

moment values of $3.2 \mu_B$ for these adducts suggesting octahedral symmetry. They did not succeed in isolating an adduct with 2-picoline, however, which was attributed to steric hindrance.

On the basis of this discussion, it is concluded that the diadducts formed by pyridines with nickel 8-quinolinates are hexacoordinated, giving rise to an octahedral structure. It is quite probable, in the extraction system, that nickel(II) might have formed a pentacoordinated monoadduct of pyridine with 8-quinaldine (2-methyl analogue) as observed earlier in the spectrophotometric study of nickel chelates. But since the six-coordinate structure is more stable and favorable than the pentacoordinate structure, particularly, in the weak ligand field of pyridine, nickel(II) achieves hexacoordination in the course of extraction. All these findings show that adduct formation, in general, increases the hydrophobic character of the metal chelates and enhances the extraction of a metal ion.

Registry No. NiQ₂·2(pyridine), 66700-88-7; NiQ₂·2(2-picoline), 66632-51-7; NiQ₂·2(2,4-lutidine), 66674-75-7; NiQ₂·2(2,4,6-collidine),

66632-50-6; Ni(2-methyl-Q)₂·2(pyridine), 66632-49-3; Ni(2-methyl-Q)₂·2(2-picoline), 66632-48-2; Ni(2-methyl-Q)₂·2(2,4-lutidine), 66632-64-2; Ni(2-methyl-Q)₂·2(2,4,6-collidine), 66632-63-1; Ni(4-methyl-Q)₂·2(pyridine), 66632-62-0; Ni(4-methyl-Q)₂·2(2-picoline), 66632-61-9; Ni(4-methyl-Q)₂·2(2,4-lutidine), 66632-60-8; Ni(4-methyl-Q)₂·2(2,4,6-collidine), 66632-59-5; Ni(5-chloro-Q)₂·2(pyridine), 66632-58-4; Ni(5-chloro-Q)₂·2(2-picoline), 66632-57-3; Ni(5-chloro-Q)₂·2(2,4-lutidine), 66632-56-2; Ni(5-chloro-Q)₂·2(2,4,6-collidine), 66632-55-1; Ni(5-nitro-Q)₂·2(pyridine), 66632-71-1; Ni(5-nitro-Q)₂·2(2-picoline), 66632-70-0; Ni(5-nitro-Q)₂·2(2,4-picoline), 66632-69-7; Ni(5-nitro-Q)₂·2(2,4,6-collidine), 66632-68-6.

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Kinetic Parameters for the Reactions of U(III) with Ru(NH₃)₆³⁺, Ru(NH₃)₅OH₂³⁺, and Ru(en)₃³⁺ in Trifluoromethanesulfonate Media

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The rates of the reactions between U(III) and aquopentaammineruthenium(III), hexaammineruthenium(III), and tris(ethylenediamine)ruthenium(III) are reported. In all three reactions the observed rates show a first-order dependence on each reactant. Over the acid range investigated ($[H^+] = 0.02\text{--}1.0$ M, except for Ru(en)₃³⁺ where $[H^+] = 0.1\text{--}1.0$ M), no acid dependence is observed and over the temperature range investigated (5–40 °C), no temperature dependence is observed. The reaction parameters (rate at 25 °C in M⁻¹ s⁻¹, ΔH^\ddagger in kcal/mol, ΔS^\ddagger in eu) are as follow: In 1 M HCF₃SO₃, $k = (1.11 \pm 0.33) \times 10^4$, $\Delta H^\ddagger = -0.6 \pm 1.4$, and $\Delta S^\ddagger = -38 \pm 5$ for U³⁺ + Ru(NH₃)₅OH₂³⁺; $k = (1.10 \pm 0.46) \times 10^4$, $\Delta H^\ddagger = 1.0 \pm 0.7$, and $\Delta S^\ddagger = -38 \pm 2$ for U³⁺ + Ru(NH₃)₆³⁺; in 0.1 M HCF₃SO₃, $k = 1.62 \pm 0.27 \times 10^5$, $\Delta H^\ddagger = -1.3 \pm 1.3$, and $\Delta S^\ddagger = -39 \pm 4$ for U³⁺ + Ru(en)₃³⁺. The small enthalpies of activation are rationalized in terms of the Coulombic energy and solvent reorganization energy required to form the precursor complex. Ionic strength parameters derived from the reactions of aquopentaammineruthenium(III) and hexaammineruthenium(III) with U(III) in the range $I = 0.1\text{--}2.0$ M (LiCF₃SO₃) are of the magnitudes expected for reactions between two 3+ species. Rate constants derived from perchlorate media are similar to those from trifluoromethanesulfonate media, indicating that the two anions behave similarly even for reactions between highly charged species. Starting with the Marcus cross relation and the known electron self-exchange rate for Ru(NH₃)₆^{3+/2+}, the experimental results are used to calculate self-exchange rates for the other reactants. Assuming that at $I = 1.0$ M the electron self-exchange rate for Ru(NH₃)₆^{3+/2+} is 2.1×10^4 M⁻¹ s⁻¹, the calculated electron self-exchange rates (in M⁻¹ s⁻¹) are 5.9×10^5 for U^{4+/3+}, 3.6×10^4 for Ru(en)₃^{3+/2+}, and 2.9×10^3 for Ru(NH₃)₅OH₂^{3+/2+}. The results for the ruthenium self-exchange rates agree qualitatively with those obtained from a similar calculation using the analogous Np(III)–Ru(III) reaction rates, suggesting the applicability of the Marcus cross relation to reactions that differ in ΔG° by as much as 18 kcal/mol.

Introduction

The purpose of this work is to examine the reaction between some ruthenium(III) amines and U(III) in acidic aqueous media. The results are expected to shed light on two aspects of redox kinetics. First, they should help elucidate the nature of the reductant, U(III), which is of interest because its large reduction potential makes it a potentially useful and versatile reagent. The high charge, ionic nature, large size, and *f* valence electrons of this ion distinguish it from other reductants, but its reactivity patterns have not yet been broadly characterized. Second, since the reactions are outer sphere, the Marcus theory of electron transfer can be applied and the results obtained used to gain insight into the nature of both the oxidants and reductants. An example of such insight is that derived from the reactions of Np(III) with both aquopentaammineruthenium(III) and hexaammineruthenium(III),

which have already been studied.² Applying the Marcus cross relation to the rates of these two reactions and using the known self-exchange rates of hexaammineruthenium^{3+/2+} leads to a predicted value of the self-exchange rate of aquopentaammineruthenium^{3+/2+}, a number which is difficult to obtain directly.

The actinide ion U(III) is believed to be a well-behaved ionic species in solution. It is reversibly oxidized to the 4+ state by loss of an *f* electron. The 3+ state appears to undergo insignificant hydrolysis (from spectrophotometric evidence), despite the high formal charge. The 4+ state undergoes detectable hydrolysis, but in media with $[H^+] \geq 0.1$ M, the hydrolyzed forms make up only 1–2% of the total U(IV).³ There are only a few cases of 3+ ions that can behave as reductants and in these, loss of an electron is usually accompanied by a significant structural change—such as addition

of an "yl" oxygen ligand and an overall decrease in charge; this phenomenon is generally manifested in a complicated rate law. The U(III) ion offers a unique opportunity to examine—without complications due to the addition of oxygen to the reductant—reductions by 3+ aquo ions.

The Marcus cross relation is usually used in the form⁴

$$k_{12} = (k_{11}k_{22}fK_{12})^{1/2} \quad (1)$$

where

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)}$$

k_{11} and k_{22} are the electron self-exchange rates for the oxidant and reductant, k_{12} and K_{12} are the rate and equilibrium constants, respectively, of the reaction of the oxidant with the reductant, and Z is the collision frequency, taken by Marcus to be $2.5 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C in water. When Marcus cross relation expressions for two reactions involving a common reactant are combined, the self-exchange rate of the common reactant cancels and only one of the two remaining self-exchange rates needs to be known in order to determine the other. The most important assumption made in deriving eq 1 is that inner- and outer-sphere rearrangements undergone by the reactants during the cross reaction will be similar to those undergone by each reactant during its self-exchange reaction. The fraction $1/2$ is introduced by the further assumption that the contribution of each reactant to the activation barrier of the cross reaction will be equal to its contribution to the activation barrier of its self-exchange reaction. This latter assumption is expected to break down in cross reactions with very large values of K_{12} ,⁵ but exactly how large K_{12} must be before the cross relation breaks down has not been established.

The difference in reduction potential between U(III) and Np(III) is almost 0.8 V or 18 kcal/mol.⁶ Whether or not the predictions made using eq 1 and the U(III)–Ru(III) reaction rates agree with those made using the Np(III)–Ru(III) reaction rates will shed some light on the question of the limitation(s) imposed on the Marcus cross relation by the magnitude of K_{12} .

Experimental Section

Standard Reagents. Unless otherwise specified, all chemicals were Fisher Certified or Baker Analyzed reagent grade. Water was distilled a second time from alkaline permanganate. Perchloric acid solutions were prepared from G. F. Smith doubly vacuum distilled perchloric acid. Lithium perchlorate solutions were prepared from lithium carbonate and perchloric acid. The salt so formed was recrystallized twice from water. The preparation of the trifluoromethanesulfonic acid and the amalgamated zinc were described previously.⁷ Standard lithium trifluoromethanesulfonate was prepared from weighed lithium carbonate and trifluoromethanesulfonic acid and standardized by gravimetric determination of the tetraphenylarsonium salt.

Ruthenium(III) Salts. The tris(ethylenediamine)ruthenium(III) complex was prepared as described previously:⁷ spectral data λ_{max} 310.0 nm, ϵ 320 $\text{M}^{-1} \text{ cm}^{-1}$. **Caution!** An attempt to isolate the perchlorate salt of this complex resulted in an explosion.

Hexaammineruthenium(III) trifluoromethanesulfonate was prepared by literature methods² and recrystallized from 0.4 M HCF_3SO_3 ; spectral data λ_{max} 280 nm, ϵ 470 $\text{M}^{-1} \text{ cm}^{-1}$. Aquopentaammineruthenium(III) trifluoromethanesulfonate was prepared as described in the literature;² spectral data λ_{max} 270 nm, ϵ 760 $\text{M}^{-1} \text{ cm}^{-1}$.

Uranium(III). Stock solutions of U(VI) were prepared from uranium oxide, red (UO_3) (Alfa Ventron), which was dissolved in 6 equiv of acid so that the solutions would contain no excess acid when reduced to U(III). Reactant solutions were prepared by diluting aliquots of the stock with appropriate amounts of acid, lithium solutions, and water and deaerating for 20 min before adding zinc amalgam. Reduction to U(III) was essentially complete after 30 min, as judged from the visible absorption spectrum.

Procedures. The inert-gas line, flasks, gastight syringes, and Teflon needles used in this work have been described previously.⁷

Measurements on air-sensitive solutions utilizing a Cary 14 spectrophotometer were done in specially designed cells as described by Newton and Baker.⁸ Cell contents were homogenized within 5 s by magnetic stirring. Rapid reactions were monitored in a Durrum-Gibson stopped-flow spectrophotometer, and oscilloscope traces were recorded on film.

The temperature of the Cary 14 cell compartment was maintained within 0.1 °C with a Haake Model FK-2 circulating bath. A Lauda-Brinkmann Model K-2R circulating bath was used to regulate temperature for the stopped-flow apparatus. For determinations at 25 °C, the Kel-F valve block was allowed to equilibrate for at least 90 min. For determinations at other temperatures, 4 h of equilibration was allowed. At 5 and 40 °C, temperature regulation was only ± 2 °C.

In handling U(III) in the stopped-flow apparatus, it was necessary to flush the flow system several times with deaerated solutions to remove oxygen present in the liquid films that adhere to the surfaces of the syringes and flow system. Rinsing was continued until no transmittance change occurred at wavelengths diagnostic for U(III). Solutions of $1 \times 10^{-4} \text{ M U(III)}$ held in the drive syringes for 30 min decomposed about 15%. Decomposition of solutions of $1 \times 10^{-4} \text{ M U(III)}$ held in the reaction cuvette, however, indicated that oxygen leaks into the cuvette at the rate of 1×10^{-6} mequiv/(mL s). This rate of leakage is insignificant on the time scale of the U(III)–Ru(III) reactions. From the transmittance increase observed when U(III) and "deaerated" 0.1 M HClO_4 are mixed, it is estimated that about 2.7×10^{-6} equiv/L of molecular oxygen remains in deaerated solutions that have been introduced into the drive syringes. By monitoring the reaction of U(III) with air-saturated 0.1 M HClO_4 , an estimate of $8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was made for the rate of reaction between U(III) and O_2 at 25 °C. From this rate constant, the contribution made by $2.7 \times 10^{-6} \text{ M O}_2$ to the observed rate of reaction between U(III) and Ru(III) was estimated to be $\leq 5\%$. This is within the uncertainty limits associated with the rate constants of the U(III)–Ru(III) reactions. The U(III) was usually the limiting reagent, thereby avoiding drift in T_∞ . Unless otherwise noted, the reactions were monitored at 350 nm, where large values of $\Delta\epsilon$ produced large transmittance changes even under dilute concentration. The U(III) absorbs strongly ($\Delta\epsilon \geq 1600 \text{ M}^{-1} \text{ cm}^{-1}$) throughout the UV region of the spectrum. The small value of $\Delta\epsilon$ for the ruthenium reactants and the necessity of dealing with the O_2 impurity makes it impossible to work under conditions where the ruthenium could be monitored. Experiments following the change in transmittance at 520 nm (another U(III) maximum), however, indicate no wavelength dependence. The average rate constants, k_{obsd} , reported are the average of two or more independent determinations. An independent determination in this work, k_{obsd} , is itself the average of two to eight determinations made by the combination of a particular U(III) and Ru(III) solution and including at least two different fillings of the reservoir syringes.

Calculations. All reaction parameters were determined using a CDC 6400 digital computer and the Los Alamos Scientific Laboratory nonlinear least-squares program⁹ with necessary subroutines. The general procedure is to fit an equation of the form $Y = f(z, p_1, p_2, \dots, p_n)$, where Y is the experimental observable, z is the independent variable, and p_1 – p_n are parameters whose values are adjusted by minimizing the sum $(Y_{i\text{obsd}} - Y_{i\text{calcd}})^2$. The specific forms of the function f used in this work are given below.

The integrated form of rate law for a second-order reaction (first order in each reactant) is

$$\ln \left[\frac{B_0 - A_0 + xA_0}{xB_0} \right] = (B_0 - A_0)kt \quad (2)$$

where A is the limiting reagent, A_0 and B_0 are the initial concentrations of the two reactants, and $x = [A]/A_0$. Solving for x yields

$$x = \frac{A_0 - B_0}{A_0 - B_0(\exp((B_0 - A_0)kt))} \quad (3)$$

The experimental observable is the transmittance T :

$$x = \frac{\log T - \log T_\infty}{\log T_0 - \log T_\infty} \quad (4)$$

Then $T = T_\infty(T_0/T_\infty)^x$, where x is given by eq 3. The initial concentration of U(III) (the limiting reagent) is variable because of its

reactivity toward O₂. The expression for A₀ in eq 2 is therefore replaced by

$$A_0 = (1/\Delta\epsilon) \log (T_\infty/T_0) \quad (5)$$

where for 1:1 stoichiometry $\Delta\epsilon$ is the difference in molar absorptivities between the reactants and the products. The adjustable parameters were taken as T_∞, T₀, and the second-order rate constant *k*.

The equation used for the calculation of the ionic strength dependence is

$$k = k_0 \exp \left(\frac{2AZ_a Z_b(I)^{1/2}}{1 + Ba(I)^{1/2}} + \gamma I \right) \quad (6)$$

where *k*₀, *a*⁰, and γ are adjustable parameters, the ionic strength *I* is the independent variable, and *A* and *B* are constants depending only on the solvent, with values at 25 °C of 0.512 M^{-1/2} and 32.91 Å⁻¹ M^{-1/2}, respectively.¹⁰

The Eyring activation parameters were determined using the equation

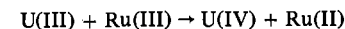
$$k = \frac{k_b T}{h} \exp \left[\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \right] \quad (7)$$

ΔH^\ddagger and ΔS^\ddagger are the adjustable parameters, *k*_b/*h* = 2.085 × 10¹⁰, *R* = 1.9871 cal deg⁻¹ mol⁻¹, and temperature is the independent variable.

Results and Discussion

Stoichiometry. The stoichiometry was determined using the Cary 14 spectrophotometer and specially designed cells whose contents can be magnetically stirred. Ru(III), which was added last, was the limiting reagent. Under these conditions, for 1:1 stoichiometry, the experimentally determined value of the change in molar absorptivity, $\Delta\epsilon$, is (OD_i - OD_∞)/*C*_i, where *C*_i is the initial concentration of the Ru(III) reactant. U(III) is the only species which contributes to OD_i. The values of $\Delta\epsilon$ (=ε_{U(III)} - ε_{Ru(III)}) determined from the individual molar absorptivities, and those obtained directly, are (in M⁻¹ cm⁻¹) respectively, for Ru(NH₃)₅OH₂³⁺, 1530 and 1501 ± 30, for Ru(NH₃)₆³⁺, 1504 and 1482 ± 111, and for Ru(en)₃³⁺, 1460 and 1475 ± 24. The agreement between the calculated and observed values indicates 1:1 stoichiometry.

No spectrophotometric evidence was obtained to verify ruthenium(II) as the product. It was also impossible to verify the stoichiometry of the [Ru(NH₃)_n(H₂O)_{6-n}]³⁺ + U³⁺ reactions (*n* = 5, 6) in perchlorate media, since in this case U(III) was rapidly consumed by the products of the ClO₄⁻ + Ru(II) reaction.¹¹



Kinetics. The reactant dependence was examined extensively in 0.1 M HCF₃SO₃. The ratio of initial concentrations, [Ru(III)]_i/[U(III)]_i, varied from 40 to 1 for the aquopentaamine- and tris(ethylenediamine)ruthenium(III) complexes and from 20 to 0.3 for the hexaammineruthenium(III) complex. The initial U(III) concentrations were in the range (0.5–20) × 10⁻⁴ M in the study of the aquopentaamine and hexaammineruthenium(III) complexes and (0.5–5) × 10⁻⁴ M for the tris(ethylenediamine)ruthenium(III) complex. The rate curves were adequately described in all cases by a rate law first order in each reactant. The least-squares estimates of the second-order rate constant showed no variation attributable to the absolute concentration of either reactant or the ratios of concentration. The rate constants, \bar{k}_{obsd} , obtained under a variety of conditions are summarized in Table I.

Specific features to be noted are as follow: (1) no acid dependence is observed for any of the reactions in the range [H⁺] = 0.1–1.0 M; (2) the rate constants are not significantly

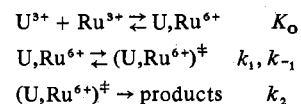
Table I. Summary of Observed Rates^a for the Reactions U(III) + Ru(III) → U(IV) + Ru(II)

[H ⁺], M	<i>I</i> , M	<i>T</i> , °C	10 ⁻⁴ \bar{k}_{obsd} or 10 ⁻⁴ <i>k</i> _{obsd} , M ⁻¹ s ⁻¹		
			Ru(NH ₃) ₅ OH ₂ ³⁺	Ru(NH ₃) ₆ ³⁺	Ru(en) ₃ ³⁺
CF ₃ SO ₃ ⁻ Medium					
0.1	0.1	6	1.11 ± 0.11 (2)	2.38 ± 0.21 (3)	17.1 ± 0.6 (8) ^b
		25	1.15 ± 0.11 (20)	2.29 ± 0.27 (9)	16.3 ± 2.8 (20)
		40	1.13 ± 0.04 (4) ^b	2.11 ± 0.12 (2)	15.6 ± 0.5 (8) ^b
1.0	1.0	6	8.21 ± 0.52 (6) ^b	19.5 ± 3.1 (5) ^b	81.8 ± 8.5 (8) ^b
		25	7.70 ± 0.46 (5)	15.0 ± 1.1 (1) ^b	84 ± 11 (6) ^b
		40	10.3 ± 1.0 (4) ^b	16.4 ± 1.1 (2)	80.7 ± 9.8 (8) ^b
0.1	1.0	25	8.44 ± 1.11 (2)	15.7 ± 0.84 (2)	88.3 ± 6.2 (3) ^b
ClO ₄ ⁻ Medium					
0.1	0.1	6	1.79 ± 0.05 (8) ^b	4.13 ± 0.06 (2) ^b	
		25	1.75 ± 0.10 (3)	3.28 ± 0.15 (3)	
		40	1.74 ± 0.10 (2)	3.26 ± 0.04 (2)	
1.0	1.0	6	11.6 ± 0.5 (4) ^b		
		25	11.11 ± 0.3 (3)		
		40	13.8 ± 0.3 (6) ^b		
0.1	1.0	25	10.4 ± 0.3 (2)		

^a The uncertainty is the standard deviation of the *n* determinations from which the average is calculated. Unless noted otherwise, the *n* determinations are independent (\bar{k}_{obsd}). ^b Calculated from *n* dependent determinations (*k*_{obsd}).

temperature dependent in the range 5–40 °C; and (3) at constant ionic strength, changing from CF₃SO₃⁻ to ClO₄⁻ media increases the rate constant by less than a factor of 2. Second-order rate constants have been reported by Adegite et al.¹² for the reactions of U(III) with Ru(NH₃)₆³⁺ and Ru(NH₃)₅OH₂³⁺ under conditions similar to ours (*I* = 0.25 M, HClO₄, 25 °C, [U(III)]_i = (1–2) × 10⁻⁵ M, [Ru(III)]_i = (1–3) × 10⁻⁴ M). They also found no acid dependence for these reactions in the range [H⁺] = 0.1–0.25, but the second-order rate constants they report are 1 × 10⁵ M⁻¹ s⁻¹ (U³⁺ + Ru(NH₃)₆³⁺) and 1.6 × 10⁵ M⁻¹ s⁻¹ (U³⁺ + Ru(NH₃)₅OH₂³⁺) which are much higher than those we obtain. Our value for the aquopentaammineruthenium(III) complex in 0.1 M HClO₄, *I* = 0.25, is 3.46 × 10⁴ M⁻¹ s⁻¹ and for the hexaammineruthenium(III) reaction in 0.1 M HCF₃SO₃, *I* = 0.25, it is 4.66 × 10⁴ M⁻¹ s⁻¹, which is expected to be about a factor of 2 lower than in ClO₄⁻ media. Our spectral data for the aquopentaammineruthenium(III) complex agree with those reported by Adegite; hence, the cause of the discrepancy is not apparent. It should be noted, however, that since their initial concentrations of U(III) were a factor of 4–10 times lower than ours, reaction of U(III) with oxidizing impurities or molecular oxygen would be more significant in their system. For the aquopentaammineruthenium(III)–U(III) reaction, they mention contamination of the [Ru(NH₃)₅OH₂](ClO₄)₃ salt with the pentaamminechloro complex. Our starting material was the CF₃SO₃⁻ salt and it is likely that this material is of superior purity.

Activation parameters obtained for the title reactions are summarized in Table II. All enthalpies of activation are within 2 kcal/mol of zero, indicating that the reaction barrier is primarily entropic in nature. Small and even negative enthalpies of activation have been observed by other workers. In the U(III)–Ru(III) cases, because of the large formal charges on the reactants and activated complexes, it is possible to rationalize the magnitudes of the activation enthalpies in terms of the outer-sphere association constant *K*_o in the scheme¹³



A method for calculating *K*_o has been suggested by Hyde and

Table II. Activation Parameters for Reactions between U(III) and the Ruthenium(III) Amine Complexes^a

Ru reactant	medium	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol deg)	% dev ^c	n_k^d
Ru(NH ₃) ₆ ³⁺	0.1 M HCF ₃ SO ₃	-0.9 ± 0.3	-41 ± 1	14.7	15
Ru(NH ₃) ₆ ³⁺	1.0 M HCF ₃ SO ₃	-0.9 ± 0.7	-38 ± 2	6	4
Ru(NH ₃) ₆ ³⁺	0.1 M HClO ₄	-1.9 ± 0.2	-44.0 ± 0.6	3.5	6
Ru(NH ₃) ₅ OH ₂ ³⁺	0.1 M HCF ₃ SO ₃	0.3 ± 1.0	-39 ± 3	0.6	26
Ru(NH ₃) ₅ OH ₂ ³⁺	1.0 M HCF ₃ SO ₃	-0.6 ± 1.4	-38 ± 5	30.7	7
Ru(NH ₃) ₅ OH ₂ ³⁺	0.1 M HClO ₄	-0.6 ± 0.3	-41.2 ± 1.1	8.5	6
Ru(NH ₃) ₅ OH ₂ ³⁺	1.0 M HClO ₄	0.75 ± 0.82	-33 ± 3	31.3	5
Ru(en) ₃ ³⁺	0.1 M HCF ₃ SO ₃	-1.3 ± 1	-39 ± 4	29	22
Ru(en) ₃ ³⁺	1.0 M HCF ₃ SO ₃	0 ^b	-31.4 ± 0.1	1.1	3

^a The data used in these calculations are given in Table I. ^b Fixed. ^c Average difference between experimental values of k and those calculated using these activation parameters. ^d Number of values of the rate constant used in determining the activation parameters.

Table III. Variation of Rate Constant with Ionic Strength for the Reactions Ru(III) + U(III) \rightleftharpoons Ru(II) + U(IV)^a

I, M	RuA ₆ ³⁺ , CF ₃ SO ₃ ⁻		RuA ₅ H ₂ O ³⁺ , CF ₃ SO ₃ ⁻		RuA ₅ H ₂ O ³⁺ , ClO ₄ ⁻	
	10 ⁻⁴ k_{obsd}	10 ⁻⁴ k_{calcd}^b	10 ⁻⁴ k_{obsd}	10 ⁻⁴ k_{calcd}^c	10 ⁻⁴ k_{obsd}	10 ⁻⁴ k_{calcd}^d
0.1	2.04 ± 0.06	2.18 ± 0.09	1.06 ± 0.02	0.89 ± 0.12	1.63 ± 0.07	1.62 ± 0.05
0.175	3.43 ± 0.12	3.47 ± 0.10	1.81 ± 0.05	1.54 ± 0.15	2.59 ± 0.05	2.58 ± 0.06
0.250	4.66 ± 0.27	4.66 ± 0.10	2.44 ± 0.06	2.20 ± 0.15	3.46 ± 0.04	3.47 ± 0.06
0.375	6.63 ± 0.03	6.53 ± 0.09	3.24 ± 0.04	3.27 ± 0.15	4.66 ± 0.04	4.78 ± 0.05
0.50	8.51 ± 0.07	8.31 ± 0.09	4.18 ± 0.12	4.29 ± 0.13	6.04 ± 0.13	5.99 ± 0.05
0.75	11.65 ± 0.30	11.77 ± 0.10	5.96 ± 0.06	6.25 ± 0.15	8.11 ± 0.001	8.12 ± 0.06
1.0	15.2 ± 0.02	15.26 ± 0.12	7.70 ± 0.46	8.09 ± 0.18	10.2 ± 0.1	10.01 ± 0.07
1.5	22.9 ± 0.8	22.80 ± 0.13	2.27 ± 0.08	14.55 ± 0.19	13.2 ± 0.1	13.39 ± 0.06
2.0	31.5 ± 0.4	31.55 ± 0.26	4.56 ± 0.13	14.84 ± 0.27	16.5 ± 0.3	16.48 ± 0.10

^a Conditions: $T = 25^\circ\text{C}$, $[\text{H}^+] = 0.1\text{ M}$. ^b Calculated from the least-squares values of the parameters: $k_0 = 820 \pm 76$, $a = 10.24 \pm 0.33$, $\gamma = 0.164 \pm 0.012$. ^c Calculated from the least-squares values of the parameters: $k_0 = 237 \pm 62$, $a = 8.23 \pm 0.71$, $\gamma = 0.051 \pm 0.038$. ^d Calculated from the least-squares values of the parameters: $k_0 = 570 \pm 38$, $a = 9.71 \pm 0.23$, $\gamma = 0.052 \pm 0.009$.

Sykes¹⁴ for cases in which both reactants are positively charged. They used a modified form of an equation developed by Fuoss¹⁵ to obtain the expressions

$$\Delta H_0 = -(0.47 \pm 0.11)Z_1Z_2 \text{ kcal/mol}$$

$$\Delta S_0 = -2.3 - (3.65 \pm 0.35)Z_1Z_2 \text{ cal/(deg mol)}$$

for the conditions $T = 25^\circ\text{C}$, $I = 0-0.5\text{ M}$, and an internuclear distance of 5 Å. These equations attempt to include contributions made by the solvent as the outer-sphere complex forms. For positively charged reactants both the enthalpy and entropy term will be negative; in the case of $Z_1 = Z_2 = +3$, $\Delta H_0 = -4.23 \pm 0.99$ kcal/mol and $\Delta S_0 = -35.1 \pm 3.1$ cal/(mol deg) (if a 5-Å separation is again assumed). The negative activation energies obtained for the U(III)-Ru(III) systems are about -2 kcal/mol, which is of the same magnitude as the calculated value. This suggests that the enthalpy of formation of the outer-sphere complex makes a highly significant contribution to the overall enthalpy of activation and that once it is formed the subsequent reaction does not encounter significant enthalpic barriers. This is consistent with the intuitive notion that no large enthalpic barrier to electron transfer is expected since (1) neither reactant undergoes structural changes in forming the corresponding product and (2) no spin change is involved in going from reactants to products.

The data pertinent to the calculation of the ionic strength dependence are given in Table III. For both CF₃SO₃⁻ and ClO₄⁻ media, the values of a° and γ are within the range of those observed by Newton¹⁶ for reactions involving at least one actinide ion. Although less popular for kinetic experiments than perchlorate ion, the trifluoromethanesulfonate ion is likely a more versatile anion since, besides being noncomplexing, it is thermodynamically a poor oxidizing agent. An examination of the ionic strength parameters for Ru(NH₃)₅H₂O³⁺ affords a quantitative comparison of the two anions. At high ionic strength, the rate of change of the observed rate constant with μ is the same, as shown by the values of the empirical factor γ which are essentially the same. The values of a° are both within the range observed¹⁶ for electron-transfer reactions;

although this parameter has units of length, it cannot literally be taken as the mean distance of approach; in reactions of high (>0.2 M) ionic strength its physical significance is unclear. The parameter k_0 , the rate extrapolated to zero ionic strength, should have some physical significance. It would be expected that the rate of reaction would extrapolate to the same k_0 value. Such behavior is commonly observed for electron-transfer reactions studied in both lithium and sodium perchlorate solutions. However, in these cases, since the variable species (Li⁺ or Na⁺) is positively charged, it is probable that its association with the reactants and activated complex is negligible. In the present case, the high positive charge of the activated complex almost certainly requires the association of one or more anions in order to reduce the electrostatic barrier, and equal values of k_0 would not necessarily be expected.

The general similarity of the two media is also suggested by the activation parameters. While the enthalpy of activation generally reflects the faster rate in the perchlorate medium, the similarity of the entropies of activation at a given ionic strength disallows any significant difference in the net activation process as the anion is changed from perchlorate to trifluoromethylsulfonate. The results of this study therefore emphasize the similarities and utility of trifluoromethanesulfonate as innocent anions in electron-transfer reactions between cations.¹⁷ Quite likely, kinetic results obtained in a trifluoromethylsulfonate medium can be compared directly with results obtained in a perchlorate medium, without making any allowance for the difference in anion.

Calculations Using the Marcus Cross Relation. The parameters obtained for these reactions closely resemble those of the corresponding Np(III) reactions (Table IV) in that none shows an acid dependence and all have small enthalpies of activation. Also, for both sets, the rates increase in the same order, $k_{\text{Ru(NH}_3)_5\text{OH}_2} < k_{\text{Ru(NH}_3)_6} < k_{\text{Ru(en)}_3}$, which is not the order of increasing thermodynamic potential,^{2,7} $K_{\text{Ru(NH}_3)_6} < K_{\text{Ru(NH}_3)_5\text{OH}_2} < K_{\text{Ru(en)}_3}$. Assuming that the Marcus cross relation is applicable, this last result indicates that the self-exchange rate of the aquopentaammineruthenium complex is less than that of the hexaammineruthenium complex.

Table IV. Comparison of U(III) and Np(III) Reaction Parameters^a

	U(III)	Np(III)
	Ru(NH ₃) ₅ OH ₂ ³⁺	
$k(25^\circ\text{C}), \text{M}^{-1} \text{s}^{-1}$	$(7.70 \pm 0.46) \times 10^4$	0.27 ± 0.19
$\Delta H^\ddagger, \text{kcal/mol}$	-0.60 ± 1	4.2 ± 0.3
$\Delta S^\ddagger, \text{cal/(mol deg)}$	-38.2 ± 5	-46.9 ± 0.9
rel k_{ex}^e	$0.406^c/0.138^d$	0.12
	Ru(NH ₃) ₆ ³⁺	
$k(25^\circ\text{C}), \text{M}^{-1} \text{s}^{-1}$	$(15.0 \pm 1.1) \times 10^4$	0.305 ± 0.036^b
$\Delta H^\ddagger, \text{kcal/mol}$	-0.90 ± 0.69	3.9 ± 1.0^b
$\Delta S^\ddagger, \text{cal/(mol deg)}$	-37.7 ± 2.2	-48.1 ± 3.5^b
	Ru(en) ₃ ³⁺	
$k(25^\circ\text{C}), \text{M}^{-1} \text{s}^{-1}$	$(84 \pm 11) \times 10^4$	8.49 ± 0.10
$\Delta H^\ddagger, \text{kcal/mol}$	0	1.41 ± 0.18
$\Delta S^\ddagger, \text{cal/(mol deg)}$	-31.4 ± 0.1	-49.5 ± 0.6
rel k_{ex}^e	$2.56^c/1.73^d$	5

^a In 1.0 M HCF₃SO₃, unless noted otherwise. ^b In 0.5 M HCF₃SO₃. ^c Using $10 \text{ M}^{-1} \text{ s}^{-1}$ for k_{ex}^{U} . ^d Using $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for k_{ex}^{U} . ^e $k_{\text{ex}}^{\text{Ru}^{3+/2+}}/k_{\text{ex}}^{\text{Ru}(\text{NH}_3)_6^{3+/2+}}$, where k_{ex} is the electron-transfer rate for self-exchange.

Using the Marcus cross relation, eq 1, and the rates of the analogous Np(III)-Ru(III) reactions (in which K_{eq} is close to unity), we previously calculated⁷ values for the electron self-exchange rates of Ru(NH₃)₅H₂O^{3+/2+} and Ru(en)₃^{3+/2+} relative to that of Ru(NH₃)₆^{3+/2+}. It is of interest to determine whether or not the estimates of Ru^{2+/3+} self-exchange rates made from the Np(III)-Ru(III) reaction rates⁷ agree with those that can be made from the U(III)-Ru(III) reaction rates, where the driving force is much larger. The following expression may be derived from the Marcus cross relation:

$$k_{\text{ex}}^{\text{Ru}} = k_{\text{ex}}^{\text{RuA}_6} \left(\frac{k^2_{\text{U-Ru}}}{k^2_{\text{U-RuA}_6}} \right) \left(\frac{f_{\text{U-RuA}_6}}{f_{\text{U-Ru}}} \right) \left(\frac{Q_{\text{U-RuA}_6}}{Q_{\text{U-Ru}}} \right) \quad (8)$$

The value for $k_{\text{ex}}^{\text{RuA}_6}$ is taken from Meyer and Taube,¹⁸ corrected for ionic strength.⁷ The calculation was performed twice using values for k_{ex}^{U} of 10^{-4} and $10 \text{ M}^{-1} \text{ s}^{-1}$ in order to determine whether or not the choice of k_{ex}^{U} significantly alters the results. As seen in Table IV, regardless of the choice of k_{ex}^{U} , the values calculated from U(III)-Ru(III) data show the same trend as those calculated from the Np(III)-Ru(III) data—namely, these data predict that the self-exchange rate for Ru(en)₃^{3+/2+} will be faster than that for Ru(NH₃)₆^{2+/3+}.

Sutin et al. have recently¹⁷ pointed out that exchange reaction rates obtained from the Marcus cross relation are likely to be much less accurate than cross reaction rates. As an example, they calculate exchange rates (in $\text{M}^{-1} \text{ s}^{-1}$) for Eu^{2+/3+} ranging from 9×10^{-4} to 1.6×10^{-8} for reactions ranging in overall free energy from 4.38 to 18.45 kcal/mol. In our reactions, the free energy of the U³⁺-Ru(en)₃³⁺ reaction is 18.4 kcal/mol and that of the analogous Np³⁺ reaction is 0.28 kcal/mol. The fact that the exchange rates of the ruthenium complexes calculated from these data are quite similar (differing only by factors of 2 or 3) suggests that differences in the nature of the oxidants rather than just differences in free energy may be responsible for the variable values calculated¹⁷ for the Eu^{2+/3+} self-exchange rate.

The U^{4+/3+} exchange rate k_{ex}^{U} has recently been reported¹⁹ to be $1.61 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 0.25 \text{ M}$. This value was obtained by extrapolation of a plot of $\log k_{12} - 0.5(\log k_{22} + \log f)$ vs. $\log K_{12}$.¹⁹ All reactions used in this plot are not established as outer-sphere reactions and all values used were not corrected to the same ionic strength. Also, the slope of such a plot should be 0.5⁴ but instead is 0.3.¹⁹ Hence, the value of k_{ex}^{U} ($=1.61 \text{ M}^{-1} \text{ s}^{-1}$) derived by extrapolation to $\log K_{12} = 0$ is highly questionable. Other workers²⁰ have assumed that the self-exchange rates of the actinide 3+/4+ couples of U, Np, and

Pu are similar and have used Keenan's²¹ experimentally determined value for the Pu^{3+/4+} self-exchange rate (in $\text{M}^{-1} \text{ s}^{-1}$: 22 ± 88 at 25°C , 380 ± 80 at 12.5°C , and 180 ± 70 at 0°C , all at $I = 1.0 \text{ M}$) as an estimate of the U^{3+/4+} self-exchange rate. However, Keenan's values were obtained under difficult experimental conditions where the major path was inversely dependent on the acid concentration. We have chosen to calculate a value of k_{ex}^{U} from the U³⁺-Ru(NH₃)₆³⁺ reaction rate, the Ru(NH₃)₆^{3+/2+} electron self-exchange rate, and the Marcus cross relation, using an iterative procedure¹⁷ to obtain a value for $f_{\text{U-Ru}}$ which contains k_{ex}^{U} :

$$k_{\text{ex}}^{\text{U}} = \frac{k^2_{\text{U-Ru}}}{k_{\text{ex}}^{\text{Ru}} f_{\text{U-Ru}} Q_{\text{U-Ru}}} \quad (9)$$

To perform the calculation at $I = 1.0 \text{ M}$ requires an estimate of $k_{\text{ex}}^{\text{Ru}}$ at this ionic strength. The reported values¹⁸ are $840 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 0.013 \text{ M}$ and $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 0.16 \text{ M}$. Extrapolating each of these values (using eq 6 with values of 7 Å and 0.13 M⁻¹ as estimates of a° and γ respectively) and averaging resulting values yield an estimate of $k_{\text{ex}}^{\text{Ru}}$ (Ru(NH₃)₆^{3+/2+}) = $2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 1.0 \text{ M}$. Using the rate and equilibrium²⁶ parameters associated with the U³⁺-Ru(NH₃)₆³⁺ reaction ($k_{12} = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $K_{12} = 6.22 \times 10^{11}$), the calculation results in a value for k_{ex}^{U} of $5.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ($f = 0.03$) at $I = 1.0 \text{ M}$. This value is 10^4 times lower than that obtained by the graphical¹⁹ method. For the sake of comparison, the calculation was also made for the Np³⁺/Np⁴⁺ self-exchange rate from the rate of the Np³⁺-Ru(NH₃)₆³⁺ reaction ($k_{12} = 0.55 \text{ M}^{-1} \text{ s}^{-1}$ at 1.0 M ionic strength⁷). In this case, the f term is approximately unity. The calculated value for the Np³⁺/Np⁴⁺ exchange rate is $4.6 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. This is close to our calculated U^{3+/4+} self-exchange rate, a similarity which is consistent with the assumption that the 3+/4+ exchange rates of U, Np, and Pu are similar.²⁰ These low values can be rationalized in terms of the heavily shielded environment of f electrons and are also closer in value to the self-exchange rate of Eu^{2+/3+} of $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 39°C estimated by Sutin.¹⁷ We therefore believe that our value $k_{\text{ex}}^{\text{U}} \approx 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ is a better approximation than those obtained previously.^{19,20}

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Registry No. Ru(NH₃)₅OH₂³⁺, 25590-52-7; Ru(en)₃³⁺, 21393-87-3; Ru(NH₃)₆³⁺, 18943-33-4; U³⁺, 22578-81-0; Np³⁺, 21377-65-1.

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Photosolvolysis of *trans*-Tetrathiocyanatodiamminechromium(III) and *trans*-Dithiocyanatobis(ethylenediamine)chromium(III) Ions: Nucleophilicity and Solvent Orientation¹

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Photorelease of thiocyanate from two similar complexes which differ with respect to sign of charge, *trans*-[Cr(NCS)₄(NH₃)₂]⁻ and *trans*-[Cr(en)₂(NCS)₂]⁺, has been studied in several solvents: H₂O, Me₂SO, DMF, CH₃CN, CH₃NO₂, and H₂O-glycerol. The quantum yield for reaction of the cation is a linear function of the Guttmann donor number of the solvent, supporting the associative mechanism for photosubstitution at Cr(III) which has been suggested on the basis of stereochemistry. But attack on a very short-lived species is indicated by the fact that reaction of the otherwise similar anion correlates only with solvent fluidity (inverse viscosity). This suggests that only solvent molecules which are correctly oriented toward the center can achieve nucleophilic attack. In this context, the lack of temperature dependence in a reaction of the cation is significant. This photonucleophilic attack is not an activated process analogous to thermal nucleophilic attack. The role of a good nucleophile appears to be to select the reactive relaxation channel.

Introduction

The suggestion has been made, primarily on the basis of stereochemistry, that the well-known³ photosubstitution reactions of six-coordinate Cr(III) complexes are *associative*.⁴ Only one publication so far has reported measurements of the relative reactivity of different nucleophiles toward a Cr(III) center.⁵ This question, photonucleophilicity, is interesting because important differences from nucleophilicity in thermal reactions may arise. A nucleophile in a thermal reaction lowers the barrier for substitution by stabilization of the transition state through new bond formation. A nucleophile in a photoreaction may be involved with an excited state which is at an energy well above the thermal substitution barrier. In that case, it may play a role in selection of a relaxation channel rather than in lowering a barrier.

In this paper, we examined two compounds similar to two examined in several solvent mixtures by Wong and Kirk.⁴ In their studies, quantitative comparison of solvent nucleophilicities could not be accomplished because of complications with preferential solvation and steric effects. The complexities of preferential solvation in CH₃CN-H₂O mixtures and alcohol-water mixtures are known with respect to Cr(III) complexes.⁶ We have chosen single solvent systems for most of these studies and sought a wide range of probable solvent nucleophilicity. The limit on the range was finally imposed by complex salt solubilities. The reaction monitored is thiocyanate release which has been observed as a consequence of irradiation of the first quartet ligand field band of the complexes.^{7,8}

Experimental Section

Materials. K[Cr(NH₃)₂(NCS)₄] was obtained from the ammonium salt by reprecipitation with potassium nitrate⁹ and twice recrystallized from warm water. *trans*-[Cr(en)₂(NCS)₂]Cl was prepared from Cr(en)₃(NCS)₃ according to the method reported in the literature.¹⁰ *trans*-[Cr(en)₂(NCS)₂]ClO₄ for use in CH₃CN and *trans*-[Cr(en)₂(NCS)₂]BPh₄ for use in CH₃NO₂ were obtained with HClO₄ and sodium tetraphenylboride, respectively. The solvents were all reagent grade and were used without further purification.

Table I. Extinction Coefficient Values of the Iron(III) Thiocyanate Species in Different Water-Solvent Mixtures

solvent	ϵ , M ⁻¹ cm ⁻¹	λ , nm
H ₂ O ^a	4.3×10^3	450
20% CH ₃ CN/80% H ₂ O	4.1×10^3	450
20% CH ₃ NO/30% CH ₃ OH	3.1×10^3	510
20% DMF/80% H ₂ O	2.3×10^3	510
20% Me ₂ SO/80% H ₂ O	2.1×10^3	510

^a This value also applies to water-glycerol mixtures.

Table II. Quantum Yields for Photosolvolysis of [Cr(NH₃)₂(NCS)₄]⁻ and *trans*-[Cr(en)₂(NCS)₂]⁺

solvent	[Cr(NH ₃) ₂ (NCS) ₄] ⁻ ϕ	[Cr(en) ₂ (NCS) ₂] ⁺ ϕ	η , ^b cP	DN ^c
H ₂ O	0.311 ± 0.003^a	0.152 ± 0.002	8.93	33
Me ₂ SO	0.135 ± 0.002	0.141 ± 0.001	19.8	29.8
DMF	0.184 ± 0.002	0.120 ± 0.006	7.96	26.6
CH ₃ CN	0.257 ± 0.001	0.061 ± 0.003	3.45	14.1
CH ₃ NO ₂	0.216 ± 0.002	0.021 ± 0.003	6.08	2.7

^a Value from ref 9. ^b Value from ref 12. ^c DN = donor number. Value from ref 11.

Photolyses. The solutions to be photolyzed were made up just prior to use and were irradiated for 15–40 min in a 5-cm quartz vessel. The light source was a xenon lamp; the irradiation wavelength was 465 nm and was selected by means of a Jarrel-Ash 1/4-m grating monochromator. The intensity of the light before and after irradiation was measured by Reineckate actinometry.⁹ In order to avoid interference by the products, the extent of the photosolvolysis never exceeded 4%. The quantum yields were determined by spectrophotometric analysis of the released SCN⁻ as the complex "Fe(SCN)²⁺" in aqueous perchloric acid. Aliquots of the reacting solution were withdrawn and diluted by a factor of 5 with the analytical solution. A value of 4.3×10^3 M⁻¹ for the extinction coefficient of Fe(SCN)²⁺ in water at 450 nm was used. The analytical system was calibrated in each of the nonaqueous solvents with standard thiocyanate solutions at 510 nm. At this wavelength the complex Fe(SCN)²⁺ was the only absorbing species in the mixture and the calibration curve was linear. When the solvent was nitromethane, the aliquot of solution to be examined had to be made 30% in methanol in order to make