the overlap of a singly occupied R orbital with the π^* SOMO of OF.[13] According to this view, releasing R groups will simultaneously increase the paramagnetic shielding around the fluorine atom *and* the antibonding character of the bond; that is, they will decrease ^{19}F NMR chemical shifts and O–F bond dissociation energies (Figure 1).

This analysis resembles an earlier proposal accounting for trends in bond lengths and force constants in nitrosyls and peroxides.[14] These compounds derive from NO and O_2, which also possess π^* SOMO's. As a contradistinction, the present correlation, probing simultaneously into bond stability and electron distribution, actually discloses the concomitant variations in the population of the relevant π^* MO rather than invoking them.

The ^{19}F nuclear magnetic resonance absorption data for the OF group presented in Table I typically show a large downfield shift relative to trichlorofluoromethane and are out of the range of most other fluorine NMR absorptions.[7] This feature allows the unambiguous assignment of OF absorptions.

The available thermochemistry on the OF bond in CF_3OF, SF_5OF, FSO_2OF, and NO_2OF has been recently reexamined,[4] and the corresponding D_{RO-F} values, calculated from experimental activation energies E and OF stretching vibrational frequencies ν_s as $D = E + 0.5h\nu_s$, are considered reliable to within 1 kcal/mol. Similarly, a lower bound for D_{RO-F} in difluoroxydifluoromethane, $CF_2(OF)_2$, can be derived from a study of its thermal decomposition[15] by assuming a normal A factor ($A = 10^{15.3}$ s^{-1}) for the unimolecular fission of each O–F bond.[4] A linear function between D_{RO-F} (kcal/mol) and ϕ (ppm) relative to Cl_3CF (eq 1) describes well the proposed

$$D = 48.8 + 0.126(\phi + 140) \qquad (1)$$

correlation in the ranges 34.7–47.6 kcal/mol and −147.1 to −249.0 ppm (Figure 1). Equally important, when eq 1 is combined with extensive data on ^{19}F NMR of fluoroxy compounds,[7] the rates of thermal decomposition predicted from the expression $\log k$ (s^{-1}) $= 15.3 - E/\theta$ ($\theta = 10^{-3}(4.575T)$ mol kcal^{-1}) are clearly consistent with a large body of qualitative observations. Thus, for example, the greater thermal stability of fluoroxyfluoroalkanes relative to perfluoroacyl hypofluorites[1] certainly reflects their upfield OF fluorine shifts (Table I). In Table I we present estimated values of D for some representative fluoroxy compounds.

On this basis, from the measured value of the ^{19}F shift in ClO_3OF, $\phi = -219.4$ ppm,[16] and using eq 1, we estimate an activation energy for the O–F homolysis of about 37.5 kcal/mol and would predict a fairly stable species below 400 K if this process were rate determining. Since measured rates are more than a factor of 10^3 larger than estimated values, one is led to conclude that perchloryl hypofluorite pyrolysis occurs via a complex mechanism rather than a simple unimolecular reaction in full agreement with experimental observations.[17] It is apparent that eq 1 provides a valuable guide toward the kinetics and thermochemistry of fluoroxy compounds. An extension of these ideas is under way.

Registry No. Fluorine, 7782-41-4; oxygen, 7782-44-7.

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Kinetics and Mechanism of the Oxidation of Europium(II) Ions and of the Reduction of Europium(III) Ions by 2-Hydroxy-2-propyl Radicals

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The kinetics of the reactions of Eu^{3+} and Eu^{2+} with 2-hydroxy-2-propyl radicals in H_2O and D_2O have been studied by competition methods based on homolysis of (2-hydroxy-2-propyl)pentaaquochromium(III) ions. The radicals react with Eu^{3+} to form Eu^{2+} and acetone with rate constants (±15%) of 3.7×10^4 M^{-1} s^{-1} in H_2O and 8.8×10^3 M^{-1} s^{-1} in D_2O and with Eu^{2+} to form Eu^{3+} and 2-propanol with rate constants of 1.5×10^5 M^{-1} s^{-1} in H_2O and 3.1×10^4 M^{-1} s^{-1} in D_2O at 25 °C. The reduction of Cr^{3+} by $\cdot C(CH_3)_2OH$ is characterized by the rate constant $(5.6 \pm 1.4) \times 10^2$ M^{-1} s^{-1}. Mechanisms consistent with the kinetic data have been formulated.

Introduction

The oxidation–reduction reactions occurring between Eu^{3+} or Eu^{2+} ions and carbon-centered free radicals have received very little attention. The only information we have found concerns a semiquantitative pulse radiolytic study[1] that reports the reduction of Eu^{3+} to Eu^{2+} by the carboxylate radical anion $\cdot CO_2^-$ ($Eu^{3+} + \cdot CO_2^- \rightarrow Eu^{2+} + CO_2$) as having $k > 7 \times 10^6$ M^{-1} s^{-1}. The availability of the 2-hydroxy-2-propyl radical from the homolytic decomposition of an organochromium(III) complex has provided a useful method for studying less reactive substrates, and thus a method of evaluating rate constants for the reaction of a series of cobalt(III) complexes[2a] and pyridinium ions[2b] and for the oxidation of vanadium(II) ions.[3] We

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have now employed the method to study the oxidation-reduction reactivity of Eu^{3+} and Eu^{2+}.

The organochromium complexes[4-8] $(H_2O)_5CrR^{2+}$ undergo acidolysis and homolysis in acidic aqueous solutions.[7,9] The extent of the two reactions depends on the identity of the group R; in the case at hand, R = $C(CH_3)_2OH$, the respective reactions 1 (acidolysis) and 2 (homolysis) and their rate constants are known.[7,10]

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_3O^+ \xrightarrow{k_A} Cr(H_2O)_6^{3+} + (CH_3)_2CHOH \quad (1)$$

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_2O \underset{k_{Cr}}{\overset{k_H}{\rightleftharpoons}} Cr(H_2O)_6^{2+} + \cdot C(CH_3)_2OH \quad (2)$$

The homolysis reaction produces a low, steady-state concentration of the carbon-centered free radical. The rate constant for the reaction of desired substrate can then be determined by studying the kinetic competition between Cr^{2+} (reverse of eq 2) and the given substrate (Eu^{2+} or Eu^{3+}) for the radical. In the present work we report results showing that the reactions given by eq 3 and 4 occur as written and

$$Eu(aq)^{3+} + \cdot C(CH_3)_2OH \rightarrow Eu(aq)^{2+} + (CH_3)_2CO + H^+ \quad (3)$$

$$Eu(aq)^{2+} + \cdot C(CH_3)_2OH \xrightarrow{(+H^+)} Eu(aq)^{3+} + (CH_3)_2CHOH \quad (4)$$

$$Cr(H_2O)_6^{3+} + \cdot C(CH_3)_2OH \rightarrow Cr(H_2O)_6^{2+} + (CH_3)_2CO + H^+ \quad (5)$$

also present some evidence for eq 5, although it is so much slower as to be barely perceptible. The rate constants for eq 3 and 4 were evaluated by using the competition technique in both H_2O and D_2O solutions.

Experimental Section

Solutions containing the organochromium complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$ were prepared[2,4] from the reaction of chromium(II) ions with hydrogen peroxide in aqueous perchloric acid or hydrochloric acid solutions containing 2-propanol (~1 M). The Eu^{3+} solutions were prepared by dissolving weighed amounts of europium(III) oxide in perchloric or hydrochloric acid solutions. Solutions of Cr^{2+} and Eu^{2+} were prepared by reducing a known concentration of M^{3+} with amalgamated zinc under an atmosphere of Cr^{2+}-scrubbed nitrogen. Because Eu^{2+} is oxidized by perchloric acid,[11,12] no solution over 3 h old was used, and some experiments were performed in hydrochloric acid solutions. The same results were obtained in 0.037 M hydrochloric acid as in perchloric acid of the same concentration.

The quantitative reduction of Eu^{3+} to Eu^{2+} was checked by its absorption spectrum, which agreed with ones published.[12,13] This reduction was further checked by using Eu^{2+} to reduce an excess of $Co(NH_3)_5Cl^{2+}$; the yield of Co^{2+}, determined as $Co(NCS)_4^{2-}$ with ϵ 1842 M^{-1} cm^{-1} at 623 nm,[14] confirmed that reduction to Eu^{2+} was quantitative. Our most precise values of the wavelength maxima and molar absorptivities of Eu^{2+} are λ 320 and 248 nm (ϵ 6.42×10^2 and 1.66×10^3 M^{-1} cm^{-1}, respectively, in 0.037 M $HClO_4$, and 6.15×10^2 and 1.75×10^3 M^{-1} cm^{-1}, respectively, in 0.037 M HCl).

The kinetic measurements were made with a Cary Model 219 recording spectrophotometer with a thermostated cell compartment. The data were collected at λ 407 nm, an absorption maximum for $CrC(CH_3)_2OH^{2+}$ (ϵ 7.0×10^2 M^{-1} cm^{-1}), with the reaction temperature controlled at 25.0 ± 0.1 °C. The ionic strength was governed largely by the concentrations of perchloric or hydrochloric acid, which were set at 0.40 and 0.037 M, respectively, for the reactions of Eu^{3+} and Eu^{2+}. The slow reaction of Cr^{3+} with $\cdot C(CH_3)_2OH$ necessitates the use of high $[Cr^{3+}]$ to realize measurable kinetic effects. These measurements were done at a constant $[Cr^{3+}] = 0.0696$ M and at a constant $[H^+] = 0.200$ M, the applicable ionic strength thus being 0.618-0.622 M. Reactions run in D_2O were prepared from 99.83% D_2O; the final solutions used in the kinetic determinations had a mole fraction of deuterium of at least 0.96.

Results and Interpretation

Products and Stoichiometry. The decomposition of $Cr(C(CH_3)_2OH^{2+}$ in the presence of excess Eu^{3+} yields Eu^{2+}. The organic product was assumed to be acetone, as expected from this radical and demonstrated in related reactions.[2a,3] The spectrum of the final reaction solution confirmed the production of Eu^{2+}, and its concentration was determined both directly, based on the values of the molar absorptivities at λ 248 and 320 nm, and indirectly from the Co^{2+} produced by reaction of that solution with $Co(NH_3)_5Cl^{2+}$. With due allowance for the proportion of reaction proceeding by the concurrent nonradical pathway (eq 1) and with the rate constants given in the next section, the observed yield of Eu^{2+} is 96% of that expected from eq 3. Decomposition of $CrC(CH_3)_2OH^{2+}$ in the presence of excess Eu^{2+} produces Eu^{3+}, eq 4, as confirmed by the appearance of a small spike at a sharp absorption maximum of Eu^{3+} (λ 393 nm, ϵ ~3 M^{-1} cm^{-1}) on top of the broader absorption of the remaining Eu^{2+}. A reliable estimate of the Eu^{3+} concentration could not be made from its weak absorbance, however; hence the Eu^{2+} remaining was determined as before and the Eu^{3+} formed calculated by diffference. Again, the value of $[Eu^{3+}]_\infty$ was 96% of that expected from eq 4.

Kinetics. In the case of Eu^{3+} the relevant reactions are those in eq 1, 2, and 3. (Note that self-reaction between a pair of free radicals is not important under the experimental conditions employed, since the added quantities of the reactive Eu^{3+} (or Eu^{2+}) and Cr^{2+} keep the radical concentration quite low.) With the steady-state approximation applied to the concentration of the free-radical intermediate, the expected rate law is

$$\frac{-d[CrC(CH_3)_2OH^{2+}]}{dt} = \left(k_A + \frac{k_H k_3[Eu^{3+}]}{k_{Cr}[Cr^{2+}] + k_3[Eu^{3+}]}\right)[CrC(CH_3)_2OH^{2+}] \quad (6)$$

where k_A represents the rate constant for eq 1 (at a given $[H^+]$ and ionic strength) and k_H and k_{Cr} are the respective forward and reverse rate constants for eq 2. A similar equation, with $k_4[Eu^{2+}]$ in place of $k_3[Eu^{3+}]$, applies to the decomposition of the organochromium cation in the presence of Eu^{2+}, when the reactions of eq 1, 2, and 4 are the only important ones. Thus the decomposition of $CrC(CH_3)_2OH^{2+}$ is, according to these equations, expected to follow pseudo-first-order kinetics when the initial concentrations of Eu^{3+} (or Eu^{2+}) and Cr^{2+} are much larger than that of $CrC(CH_3)_2OH^{2+}$, as was the case

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Table I. Kinetic Data[a] for the Reduction of Eu^{3+} by $\cdot C(CH_3)_2OH$ in H_2O and D_2O at 25.0 °C

$10^3[Cr^{2+}]/[Eu^{3+}]$	10^3k_{obsd}, s^{-1}	
	H_2O	D_2O
2.50		9.75
3.40		8.10
7.10		5.30
8.20	16.0	
10.5		4.37
14.2	11.5	3.80
20.0	9.70	
21.4		3.23
25.0		3.05
26.0	8.60	
35.0	7.80	
38.9	7.60	
∞[b]	5.30	2.10

[a] Conditions: 0.400 M $HClO_4$, 1.14 M 2-propanol, $[CrC(CH_3)_2OH^{2+}]_0 = 8.0 \times 10^{-4}$ M; range $1.76 < 10^2\,[Eu^{3+}]_0 < 3.52$ M and $0.10 < 10^3\,[Cr^{2+}]_0 < 4.0$ M. [b] This represents k_A, the rate constant for the acidolysis reaction (eq 1), determined under the identical experimental conditions.

Table II. Kinetic Data[a] for the Oxidation of Eu^{2+} by $\cdot C(CH_3)_2OH$ in H_2O and D_2O at 25.0 °C

$10^2[Cr^{2+}]/[Eu^{2+}]$	10^3k_{obsd}, s^{-1}	
	H_2O	D_2O
4.02	12.7	
5.60	10.0	
5.70		2.40
6.25	8.93	
8.40		1.75
8.70	7.74	
9.90	7.40	
11.30		1.60
14.05	6.25	
14.25		1.47
15.63	5.95	
19.90		1.30
20.10	5.50	
20.30	5.50	
27.50	4.95	
28.50		1.19
35.04	4.70	
40.00	4.44	
∞[b]	3.55	0.91

[a] Conditions: 0.0370 M HCl or $HClO_4$, 3.0 M 2-propanol, $[CrC(CH_3)_2OH^{2+}]_0 = 8.0 \times 10^{-4}$ M; range $3.0 < 10^3\,[Eu^{2+}]_0 < 4.5$ M and $0.10 < 10^3\,[Cr^{2+}] < 2.0$ M. [b] See Table I, footnote *b*.

in practice. This expectation was, in fact, realized, and each such run afforded a value of a pseudo-first-order rate constant k_{obsd} ($=-d \ln [CrC(CH_3)_2OH^{2+}]/dt$), which is the quantity within the parentheses of eq 6. The values of k_{obsd} varied with the concentration of Eu^{3+} (or Eu^{2+}) and Cr^{2+} (Tables I and II), as would be expected. Rearrangement of eq 6 gives

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_H} + \frac{k_{Cr}}{k_H k_{Eu}} \frac{[Cr^{2+}]}{[Eu]} \tag{7}$$

where $k_{Eu}[Eu]$ is now a generic notation for either $k_3[Eu^{3+}]$ or $k_4[Eu^{2+}]$, depending on which experiment was being run. The acidolysis rate constant k_A is actually $[H^+]$ dependent ($k_A = k_{1A} + k_{2A}[H^+]$), and was determined under each precise set of experimental conditions used. A plot of $(k_{obsd} - k_A)^{-1}$ vs. the ratio $[Cr^{2+}]/[Eu]$ is thus predicted to be a straight line. The plot appears in Figure 1. The preceding description is a useful one for illustrative purposes, but the algebraic form of eq 7 is not the optimum for precise numerical analysis. The full expression for k_{obsd} from eq 6 is

$$k_{obsd} = k_{1A} + k_{2A}[H^+] + \frac{k_H}{1 + (k_{Cr}/k_{Eu})[Cr^{2+}]/[Eu]} \tag{8}$$

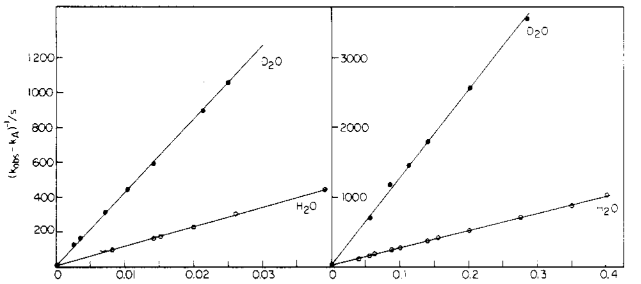

Figure 1. Plots of the kinetic data in a linearized fashion in accord with eq 7. The left portion of the graph depicts the kinetic data for the reduction of $Eu(aq)^{3+}$ in H_2O and D_2O and the right portion for the oxidation of $Eu(aq)^{2+}$.

Table III. Rate Constants for the Reactions of Various Complexes with 2-Hydroxy-2-propyl Radicals in H_2O and D_2O at 25 °C

reactant	$k_{H_2O}/$ $(M^{-1}\,s^{-1})$	$k_{D_2O}{}^a/$ $(M^{-1}\,s^{-1})$	k_{H_2O}/k_{D_2O}	ref
$Eu(aq)^{3+}$	3.7×10^4	8.8×10^3	4.2	*b*
$Eu(aq)^{2+}$	1.53×10^5	3.1×10^4	4.8	*b*
$V(H_2O)_6{}^{2+}$	2.1×10^5	$3.6 \times 10^{4\,c}$	$\sim 6.0^d$	3
$Co(NH_3)_6{}^{3+}$	4.1×10^5	4.5×10^5	0.91	2
$Co(ND_3)_6{}^{3+}$	3.0×10^5	2.4×10^5	1.25	2
$Cr(H_2O)_6{}^{3+}$	5.6×10^2			*b*
$Cr(H_2O)_6{}^{2+}$	5.1×10^7		$(\sim 1.0)^e$	15

[a] The values listed for D_2O assume that the rate constant k_{Cr} for $Cr^{2+} + \cdot C(CH_3)_2OH \rightarrow CrC(CH_3)_2OH^{2+}$ is the same in D_2O as in H_2O. [b] This work. [c] In 92% D_2O. [d] Extrapolated to 96% D_2O, where the other values were determined. [e] Assumed value (see text).

in which the acid dependence[2a,4,7,10] of k_A has been stated explicitly. The numerical fit of all the kinetic data used to calculate the best value of the ratio k_{Cr}/k_{Eu} was based on a nonlinear least-squares analysis according to eq 8. The known rate constants were fixed at their established values: $k_H = 0.127 \pm 0.003\ s^{-1}$ at 25.0 °C[7] and k_A as appropriate to the conditions employed (ref 10; Tables I and II). The ratios at 25.0 °C are $k_{Cr}/k_3 = (1.37 \pm 0.02) \times 10^3$ and $k_{Cr}/k_4 = (3.33 \pm 0.04) \times 10^2$, where the uncertainties shown represent one standard deviation.

Analogous experiments in D_2O yield $(5.82 \pm 0.17) \times 10^3$ and $(1.63 \pm 0.05) \times 10^2$, respectively. The ratios in D_2O were calculated by using the same value for k_H as in H_2O, as shown previously[2a] and further verified by the common intercept for each reaction as shown in Figure 1. On the other hand, k_A is strongly isotope dependent,[2a,9,15] the values used being those in Tables I and II.

The individual rate constants are calculated from the experimentally determined ratios with the directly measured value $k_{Cr} = 5.1 \times 10^7$ (±15%) $M^{-1}\,s^{-1}$ at 22 ± 2 °C[16]. The accuracy of k_3 and k_4 is thus probably ±15%, as compared to the more precisely known ratios, k_{Cr}/k_3 and k_{Cr}/k_4. If it is assumed that $k_{Cr}(H_2O) \approx k_{Cr}(D_2O)$, the kinetic isotope effects associated with the rate constant for the europium reactions are $k_3(H_2O)/k_3(D_2O) = 4.23 \pm 0.17$ and $k_4(H_2O)/k_4(D_2O) = 4.84 \pm 0.21$. The values are given in Table III.

Reduction of $Cr(H_2O)_6{}^{3+}$. Preliminary experiments showed that $\cdot C(CH_3)_2OH$ reacts with Cr^{3+} much more slowly than with $Eu(aq)^{3+}$, if at all. This requires the use of high ratios of $[Cr^{3+}]/[Cr^{2+}]$, and particular efforts to ensure that any systematic variation of k_{obsd} is not due to activity effects since

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the determination of k_5 is based on small differences. Thus a series of determinations using a high and constant concentration of chromium(III) ions, 6.96×10^{-2} M, and a constant reaction medium (0.200 M perchloric acid, 1.13 M 2-propanol) was carried out. The principal variable was $[Cr^{2+}]$, ranging between 1.8×10^{-4} and 3.0×10^{-3}. The kinetic data are as follows, where k_5 was calculated by using $k_A = 4.30 \times 10^{-3}$ s^{-1}:

$[Cr^{2+}]$/M	k_{obsd}/s^{-1}	$k_5/(M^{-1}\ s^{-1})$
1.8×10^{-4}	4.75×10^{-3}	4.13×10^2
8.8×10^{-4}	4.46×10^{-3}	6.0×10^2
2.96×10^{-3}	4.38×10^{-3}	6.8×10^2
		av $(5.6 \pm 1.4) \times 10^2$

The very low rate constant of the reaction of eq 5 could have previously been inferred since it is never a factor in other competition or kinetic experiments involving $CrC(CH_3)_2OH^{2+}$ in solutions containing low but variable concentrations of $Cr(H_2O)_6^{3+}$.

Europium-Catalyzed Disproportionation of $\cdot C(CH_3)_2OH$? The summation of eq 3 and 4 is equivalent to disproportionation of the aliphatic radicals, eq 9. This spontaneous reaction

$$2\cdot C(CH_3)_2OH \rightarrow (CH_3)_2CHOH + (CH_3)_2CO \quad (9)$$

has a very high rate constant, $k_9 = 6.5 \pm 0.5) \times 10^9$ M^{-1} s^{-1},[17] but is not important as a direct reaction in this work owing to the low concentration of the free radical which prevails throughout.

On the other hand, the sequential occurrence of the two reactions noted, eq 3 and 4, leads to the same overall net reaction; if it occurs to a major extent it would then constitute a europium-catalyzed pathway for free-radical disproportionation. Reaction conditions were selected to minimize its importance. In retrospect, the easiest way to gauge the success of the experimental control is to examine the summation $k_3[Eu^{3+}] + k_4[Eu^{2+}]$, which would be the catalyzed rate constant. In experiments dealing with reaction 4 (Table II), the first term never contributes more than 6.0% to the sum. In the Eu^{3+} experiments (Table I), the second term never amounts to more than 10.1%. Both figures apply at the midpoint of the kinetic runs. It is clear from this analysis that the catalyzed disproportionation reaction does not make an appreciable contribution under the concentration conditions used for kinetic evaluations.

Discussion

Reaction Mechanisms. The rate constants for the reactions in which $Eu(aq)^{3+}$ and $Cr(H_2O)_6^{3+}$ are reduced by $\cdot C(CH_3)_2OH$ differ by a factor of nearly 10^2. A similar qualitative difference was found[1] in comparing the ready reaction of $\cdot CO_2^-/\cdot COOH$ with Eu^{3+} under conditions where Cr^{3+} does not react. An outer-sphere electron transfer mechanism is often assigned to reactions in which $\cdot(CH_3)_2OH$ functions as a reducing agent. Alternatively electron transfer may occur within a charge-transfer complex. The lower reactivity of Cr^{3+} may well be a consequence of a slower self-exchange for Cr^{3+}/Cr^{2+} as compared to Eu^{3+}/Eu^{2+} and to the much greater tendency for the latter to involve major contributions from nonadiabaticity. Similar arguments have been advanced[18] to account for the differences in the solvent isotope effects for the electrochemical self-exchange rate constants for Cr^{3+}/Cr^{2+} as compared to Eu^{3+}/Eu^{2+}.

The oxidation of $Eu(aq)^{2+}$ by $\cdot C(CH_3)_2OH$ appears, like the oxidation of $V(H_2O)_6^{2+}$,[3] to proceed by a hydrogen atom abstraction mechanism, as depicted in eq 10. Evidence for

$$Eu(H_2O)_x^{2+} + \cdot C(CH_3)_2OH \rightarrow EuOH^{2+} + (CH_3)_2C\mathit{H}OH \quad (10)$$

this consists, in part, of the large kinetic isotope effects, 4.8 for Eu^{2+} and 6.0 for V^{2+} (Table III). It is possible to account more quantitatively for the kinetic isotope effects found here in terms of isotope fractionation factor theory,[15,19] but those results will be given elsewhere.[20]

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Registry No. Europium, 7440-53-1; 2-hydroxy-2-propyl, 5131-95-3.

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Kinetics of Coordinated-Base-Catalyzed and Free-Base-Catalyzed Configurational Conversions of a Tetraamine Macrocyclic Ligand Complex of Copper(II)

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In order to investigate the effect of coordinated hydroxide ion and free hydroxide ion in configurational conversion of a tetraamine macrocyclic ligand complex, the kinetics of the blue-to-red interconversion of the copper(II) complex of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane has been examined spectrophotometrically for $[OH^-]$ between 1.99×10^{-4} and 5.00 M. All the data are satisfactorily fitted by the rate law $R = (k_1K_{OH}[OH^-] + k_2K_{OH}[OH^-]^2)(1 + K_{OH}[OH^-])^{-1}([[Cu(tet\ a)(blue)]^{2+}] + [[Cu(tet\ a)(OH)(blue)]^+])$, with $k_1 = 5.51$ s^{-1}, $k_2 = 0.84$ M^{-1} s^{-1}, and $K_{OH} = 51.6$ M^{-1} at 25.0 °C and $\mu = 5.0$ M ($NaNO_3 + NaOH$). The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for k_1 are 10.8 kcal mol^{-1} and −19.0 eu, respectively. These small $\Delta H^\ddagger$ and negative $\Delta S^\ddagger$ values suggest a concerted coordinated-base-catalyzed mechanism in which intramolecular hydrogen bonding, nitrogen inversion, solvation, and ring conformational changes occur. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for k_2 are 22.8 kcal mol^{-1} and 17.5 eu, respectively. These activation parameters are consistent with the desolvation that takes place in the reaction of $[Cu(tet\ a)(OH)(blue)]^+$ with free hydroxide ion.

Introduction

The extreme kinetic inertness and very high thermodynamic stability of tetraamine macrocyclic ligand complexes are significant for inorganic stereochemistry,[1] since they greatly enhance the number of potentially isolable isomers.[2] Thus, these complexes provide stimulating examples for studying

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[1] Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540; **1970**, *92*, 2151.

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