# Kinetics and Mechanism of the Reaction of Europium(II) and Oxovanadium(IV) Ions in Solutions Containing Perchlorate and/or Complexing Anions[1a]

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**Abstract:** The oxidation of Eu$^{2+}$ by VO$^{2+}$ occurs according to a rate expression $k[\mathrm{Eu}^{2+}][\mathrm{VO}^{2+}]$, with $k = 2.64 \pm 0.09 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ at 25.0° and unit ionic strength. The products are Eu$^{3+}$ and V$^{3+}$; subsequent reduction of V$^{3+}$ by Eu$^{2+}$ occurs much more slowly. Activation parameters for the reaction are $\Delta H^{\ddagger} = 2.83 \pm 0.30$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -33.4 \pm 1.0$ cal mol$^{-1}$ deg$^{-1}$. The reaction was also studied in the presence of thiocyanate, azide, and chloride ions. All three anions increase the rate of oxidation of Eu$^{2+}$, suggesting oxidation of VO(X)$^+$ by Eu$^{2+}$. In the presence of $>0.1\ M$ SCN$^-$, (H$_2$O)$_5$VNCS$^{2+}$ was detected as a product; the failure to detect VCl$^{2+}$ is probably due to its high aquation rate.

Europium(II) is a sufficiently powerful reducing agent to convert the oxovanadium(IV) ion to vanadium(II) in aqueous perchloric acid solution. The reduction proceeds in two stages; however, the second stage reaction of V(III) and Eu(II) is considerably slower.[2] The reaction of V(IV) and Eu(II) was referred to by Adin and Sykes,[2] who provided an approximate second-order rate constant, *ca.* $10^3\ M^{-1}\ \mathrm{sec}^{-1}$ at 25° in 0.2 *F* perchloric acid. In the present work we have employed the stopped-flow technique in a detailed study of the kinetics of reaction I in perchloric acid solution.

$$\mathrm{Eu}^{2+} + \mathrm{VO}^{2+} + 2\mathrm{H}^+ = \mathrm{Eu}^{3+} + \mathrm{V}^{3+} + \mathrm{H_2O} \qquad \mathrm{(I)}$$

The literature on Eu(II) reaction mechanisms has previously been concerned with the Eu(II)–Eu(III) exchange rate,[3] and the reduction of such substrates as Co(III) complexes,[4] V(III),[2] Cr(III)[2] and its complexes,[5] and Fe(III) and its complexes.[6] The general pattern resulting from the studies has not been clearly resolved and it appears that some, but not all, mechanisms involve inner-sphere transition states. The evidence for such conclusions has been indirect, however, since the oxidized product Eu(III) undergoes very rapid ligand substitution and exchange.

The reactions of VO$^{2+}$ with Cr(II),[7] V(II),[8] and Cu(I)[9] have been studied; in each case the form of the rate expression has suggested the presence of oxo or hydroxo groups in the transition state. These ligands are probably functioning as bridging groups. In the first two instances dinuclear intermediates were detected spectrophotometrically, substantiating the suggestion of inner-sphere mechanisms.

The product of the single-equivalent reduction of VO$^{2+}$ is V$^{3+}$, which is known[10,11] to undergo ligand substitution processes such as shown in reaction II at

$$\mathrm{V(H_2O)_6}^{3+} + \mathrm{X}^- = \mathrm{(H_2O)_5VX}^{2+} + \mathrm{H_2O} \qquad \mathrm{(II)}$$

rates that are low relative to electron transfer. For that reason an examination of the effect of anions other than perchlorate might be helpful toward resolving the role anions play in reactions of this type, as has been the case in earlier work.[6,12–15] If a new rate term arises upon addition of such an ion one may possibly learn about its role in the transition state by noting whether the anion is captured by the V(III) product during the course of electron transfers. Such experiments were carried out to examine the effects of thiocyanate, azide, and chloride ions in the reaction of Eu$^{2+}$ and VO$^{2+}$.

## Experimental Section

**Materials and Analyses.** Stock solutions of oxovanadium(IV) perchlorate were prepared by two independent methods. Barium perchlorate and vanadyl sulfate were mixed in approximately equivalent amounts after which the barium sulfate precipitate was removed by centrifugation and filtration. The supernatant solution, *ca.* 1 *M* in VO$^{2+}$, was tested for an excess of sulfate and barium ions, and the concentration then adjusted by addition of small quantities of VOSO$_4$ or Ba(ClO$_4$)$_2$ until a very slight excess of Ba$^{2+}$ remained. The resulting solution was filtered through a very fine glass frit. The second preparation involved the electrolytic reduction of a suspension of V$_2$O$_5$ (0.2 mol) in perchloric acid (530 ml, 2.9 *M*) using electrodes made of platinum foil.[16] The reduction was continued past the point where some V(III) was formed, at which time the solution was filtered to remove any unreacted and undissolved V$_2$O$_5$. Electroreduction was continued for a short time to ensure the complete absence of V(V), after which pure oxygen was bubbled through the solution for *ca.* 24 hr until no trace of V(III) remained unreacted. The V(IV) solution was analyzed by Ce(IV) titration in acetic acid solution according to the procedure of Sririmam and Rao.[17]

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[1] (a) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970; (c) based on the M.S. thesis of R. J. C., May 1969.

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[16] A mercury pool cathode is not suitable as V(V) reacts directly with Hg, and gives a solution containing VO$^{2+}$ and Hg$_2$$^{2+}$.

Solutions of Eu(II) were prepared and analyzed as before,[6a] with samples taken for analysis directly from the volumetric flask serving as the solution reservoir of the stopped-flow apparatus. Samples were taken during the course of each rate experiment, thereby avoiding any effect of possible air oxidation during handling or transfer procedures.

Lithium perchlorate, sodium azide, and lithium thiocyanate were prepared and purified as described in earlier publications.[6,18] Laboratory distilled water was redistilled from alkaline permanganate in a tin-lined Barnstead still. Perchloric and hydrochloric acids were reagent grade materials used without further purification.

A procedure based on the Cu(II)-catalyzed reaction[19] of $V^{3+}$ and $Co(NH_3)_5Br^{2+}$ was developed to analyze for V(III) in the spent reaction solution. The solution was made *ca.* 0.01 $M$ in $Cu^{2+}$ and 0.002 $M$ in $H^+$, and $Co(NH_3)_5Br_3$ was added to give a ratio Co(III):V(III) of 1.1 to 1.4. The solution was allowed to remain under nitrogen for *ca.* 30 min, a time sufficient[19] for the complete oxidation of the V(III) at this $[H^+]$. Identical blank solutions were prepared and the absorbances measured at 253 nm where $Co(NH_3)_5Br^{2+}$ has an absorption maximum with $\epsilon$ $1.67 \times 10^4$. The difference in absorbance of sample and blank gives directly the V(III) concentration, as the Cu(II)-catalyzed reduction occurs with a 1:1 stoichiometry.[19] In the absence of added Cu(II) no reduction of Co(III) by V(III) occurs, and no change in absorbance at 253 nm is noted.

**Conditions and Methods.** The ionic strength was maintained at 1.00 $M$ with lithium perchlorate, and the temperature of the reactant solutions was maintained by circulating thermostated water through jackets around each of the driving syringes in the stopped-flow apparatus. The reaction temperature was found to be slightly different ($<0.8°$ for $15° < T < 35°$) from the bath temperature, and the values reported here are the corrected temperatures at which the rate constants were measured.

The course of the reaction was followed spectrophotometrically, observing the decrease in absorbance at either of the uv bands of Eu(II), 320 nm ($\epsilon$ 640 $M^{-1}$ cm$^{-1}$) or 250 ($\epsilon$ 1700). At these wavelengths the molar absorptivities of other species are relatively small except at 250 nm, where $VO^{2+}$ has $\epsilon$ 230 and $V^{3+}$ $\epsilon$ 50. The treatment of the data does not require a knowledge of the molar absorptivities of any of the species involved, however. In terms of the absorbance readings, $D$, the appropriate equations are

$$\ln (D_t - D_\infty) = \ln (D_0 - D_\infty) - k[VO^{2+}]t \qquad (1)$$

$$\ln \left\{\frac{1 - \dfrac{a(D_0 - D_t)}{b(D_0 - D_\infty)}}{(D_t - D_\infty)/(D_0 - D_\infty)}\right\} = k(b - a)t \qquad (2)$$

where eq 1 applies to the pseudo-first-order case ($VO^{2+}$ in excess) and eq 2 applies to the second-order case (reactant concentrations comparable, $VO^{2+}$ in excess). The initial concentrations of $Eu^{2+}$ and $VO^{2+}$ are designated $a$ and $b$, respectively. The rate constant $k$ in eq 1 and 2 is defined by the expression

$$-\mathrm{d}[Eu^{2+}]/\mathrm{d}t = k[VO^{2+}][Eu^{2+}] \qquad (3)$$

A Cary Model 14 recording spectrophotometer was used to measure absorption spectra and for analyses. A stopped-flow apparatus employing spectrophotometric detection was used for the rate studies as described in earlier publications.[6a,18]

## Results

**Stoichiometry.** Two experiments on the stoichiometry of the reaction of $Eu^{2+}$ and $VO^{2+}$ with the latter in excess were carried out. The $V^{3+}$ present in the resulting reaction solutions was analyzed by the $Cu^{2+}$ catalysis method outlined above. The conditions and results of the experiments are as follows.

| $10^4[Eu^{2+}]_0$ | $10^4[VO^{2+}]_0$ | $10^4[V^{3+}]_\infty$ | $[Eu(II)]/[V(IV)]_{reacted}$ |
|---|---|---|---|
| 2.79 | 10.7 | 2.87 | 0.97 |
| 5.39 | 8.54 | 5.17 | 1.04 |

A different method was used to study the stoichiometry to provide an independent check and to confirm the lack of significant reduction of V(III) when Eu(II) was in excess. The absorbances of a number of solutions containing approximately the same Eu(II) concentrations, $4 \times 10^{-4}$ $M$, were measured at 320 nm. A different concentration of $VO^{2+}$ solution was added to each, and the absorbances again measured. The quantity of Eu(II) reacted, computed from the absorbance change and the molar absorptivity of Eu(II), was compared with the [V(IV)] added giving a value $[Eu(II)]_{reacted}/[V(IV)] = 1.07 \pm 0.04$ from reaction *I*, but the deviations are probably due to some air oxidation of Eu(II) upon introduction of the V(IV). Both methods of studying the reaction served to confirm that the reaction occurs in accord with reaction I within the experimental errors associated with the methods of evaluating the stoichiometric ratios.

**Rate Studies in Perchlorate Solutions.** A series of experiments was carried out at 25.0° in which the initial concentrations of $Eu^{2+}$ and $VO^{2+}$ were varied over wide limits: $5 \times 10^{-5} \leq [Eu^{2+}]_0 \leq 4.5 \times 10^{-4}$ $M$ and $1.9 \times 10^{-4} \leq [VO^{2+}]_0 \leq 4.9 \times 10^{-3}$ $M$. In all runs except one, $VO^{2+}$ was in excess. The hydrogen ion concentration in every experiment was in considerable excess, and its concentration remained essentially invariant throughout a rate run. The rate data were plotted in accord with eq 1 or 2 depending on concentration conditions, giving graphs that were linear for at least 85% of the reaction. The fit to eq 2 was also carried out using a nonlinear least-squares computer program,[20] giving results in very good agreement with the graphical method.

The results of the individual rate experiments at 25.0° are summarized in Table I. The excellent constancy of the rate constant $k$ establishes eq 3 to be a good representation of the rate law for reaction I. The

Table I. Kinetic Data for the Reaction of $Eu^{2+}$ and $VO^{2+}$ at 25.0° [a]

| —Initial concn, $M \times 10^4$— | | $\lambda$, | $10^{-3}k_2$,[c] |
|---|---|---|---|
| $VO^{2+}$ [b] | $Eu^{2+}$ | nm | $M^{-1}$ sec$^{-1}$ |
| 1.94 | 4.5 | 250, 320 | 2.52 ± 0.10 |
| 5.18 | 0.5 | 250 | 2.74 ± 0.08 |
| 5.18 | 2.0 | 320 | 2.56 ± 0.10 |
| 13.0 | 0.5 | 250 | 2.77 ± 0.12[d] |
| 13.0 | 0.5 | 250 | 2.66 ± 0.02[e] |
| 13.0 | 1.0 | 320 | 2.90 ± 0.23 |
| 13.0 | 4.0 | 320 | 2.51 ± 0.05 |
| 13.1[f] | 1.0 | 250 | 2.89 ± 0.05 |
| 13.1[f] | 1.0 | 250 | 2.74 ± 0.09[g] |
| 19.6[f] | 1.0 | 250 | 2.69 ± 0.13 |
| 32.4 | 2.0 | 280 | 2.51 ± 0.07 |
| 32.7[f] | 2.0 | 320 | 2.58 ± 0.07[d] |
| 32.7[f] | 2.0 | 320 | 2.63 ± 0.07[h] |
| 33.4 | 2.0 | 250 | 2.62 ± 0.17[i] |
| 49.0[f] | 2.0 | 320 | 2.48 ± 0.06 |
| 49.0[f] | 2.0 | 320 | 2.57 ± 0.07 |
| | | $k_2$ = | 2.64 ± 0.09 |

[a] $\mu = 1.0$ $M$, $[H^+] = 0.95$ $M$, except as noted. [b] $VO^{2+}$ prepared from the sulfate, except as noted. [c] Uncertainty represents the average deviation from the mean of four repeat determinations using the same solutions. [d] $[H^+] = 0.01$ $M$. [e] $[H^+] = 0.10$ $M$. [f] $VO^{2+}$ prepared electrolytically. [g] $[H^+] = 0.02$ $M$. [h] $[H^+] = 0.04$ $M$. [i] $[V^{3+}] = 1.3 \times 10^{-3}$ $M$ added initially.

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(20) We are grateful to Drs. T. W. Newton and R. Moore for supplying copies of the computer programs based on the report from Los Alamos Scientific Laboratory, LA2367 + Addenda.

reaction rate also proved to be independent of hydrogen ion concentration, as established by the results given in Table I which includes data for 0.01–0.95 $M$ $H^+$. The average value of $k$ at 25° is $2.64 \pm 0.09 \times 10^3$ $M^{-1}$ $sec^{-1}$.

The reaction kinetics were also studied at 15.8 and 34.2°. The rate constants are summarized in Table II and are $2.25 \pm 0.13 \times 10^3$ and $3.18 \pm 0.09 \times 10^3$ $M^{-1}$ $sec^{-1}$ at the two respective temperatures.

**Table II.** Kinetic Data for the Reaction of $Eu^{2+}$ and $VO^{2+}$ at 15.8 and 34.2° [a]

| Temp, °C | —Initial concn, $M \times 10^4$— $VO^{2+}$ [b] | $Eu^{2+}$ | λ, nm | $10^{-3}k_{-2}$,[c] $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|
| 15.8 | 13.0 | 1.0 | 250 | $2.28 \pm 0.07$ |
| 15.8 | 19.4 | 1.0 | 250 | $2.60 \pm 0.08$ |
| 15.8 | 19.4 | 2.0 | 320 | $2.35 \pm 0.03$ |
| 15.8 | 22.9[d] | 2.0 | 320 | $2.14 \pm 0.04$ |
| 15.8 | 32.7[d] | 3.0 | 320 | $2.16 \pm 0.08$[e] |
| 15.8 | 38.9 | 3.0 | 320 | $2.08 \pm 0.08$ |
| 15.8 | 49.0[d] | 4.0 | 350 | $2.14 \pm 0.05$ |
| 34.2 | 5.2 | 0.5 | 250 | $3.54 \pm 0.27$ |
| 34.2 | 13.0 | 1.0 | 250 | $3.20 \pm 0.08$ |
| 34.2 | 19.4 | 2.0 | 320 | $3.08 \pm 0.25$ |
| 34.2 | 32.7[d] | 3.0 | 320 | $3.13 \pm 0.12$[e] |
| 34.2 | 38.9 | 2.0 | 320 | $3.23 \pm 0.12$ |
| 34.2 | 49.0[d] | 4.0 | 350 | $3.06 \pm 0.08$ |

[a] $\mu = 1.0$ $M$, $[H^+] = 0.95$ $M$, except as noted. [b] $VO^{2+}$ prepared from the sulfate, except as noted. [c] Uncertainty represents the average deviation from the mean of four repeat determinations using the same solutions. [d] $VO^{2+}$ prepared electrolytically. [e] $[H^+] = 0.20$ $M$.

**Anion Effects.** Two equilibria pertain to solutions containing anions other than the presumably noncomplexing perchlorate ion. Vanadium(IV) undergoes complexation, as shown in reaction II. One of the

$$VO^{2+} + X^- = VO(X)^+ \quad K_1 \tag{II}$$

more stable complexes is that with thiocyanate ion, for which $K_1$ is *ca.* 8 $M^{-1}$.[21] A slower but more favorable equilibrium pertains to vanadium(III), reaction III.

$$V(H_2O)_6^{3+} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2O)_5VX^{2+} + H_2O \quad K_2 = k_1/k_{-1} \tag{III}$$

In principle Eu(II) will react with both $VO^{2+}$ and the complex $VOX^+$; it may also be involved in an $X^-$-catalyzed reaction not involving the species $VOX^+$. The effect of $[X^-]$ on the apparent second-order rate constant will provide some information on its role, if any, but the question remains of whether the $VX^{2+}$ produced comes from direct reduction of $VOX^+$ or from anation of $V^{3+}$ according to reaction III after its production by I. Since the rate of III is low relative to electron transfer, the answer to whether reduction of $VOX^+$ to $VX^{2+}$ occurs can be sought directly.

One such experiment to study the effect of thiocyanate ion was carried out under the following initial concentration conditions: $2 \times 10^{-4}$ $M$ $Eu^{2+}$, $3.1 \times 10^{-3}$ $M$ $VO^{2+}$, 0.01 $M$ $SCN^-$, and 0.98 $M$ $H^+$.

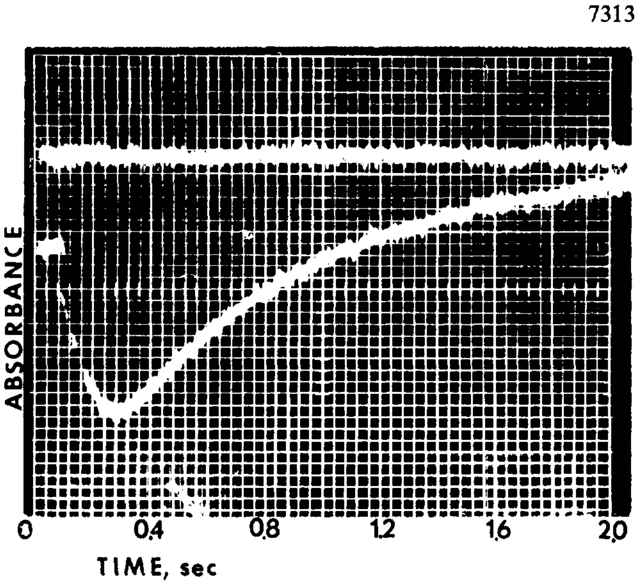

Figure 1. The absorbance as a function of time at 350 nm, $\lambda_{max}$ for $VNCS^{2+}$, in an experiment $Eu^{2+}$ + excess $VO^{2+}$ in a solution with 0.010 $M$ $SCN^-$.

The absorbance–time trace at λ 350 nm displayed a minimum as shown in Figure 1. The initial decrease corresponds to the disappearance of $Eu^{2+}$, and the subsequent increase to the formation of $(H_2O)_5VNCS^{2+}$, which has $\lambda_{max}$ 350 nm (ε 580).[10] In the second stage of the reaction $VNCS^{2+}$ is being formed according to reaction III from $V(H_2O)_6^{3+}$ first produced by reaction I. The identification of the second stage as reaction III was substantiated by the observed rate constant which was in accord with the known values. The first stage provides some indication of thiocyanate catalysis, however, as the rate constant was *ca.* $3.8 \times 10^3$ $M^{-1}$ $sec^{-1}$, somewhat larger than the value of $2.64 \times 10^3$ $M^{-1}$ $sec^{-1}$ found in the absence of thiocyanate.

When higher concentrations of $SCN^-$ were added, the pattern of the absorbance–time trace at λ 350 nm changed. At 0.10 $M$ $SCN^-$, for example, there was a continuous increase in absorbance that appeared, however, to occur at two rather separated rates. At 0.94 $M$ $SCN^-$ the increase in absorbance occurred in a single stage and corresponded to an apparent second-order rate constant $(-C_{V(IV)})^{-1}$ d ln $[Eu^{2+}]/dt$) of $1.15 \times 10^4$ $M^{-1}$ $sec^{-1}$. At $[SCN^-] = 0.01$, 0.10, and 0.94 $M$, *ca.* 10, 50, and 90% of the V(IV) is complexed; at the highest concentration higher complexes are undoubtedly present.

A few rate experiments were also carried out on solutions containing chloride and azide ions ($HN_3$). The complex $(H_2O)_5VN_3^{2+}$ also has an absorption maximum at λ 350 nm (ε ~800).[11] The absorbance-time trace in an experiment with the initial concentration conditions $Eu^{2+}$, $7.6 \times 10^{-4}$, $VO^{2+}$, $8.17 \times 10^{-3}$, $HN_3$, 0.20, and $H^+$, 0.025 $M$ went through a minimum, with the second-stage rate constant in agreement with the values[11] for $VN_3^{2+}$ in reaction III. The second-order rate constant for the first stage was $3.1 \pm 0.1 \times 10^3$ $M^{-1}$ $sec^{-1}$, again larger than in the absence of added $HN_3$.

Finally, an experiment was carried out with chloride ion added at 0.95 $M$. No spectral evidence was obtained for $(H_2O)_5VCl^{2+}$ either at 440 nm, where it is believed to have an absorption maximum,[22] or in the 250–350-nm region. The apparent second-order rate constant was $3.8 \times 10^3$ $M^{-1}$ $sec^{-1}$ at $[Cl^-] = 0.95$ $M$.

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## Interpretation and Discussion

**Activation Parameters and Reaction Mechanism.** The net activation process corresponding to eq 3 is the following

$$VO^{2+} + Eu^{2+} = [VOEu^{4+}]^{\ddagger} \qquad (IV)$$

The temperature dependence of the second-order rate constant was found to be in agreement with the Eyring relation, as the plot of ln $(k/T)$ *vs.* $1/T$ was linear. The rate constants were fit to this equation using a nonlinear least-squares computer program;[20] the resulting values are $\Delta H^{\ddagger} = 2.83 \pm 0.30$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -33.4 \pm 1.0$ cal mol$^{-1}$ deg$^{-1}$, where the uncertainties given are the standard deviations. Using the molar entropies of $Eu^{2+}$ and $VO^{2+}$ as $-18$ and $-26$ cal mol$^{-1}$ deg$^{-1}$, respectively,[23,24] the molar entropy of the transition state, $S^{\ddagger}$, is calculated to be $-77$ cal mol$^{-1}$ deg$^{-1}$, on the scale $S°(H^+) = 0$. This value falls within the range $-60$ to $-80$ noted by Newton and Baker[25] for other 4+ charged transition states in a compilation of data for actinide element reactions. For other reductions of $VO^{2+}$, similar values were found; the transition states $[VOV^{4+}]^{\ddagger}$ and $[VOHCu^{4+}]^{\ddagger}$ have respective[8,9] $S^{\ddagger}$ values of $-66$ and $-73$ cal mol$^{-1}$ deg$^{-1}$.

The rate-determining step is that shown in reaction IV; the two protons needed to complete reaction I must occur in one or more subsequent reaction steps that convert this transition state, or an intermediate of the same composition, to products. The similarities to related reactions, such as the reduction of $VO^{2+}$ by $V^{2+}$[8] or by $Cr^{2+}$,[7] suggest that the reaction may proceed by an inner-sphere mechanism. A dinuclear intermediate involving oxo and/or hydroxo bridging may possibly be involved, but its existence has not been established. Such an intermediate would likely decompose quite rapidly,[7] reaction V, as the more labile

$$VOEu^{4+} + 2H^+ = V^{3+} + Eu^{3+} + H_2O \qquad (V)$$

partner, $Eu^{3+}$, undergoes rapid solvent exchange. In this instance an inner-sphere reaction can be proposed in the absence of a dominant $1/[H^+]$ rate dependence, for the reduction of an oxo ion does not require the same rearrangement of protons as a simple hydrated cation does.

**Role of Complexing Anions.** The minimum in the absorbance time trace at λ 350 nm for 0.01 *M* $SCN^-$ establishes that reaction VI is not enormously faster

$$VO(X)^+ + Eu^{2+} = VX^{2+} + Eu^{3+} + H_2O \qquad (VI)$$

than I; had such been the case $VNCS^{2+}$ would have been the major product and one would have seen a maximum in the recorded trace corresponding first to the formation of $VNCS^{2+}$(VI) and then to its partial aquation.

On the other hand, although the delay in the formation of $VNCS^{2+}$ at 0.01 *M* $SCN^-$, depicted in Figure 1, does indicate that the reaction sequence I, III constitutes a pathway for forming $VNCS^{2+}$, this observation does not prove that this sequence occurs to the total exclusion of the "direct" reaction given in (VI). The disappearance of the minimum with increasing concentrations of $SCN^-$ establishes that a reaction such as (VI) does occur. The increase in the rate of the V(IV)–Eu(II) reaction with $[SCN^-]$ is consistent with that effect.

If one ignores the existence of higher complexes of $VO^{2+}$ and $SCN^-$ at 0.94 *M* $SCN^-$ and makes use of Furman and Garner's value[21] of $K_1$ to compute $[VONCS^+]$, the second-order rate constant for the reaction of $VO(NCS)^+$ and $Eu^{2+}$ can be estimated as $1.3 \times 10^4$ $M^{-1}$ sec$^{-1}$. Lack of an accurate value of $K_1$ for $VO^{2+}$–$NCS^-$ complexation prevents a more quantitative interpretation. At 0.94 *M* $SCN^-$ the amount of $VO^{2+}$ left uncomplexed is so small that its reduction by $Eu^{2+}$ makes but a very small contribution to the observed over-all rate. The equilibrium quotient[10] $K_2$ for $V^{3+}$–$NCS^-$ is 120 $M^{-1}$, so that formation of $VNCS^{2+}$ (and higher complexes) is so complete that subsequent shifts in the equilibrium position of III are slight and thus not observed in the reaction at high $[SCN^-]$.

It cannot be asserted, however, that the effect of $SCN^-$ is due solely to pathways that have $VNCS^{2+}$ as a product. Anions may play dual roles in reactions such as this,[12] and there may be a $SCN^-$-catalyzed pathway having $V(H_2O)_6{}^{3+}$ as a product. The uncertainties connected with the $VO^{2+}$–$SCN^-$ equilibrium constant and with the effect of high $SCN^-$ concentrations on the distribution of V(III) species renders further resolution of the effect of $SCN^-$ too uncertain for pursuit at this time.

The pattern in reactions containing $HN_3$ indicates that $VN_3{}^{2+}$ is formed *via* the sequence I, III. The second-order rate constant for the first stage is $3.1 \pm 0.1 \times 10^3$ $M^{-1}$ sec$^{-1}$. The catalytic effect of $HN_3$ probably results from a process analogous to reaction VI, although a pathway in which $VN_3{}^{2+}$ is not the product cannot be rigorously excluded.

A rate enhancement was also noted at high chloride concentration despite the fact that at 0.95 *M* $Cl^-$ both $VO^{2+}$ and $Eu^{2+}$ are largely uncomplexed. The interpretation of this effect is that a reaction such as VI occurs, but that aquation of $(H_2O)_5VCl^{2+}$ is relatively rapid. The latter suggestion finds support from the very feeble stability of this complex ($K \sim 10^{-1}$ $M^{-1}$), which taken together with a second-order formation rate constant that can be estimated as $\sim 10$ $M^{-1}$ sec$^{-1}$ (assuming $V(H_2O)_6{}^{3+}$ follows a usual pattern of octahedral substitutions) gives an aquation rate constant of $10^2$ sec$^{-1}$, a value indicating that any $VCl^{2+}$ formed *via* (VI) would be essentially completely aquated before it could be detected by its light absorption at 440 nm.

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