CH_2)_2CH(NH_2)COOH$ [a]

t, min	% aqn	t, min	% aqn
0	21	184	60
120	48		

[a] $[Ru]_0 = (1\text{-}3) \times 10^{-4}$ M; [4-cyp] = 0.1 M; $T = 25$ °C; $\mu = 0.1$ M (NaO_2CCF_3); $[H^+] = 0.01$ M (HO_2CCF_3).

In the stopped-flow experiments, a stoichiometric amount of Ce(IV) was used to oxidize $Ru(NH_3)_5Me_2SO^{2+}$ to Ru(III) and the increase in absorbance at $\lambda = 290$ nm was monitored. The rate constants were measured at several temperatures and with results as shown in Tables I and II. The rate constants obtained by the stopped-flow technique at 25 °C are in good agreement with those obtained from the cyclic voltammetry measurements. The activation parameters for the reactions as obtained from the plots of ln (k/T) vs. $1/T$ were as follows: for the Me_2SO complex, $\Delta H^{\ddagger} = 14.7 \pm 3.2$ kcal/mol, $\Delta S^{\ddagger} = -14.1 \pm 6.4$ cal/(deg mol); for the methionine sulfoxide complex, $\Delta H^{\ddagger} = 10.5 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -25 \pm 2$ cal/(deg mol).

For the study of O → S isomerization on Ru(II), the O-bound ruthenium(III) complexes were prepared by oxidizing the Ru(II) forms with a slight excess of Ce(IV) (<5%). The rate constants obtained from cyclic voltammetry measurements for the disappearance of the O-bound forms of Ru(II) are 40 ± 10 and 99 ± 10 s^{-1} for the Me_2SO and methionine sulfoxide complexes, respectively. As the results to be described in the next section show, some aquation accompanies isomerization of the O-bound forms of Ru(II). The fractions producing the aquo ion are 0.24 and 0.21 for the dimethyl sulfoxide and methionine sulfoxide complexes, respectively. With correction for the aquation, the specific rates for isomerization are 30 and 70 s^{-1}.

Aquation of $Ru(NH_3)_5OSR_2^{3+}$. The rates of aquation of $Ru(NH_3)_5OSR_2^{3+}$ were measured as follows. $Ru(NH_3)_5SOR_2^{2+}$ was first oxidized with a stoichiometric amount of Ce(IV) and left for 2 min for the S → O isomerization to go to completion, the end of this period defining $t = 0$ for aquation. The aquation reaction was left to proceed for various lengths of time, the solution was then reduced with a 10-fold excess of Cr^{2+}(aq), and $Ru(NH_3)_5OH_2^{2+}$ thus formed was scavenged by the addition of 4-cyanopyridine. The amount of $Ru(NH_3)_5OH_2^{2+}$ was determined by the formation of the 4-cyanopyridine complex ($\epsilon = 1.34 \times 10^4$ M^{-1} cm^{-1} at $\lambda_{max} = 525$ nm). The results are shown in Tables III and IV. The rate constants of the aquation were obtained from the slope of the ln (100 − % aquation) vs. time plot and were found to be 7.7×10^{-5} s^{-1} for the Me_2SO complex and 6.2×10^{-5} s^{-1}

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for the methionine sulfoxide complex.

It should be noted that there is significant aquation at zero time in each case, and we conclude that this measures the aquation that accompanies O → S isomerization in the 2+ state.

Discussion

Unexpectedly facile linkage isomerization on pentaammineruthenium(III) has been observed in other cases,[9,10] and it is therefore not surprising that it is observed in the present instance. To learn the cause of this lability, it would be useful to have a measurement of the rate of this change also for Rh(III). It is likely that the reaction proceeds through a 7-coordinate transition state, and this would have less antibonding character for a d^5 as compared to a d^6 system. Rh(III) is the only center that provides a straightforward comparison—the changes in the bond distance would be small as compared to case for Ru(III), and the πd–σd energy separation for the same ligand environment also is as close as can be arranged. The higher stability of the Ru(III)–O bond as compared to the S-bound form is expected from the estimate of the affinity of H_2S for $Ru(NH_3)_5H_2O^{3+}$, $K_{assoc} = 2.4 \times 10^{-4}$. Though K_{assoc} for $(CH_3)_2S$ is greater than for H_2S, a sharp decrease is expected when the sulfur is oxidized to the dimethyl sulfoxide state, and it is likely therefore that K_{assoc} for the latter ligand << 1. On the other hand, the affinity of Me_2SO acting as an oxygen donor to $Cr(H_2O)_6^{3+}$ has been found to be quite high,[11] and Ru(III) and Cr(III) can be expected to show roughly similar affinities.

Though the values of the activation parameters for the linkage isomerization on Ru(III) are not accurate, they do suffice to show that ΔS^* for the reaction is quite negative. This is in line with other observations. For the N → O rearrangement of nitrite on $Rh(NH_3)_5^{3+}$, $\Delta S^* = -12$ cal/(deg mol), and on $Ir(NH_3)_5^{3+}$, $\Delta S^* = -14$ cal/(deg mol).[12]

The marked preference of Me_2SO for the S bonding mode on Ru(II) would be hard to predict from first principles, and the exact magnitude of this preference has not been established. The two values of E_f do lead to the equilibrium quotient for

$$Ru(NH_3)_5OS(CH_3)_2^{2+} + Ru(NH_3)_5SO(CH_3)_2^{3+} = Ru(NH_3)_5SO(CH_3)_2^{2+} + Ru(NH_3)_5OS(CH_3)_2$$

($K_{eq} = 5 \times 10^{11}$), but this only gives us the relative preference for the two forms in the two oxidation states.

The lability of $Ru(NH_3)_5OS(CH_3)_2^{2+}$ toward aquation ($k \approx 10$ s^{-1}) is a matter of some interest, as providing a rough measure of the exchange rate for water between $Ru(NH_3)_5H_2O^{2+}$ and solvent. Because of the low charge on Ru(II), the preference for oxygen in the two cases, H_2O vs. $OS(CH_3)_2$, is likely not to be very great. The specific rate of water exchange was estimated elsewhere[13] as 3 s^{-1} at 25 °C.

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Registry No. $Ru(NH_3)_5Me_2SO^{2+}$, 44863-54-9; $[(NH_3)_5RuSO(CH_3)(CH_2CH_2CH(NH_2)COOH)](BF_4)_2$, 81230-34-4; $Ru(NH_3)_5OS(CH_3)_2^{3+}$, 81245-10-5; $Ru(NH_3)_5OS(CH_3)(CH_2CH_2CH(NH_2)COOH)^{3+}$, 81230-41-3; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1.

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Kinetics of Chlorine Transfer from Chloramine to Amines, Amino Acids, and Peptides

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The equilibria and kinetics of chlorine transfer from chloramine to give *N*-chloro derivatives of methylamine, amino acids, and peptides are determined in aqueous solution. The reactions, which are studied from pH 2 to 10, are first order in total chloramine and first order in total amine with rate constants which vary from 0.1 to 7 M^{-1} s^{-1} at 25.0 °C. The rates are independent of pH from pH 4 to 7. The results indicate that direct chlorine transfer occurs with NH_3Cl^+ as a very active chlorinating agent. The rate constants for the reactions of NH_3Cl^+ increase with the amine basicity but reach a maximum level of 2.4×10^8 M^{-1} s^{-1} (25.0 °C, 0.50 M $NaClO_4$).

Introduction

Chloramine (NH_2Cl) is formed in the process of disinfecting water by chlorination.[1] It results from the reaction of hypochlorous acid with ammonia.[2,3] Since NH_2Cl is slow to hydrolyze, is not very volatile, and is a less reactive oxidant than Cl_2 or HOCl, it persists as a source of active chlorine.[4–7] One series of possible chloramine reactions is the transfer of chlorine to other amine nitrogens (eq 1, where RNH_2 is an

$$NH_2Cl + RNH_2 \rightarrow NH_3 + RNHCl \qquad (1)$$

amine, an amino acid, or a peptide). A previous investigation[8] suggested that the transfer of chlorine from *N*-chloro-D-leucine to α-amino acids and NH_3 did not occur, even with 100-fold

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