

Relaxation Spectra of Some Uranyl and Vanadyl Complexes in Aqueous Solution^{1a}

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The temperature-jump method has been used to determine the kinetics of the reaction of UO_2^{2+} ion with monochloroacetate, sulfate, acetate, and thiocyanate and of VO^{2+} ion with thiocyanate. The UO_2^{2+} ion forms higher order complexes with the first three of these ligands, whereas for uranyl and vanadyl only the thiocyanate monocomplex is important. Bimolecular rate constants at 20° and the given ionic strength for formation of the 1-1 uranyl complex are: SO_4^{2-} , $180 \text{ M}^{-1} \text{ sec}^{-1}$ at $\mu = 0.15 \text{ M}$; $\text{ClCH}_2\text{COO}^-$, $110 \text{ M}^{-1} \text{ sec}^{-1}$ at $\mu = 0.15 \text{ M}$; SCN^- , $290 \text{ M}^{-1} \text{ sec}^{-1}$ at $\mu = 1.2 \text{ M}$; CH_3COO^- , $1050 \text{ M}^{-1} \text{ sec}^{-1}$ at $\mu = 0.15 \text{ M}$. For the reaction between vanadyl and thiocyanate the rate constant is $160 \text{ M}^{-1} \text{ sec}^{-1}$ at 20° and $\mu = 0.2 \text{ M}$. Substitution labilizes the water molecules still bound to the oxo ion, so that further substitution is speeded up. The effect, however, is not as pronounced as for divalent transition metal ions. Complexation rates for uranyl ion are most nearly typical of 3+ ions. No clear-cut correlation between the formation rate constant and ligand basicity could be demonstrated for either cation. The principal effect the oxo ion has on the rate of complexation is exerted by the rather high positive charge density on the metal, especially for uranyl. The site of nucleophilic attack on vanadyl may play a role in the kinetics of substitution.

Introduction

Many aspects of the aqueous chemistry of simple metal ions are shared by oxo ions. One of these features is the general rapidity of ligand substitution into the inner hydration sphere. Another characteristic of metal ions exhibited even more pronouncedly by oxo ions is the formation of polynuclear species. In the past, these effects acted as deterrents to systematic rate studies of these ions in solution although their equilibrium properties and chemistry in other phases have been thoroughly examined.² Recently the temperature-jump,³ dissociation field,⁴ and pressure-jump⁵ techniques have been used to expand our understanding of the dynamical aspects of equilibrium in uranyl and vanadyl systems.

By utilizing the temperature-jump method and working for the most part at low pH values in order to suppress formation of polynuclear species, it has been possible to gain some further information on the kinetics of complexation of these two oxo ions. In particular, the following reactions were studied: uranyl ion with monochloroacetate, sulfate, acetate, and thiocyanate; and vanadyl with thiocyanate. Fortunately, the stability constants for all of the systems are well described

by Ahrland for the uranyl complexes⁶⁻¹⁰ and by Garner for the vanadyl complex of thiocyanate.¹¹

Experimental Section

The temperature-jump apparatus used for the present experiments is described elsewhere.¹² The rate con-

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(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 32.

(3) M. P. Whittaker, E. M. Eyring, and E. Dibble, *J. Phys. Chem.*, **69**, 2319 (1965).

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(6) S. Ahrland, *Acta Chem. Scand.*, **3**, 783 (1949).

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(11) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **73**, 4530 (1951).

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Table I:^a Metal and Metal Indicator Blank Experiments^b

[UO ₂ ²⁺]	[KNO ₃]	pH	λ , m μ	Result	Indicator, type and concn
0.025	0.05	1.0	410	No chemical relaxation	UO ₂ ²⁺
0.025	0.05	2.0	410	No chemical relaxation	UO ₂ ²⁺
0.025	0.05	4.1	410	No chemical relaxation	UO ₂ ²⁺
0.01	0.03	1.70	525	No chemical relaxation	Metacresol purple, total concn = 2×10^{-5}
0.01	0.03	2.30	525	No chemical relaxation	Metacresol purple, total concn = 3×10^{-5}
0.01	0.03	2.70	525	$\tau = 5.6$ msec	Benzyl orange, total concn = 2×10^{-5}
0.01	0.03	4.0	590	$\tau = 5.3$ msec	Bromochlorophenol blue, total concn = 2×10^{-5}
[VO ₂ ²⁺] ^c					
0.056	...	1.55	580	No chemical relaxation	VO ₂ ²⁺
0.051	...	1.55	600	No chemical relaxation	Thymol blue, total concn = 2×10^{-5}

^a All concentrations in *M*. ^b Control experiments with ligand showed no observable effects. ^c No KNO₃ required.

stants are given for a temperature of $20^\circ \pm 1$. Although individual oscillograms could be evaluated to yield relaxation times with a relative error of $\pm 10\%$ the uncertainties inherent in the treatment of the data extend the error range to $\pm 25\%$ in many cases.

As in most applications of the temperature-jump method the change in absorbancy is oscillographically recorded and photographed.¹³ In this case, however, the shift to the new equilibrium could be followed directly without employing coupled indicators by utilizing the fact that each of the various complexes absorbed considerably more light at a given wavelength than did the uncomplexed ion. For uranyl, the monochloroacetate complexes were followed at 436 m μ , the sulfate complexes at 440 m μ , the acetate complexes at 475 m μ , and the thiocyanate complex at 500 m μ . For vanadyl, detection was carried out at 580 m μ .

Reagent grade uranyl nitrate hexahydrate, monochloroacetic acid, and sodium acetate were purchased from the Fisher Scientific Co., reagent grade potassium thiocyanate from Baker and Adamson Products, and reagent grade potassium sulfate from the J. T. Baker Chemical Co. The uranyl salt required drying in a desiccator over concentrated sulfuric acid before it could be used.

Each solution was prepared by weighing out appropriate amounts of metal nitrate and ligand, then diluting to a known volume with doubly distilled water. An inert electrolyte such as potassium nitrate was not required to adjust the ionic strength of each reaction mixture because the concentrations of the reactants were sufficiently high to ensure proper Joule heating in the cell. (In many cases, the minimum concentration

of reactants which produced a detectable effect resulted in an ionic strength greater than 0.1 *M*. Since these concentrations differed from ligand to ligand uniformity of ionic strength could not be achieved. The effect of this inconsistency on the final conclusions is not significant.) Each solution was brought to the desired pH by dropwise addition of dilute NaOH and/or dilute HNO₃.

The importance of blank or control experiments in systems where hydrolysis and polymerization may occur cannot be overemphasized. For this reason, coupled pH indicators as well as the metal ions themselves were followed in the blank determinations. The results are given in Table I. It will be noted that an effect was detected for uranyl at pH 3 and higher. This effect (which was in agreement with a previous observation⁸) did not interfere with the evaluation of the relaxation times in the pH range of this study since it was significantly shorter than the relaxational process associated with complexation.

Results

The treatment of relaxation data with specific reference to multi-step metal-ligand association has been given by Hammes and Steinfeld.¹⁴ In the following we shall indicate the salient features of this analysis, pointing out the specific instances in which the conditions of this study necessitate a change in the mathe-

(13) M. Eigen and L. De Maeyer in "Techniques of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963.

(14) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962). Cf. also ref 13.

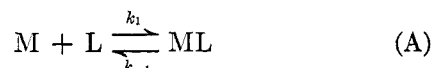
Table II:^a Relaxation Spectra of Vanadyl^b and Uranyl^c Thiocyanate at 20°

[VO ²⁺] ₀	[SCN ⁻] ₀	[VO ²⁺]	[SCN ⁻]	[VOSCN ⁺]	pH	τ_{obs} , msec	k_1 , M ⁻¹ sec ⁻¹	k_{-1} , sec ⁻¹
0.0502	0.0499	4.55×10^{-2}	4.52×10^{-2}	4.72×10^{-3}	1.70	11.1	171	74
0.0502	0.0506	4.54×10^{-2}	4.58×10^{-2}	4.80×10^{-3}	0.97	10.6	179	78
0.0301	0.0302	2.83×10^{-2}	2.84×10^{-2}	1.85×10^{-3}	1.70	15.6	130	57
$pK_L \ll 1$, $K_{ML} = 2.3$; ^d ref 11						Average: 160 ± 20 ; 70 ± 8		
[UO ₂ ²⁺] ₀	[SCN ⁻] ₀	[UO ₂ ²⁺]	[SCN ⁻]	[UO ₂ SCN ⁺]				
0.2784	0.3264	0.1396	0.1876	0.1388	2.00	7.4	260	49
0.0111	0.0131	1.0×10^{-2}	1.2×10^{-2}	1.1×10^{-3}	2.00	18.9	251	47
0.2784	0.3257	0.1398	0.1871	0.1386	2.00	5.9	325	61
0.2784	0.3257	0.1398	0.1871	0.1386	2.65	6.1	316	60
$pK_L \ll 1$, $K_{ML} = 5.3$; ref 10						Average: 290 ± 30 ; 54 ± 6		

^a All concentrations in M. ^b The approximate ionic strength is 0.2 M. ^c The approximate ionic strength is 1.2 M. ^d K_{ML} determined experimentally at an ionic strength of ~ 0.2 M and 20°.

mathematical representation of the relaxation spectra. (Charges will be neglected in writing the reactions and equations.)

(A) UO_2SCN^+ and $VOSCN^+$. The simplest system to consider is a single-step reaction of the type

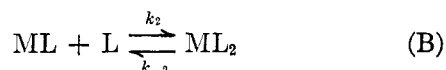


for which the reciprocal of the relaxation time is given by

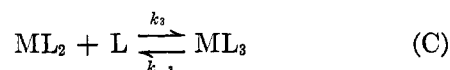
$$1/\tau = k_{-1} + k_1[(M) + (L)] \quad (1)$$

where k_{-1} and k_1 are the unimolecular and bimolecular dissociation and association rate constants, M is either UO_2^{2+} or VO^{2+} , and L is SCN^- (or anyone of the ligands subsequently treated). The data and rate constants for these systems are given in Table II.

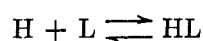
(B) $UO_2CH_2ClCOO^+$ and UO_2SO_4 . In many solutions, concentrations could be adjusted so that only a single reaction was of kinetic importance. The two possibilities to warrant our consideration in addition to reaction A are



and



The reciprocal relaxation time would then have the same form as eq 1, the subscript now being 2 or 3 and M replaced by ML or ML_2 , respectively, where required. Unlike thiocyanate, however, the other ligands studied can be protonated in solution. The appropriate equilibrium



must be included in the computation of the relaxation time. Doing so leads to a factor of $1 + a$ dividing the concentration of metal or complex in eq 1 in which

$$a = \frac{\delta(HL)}{\delta(L)} = \frac{(H)}{K_L + (L)} \quad (2)$$

where K_L is the acid dissociation constant of the ligand. The expression for the reciprocal of the relaxation time is now

$$1/\tau = k_n \left[\frac{(ML_{n-1})}{1 + a} + (L) \right] + k_{-n} \quad (3)$$

If the ligand is completely dissociated, then K_L would be very large with respect to unity, so that in the limit of complete ligand acid dissociation a becomes zero and eq 3 reduces to eq 1

$$\lim_{K_L \rightarrow \infty} \left[\frac{\delta(HL)}{\delta(L)} \right] = 0$$

Before proceeding to a consideration of multi-step reactions, we should like to point out that eq 3 is applicable to the uranyl monochloroacetate and sulfate systems, but not to the acetate system. Nevertheless, the treatment with respect to the outstanding feature shared by these three systems, namely, coupling, in which steps A, B, and C all contribute to the relaxation spectrum, applies to the acetate as well. The general solution to the rate equations for multi-step reactions has been given in two of the references previously cited (ref 13 and 14). The relaxation times of the system are found by solving the matrix equations

$$|K|\delta x = |1/\tau|\delta x \quad (4)$$

which is satisfied by the secular determinant

$$|K - (1/\tau)I| = 0 \quad (5)$$

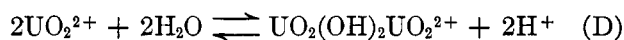
Table III:^a Relaxation Spectra of Uranyl Complexes at 20^{ab}

[UO ₂ ²⁺] ₀	[(L) + (HL)] ₀	[UO ₂ ²⁺]	[L]	[ML]	[ML ₂]	[ML ₃]	pH	τ _{obs} , msec	τ _{calcd} , msec	
Monochloroacetate										
*4.010 × 10 ⁻²	0.6077	2.23 × 10 ⁻²	2.79 × 10 ⁻²	1.50 × 10 ⁻²	2.64 × 10 ⁻³	1.73 × 10 ⁻⁴	1.36	2.22	21.4	
4.028 × 10 ⁻²	0.7015	7.99 × 10 ⁻³	9.65 × 10 ⁻³	1.85 × 10 ⁻²	1.13 × 10 ⁻³	2.54 × 10 ⁻⁴	1.90	27.8	...	
4.012 × 10 ⁻²	1.275	1.36 × 10 ⁻²	5.78 × 10 ⁻²	1.88 × 10 ⁻²	6.85 × 10 ⁻³	9.26 × 10 ⁻⁴	1.35	16.7	16.0	
6.010 × 10 ⁻²	0.1915	4.92 × 10 ⁻²	8.76 × 10 ⁻²	1.03 × 10 ⁻²	5.72 × 10 ⁻⁴	1.17 × 10 ⁻⁵	1.37	155.0	...	
*4.010 × 10 ⁻²	0.6077	1.63 × 10 ⁻²	4.61 × 10 ⁻²	1.80 × 10 ⁻²	5.24 × 10 ⁻³	5.65 × 10 ⁻⁴	1.60	17.8	...	
pK _L = 2.66, K _{ML} = 24.0, K _{ML₂} = 6.31, K _{ML₃} = 2.34; ref 7.										
Sulfate										
*4.026 × 10 ⁻²	0.2011	5.54 × 10 ⁻³	7.14 × 10 ⁻²	1.98 × 10 ⁻²	9.80 × 10 ⁻³	5.08 × 10 ⁻³	1.90	22.2	...	
4.006 × 10 ⁻²	9.063 × 10 ⁻²	1.46 × 10 ⁻²	2.83 × 10 ⁻²	2.06 × 10 ⁻²	4.04 × 10 ⁻³	8.29 × 10 ⁻⁴	1.88	44.5	...	
6.018 × 10 ⁻²	6.684 × 10 ⁻²	3.14 × 10 ⁻²	1.62 × 10 ⁻²	2.55 × 10 ⁻²	2.86 × 10 ⁻³	3.35 × 10 ⁻⁴	1.865	97.0	96.6	
*4.026 × 10 ⁻²	0.2011	1.23 × 10 ⁻²	3.50 × 10 ⁻²	2.15 × 10 ⁻²	5.20 × 10 ⁻³	1.32 × 10 ⁻³	1.35	35.6	...	
pK _L = 1.92, K _{ML} = 50.1, K _{ML₂} = 6.92, K _{ML₃} = 7.25; ref 8.										
Acetate										
[UO ₂ ²⁺] ₀	[(L) + (HL)] ₀	[UO ₂ ²⁺]	[L]	[M ₂]	[ML]	[ML ₂]	[ML ₃]	pH	τ _{obs} , msec	τ _{calcd} , msec
4.010 × 10 ⁻²	0.1200	3.37 × 10 ⁻³	1.19 × 10 ⁻³	1.88 × 10 ⁻³	9.62 × 10 ⁻³	1.09 × 10 ⁻²	1.24 × 10 ⁻²	4.07	77.7	74.1
*4.005 × 10 ⁻²	0.3610	3.69 × 10 ⁻³	1.19 × 10 ⁻²	4.70 × 10 ⁻³	1.06 × 10 ⁻²	1.20 × 10 ⁻²	1.37 × 10 ⁻²	3.23	38.9	39.7
6.020 × 10 ⁻²	0.1005	1.93 × 10 ⁻²	4.28 × 10 ⁻³	4.88 × 10 ⁻³	1.98 × 10 ⁻²	8.09 × 10 ⁻³	3.31 × 10 ⁻³	3.50	95.0	...
6.004 × 10 ⁻²	0.1024	1.96 × 10 ⁻²	4.25 × 10 ⁻³	4.60 × 10 ⁻³	1.99 × 10 ⁻²	8.08 × 10 ⁻³	3.28 × 10 ⁻³	3.52	122.0	...
*4.005 × 10 ⁻²	0.3610	1.52 × 10 ⁻³	1.83 × 10 ⁻²	2.20 × 10 ⁻³	6.66 × 10 ⁻³	1.16 × 10 ⁻²	2.02 × 10 ⁻²	3.45	31.2	...
pK _L = 4.59, K _D = 1.2 × 10 ⁻⁶ , K _{ML} = 240, K _{ML₂} = 95.5, K _{ML₃} = 95.5; ref 9.										

^a All concentrations in *M*. ^b An approximate ionic strength of 0.15 *M* was maintained for the monochloroacetate, sulfate, and acetate systems.

Here **K** is the matrix of coefficients for the linearized rate equations, δx is the column vector, $|\delta x_i\rangle$, representing the displacements of the components, and **I** is the unit matrix. The more rapid protolytic reaction coupled to the complexation enters into this reaction scheme as it did for the single-step reactions. For the uranyl with acetate, which was studied at higher pH values, another complication manifests itself.

(C) $UO_2CH_3COO^+$. Up to now, the dimerization of uranyl, which becomes significant at a pH of about 3.5 and above, has been ignored. For the reaction



we define¹⁵

$$K_D = \frac{(M_2)(H)^2}{(M)^2} = 1.2 \times 10^{-6}$$

where M_2 represents the dimer. This reaction adjusts to the new equilibrium more rapidly than the complexation reactions actually being studied (see Table I and ref 4). Its presence will therefore modify the concentrations appearing in the linearized rate equations. As before, the metal or metal-complex concentrations will be divided by a suitable factor, in this case, $1 + \alpha$. The acetate concentration will be divided by a factor $1 + \beta$, where

$$\beta = \frac{2\delta(M_2)}{\delta(M)} \quad (6)$$

These terms are explicitly

$$\alpha = \frac{4K_D(M)[(L) + (H)] + (H)^2[4(M_2) + (H)]}{(H)^2[K_L + (L)] + 4K_L[K_D(M) + (M_2)(H)]} \quad (7)$$

and

$$\beta = 4 \left\{ \frac{K_D(M)[(L) + K_L + (H)] + (M_2)(H)^2}{(H)[(H)^2 + (H)[K_L + (L)] + 4K_L(M_2)]} \right\} \quad (8)$$

In the absence of appreciable dimer α should reduce to a and β should be zero. Examination of eq 7 and 8 shows that

$$\lim_{K_D, (M_2) \rightarrow 0} \left[\frac{\delta(HL)}{\delta(L)} \right] = \frac{(H)^3}{(H)^2[K_L + (L)]} = \frac{(H)}{K_L + (L)} = a$$

and

$$\lim_{K_D, (M_2) \rightarrow 0} 2 \left[\frac{\delta(M_2)}{\delta(M)} \right] = 0$$

(D) *Evaluation of Relaxation Spectra for Multi-Step Reactions.* The experimental conditions and relaxation times for uranyl with monochloroacetate, sulfate, and acetate are listed in Table III. A trial

(15) C. F. Baes, Jr. and N. J. Meyers, *Inorg. Chem.*, **1**, 780 (1962).

and error method was used to find the best set of rate constants for calculating the relaxation times according to eq 5. The measured and calculated relaxation times are shown for comparison. The concentrations of the various species at equilibrium were calculated with the aid of an IBM 1620 computer.

In interpreting the relaxation data, it is important to determine which species, whether L or HL, or both, contribute to the relaxation spectra. Inclusion of the reaction with HL into the rate equations results in additional terms in the final expression for the reciprocal of the relaxation time. These additive terms are proportional to hydrogen ion concentration. A number of systems showing this type of behavior have been examined, of which some studies by Cavasino may be cited.¹⁶ In general, protonated ligands show smaller complexation rate constants than the corresponding deprotonated ligand. Qualitative studies were performed for each of the three ligands (the experiments that are marked with asterisks) to determine which species was principally responsible for the observed effect.

The procedure that was followed consisted of varying the pH of two identical initial experiments such that the assignment of rate constants remained nearly the same. The observed changes in the relaxation time of each system appeared to correlate with changes in L and not with HL. That is, lowering the hydrogen ion concentration, which favors the formation of L at the expense of HL, resulted in a shorter relaxation time. Alternately, raising the hydrogen ion concentration, which did not favor the formation of L, resulted in a longer relaxation time.

Obtaining a solution of the matrix equation for the case of coupled reactions is difficult when the eigenvalues are close together. For many of the systems in Table III resolution of the relaxation spectrum was not possible; consequently, for these experiments no entry appears in the column labeled $\tau_{\text{calcd.}}$. The rate constants derived from the uranyl experiments showing higher order complexing are listed in Table IV.

Table IV: Rate Constants of Uranyl Complex Reactions at 20°

Ligand	$M^{-1} \text{ sec}^{-1}$			Sec^{-1}		
	k_1	k_2	k_3	k_{-1}	k_{-2}	k_{-3}
Acetate	1050	800	200	4.4	8.4	2.1
Monochloro-acetate	110	240	80	4.4	38.0	34.0
Sulfate	180	300	160	3.6	43.0	22.0

Discussion

The formation of complexes between simple bivalent metal ions and sterically favorable ligands is usually controlled by the water exchange rate of the aquated metal ion with the ligand having a minimal influence.¹⁷ Ions with high charge to radius ratios, which may be divalent ions of small size like Be^{2+} or more highly charged ions like Fe^{3+} , tend to have slower, ligand-dependent rates of complex formation. We have endeavored to determine which situation prevails for the dipositive, oxygen-containing uranyl and vanadyl ions. Let us begin with uranyl.

The magnitude of the k_1 rate constants for the four ligands studied runs from $110 M^{-1} \text{ sec}^{-1}$ for chloroacetate to $1050 M^{-1} \text{ sec}^{-1}$ for acetate as shown in Tables II and IV. This range lies below that observed for the bivalent transition metal ions, being comparable to values obtained for ferric ion complexation.¹⁸ Moreover, the nature of the incoming ligand affects the rate of substitution, a point to which we shall return after a more detailed consideration of k_1 relative to k_2 and k_3 .

For chloroacetate and sulfate k_2 is greater than k_1 . This effect is readily understood, since previous studies have shown that substitution of negatively charged ligands into the inner coordination sphere loosens the binding between the central cation and the remaining coordinated waters.¹⁴ Since the mechanism is complicated, however, certain assumptions have to be made in order to derive the same trend between k_2 and k_3 . Specifically, the ion-pair association constant for reactions B and C would have to be known. The procedure usually employed is to calculate this value from theory, a process too uncertain for these systems. Roughly, the trend seems to prevail. The fact that k_2 is less than k_1 for acetate may reflect the screening of charge due to the unbound hydrophobic end of the acetate ion.¹⁹ This effect would be reflected in the ion pair formation constant for this and the next step. Essentially, then, the most significant feature of these results concerns the relative slowness of the substitution, as reflected in the k_1 rate constants, and we take up this point again.

Numerous studies have shown that in the crystal, the characteristic structure for uranyl is a unit con-

(16) F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965); *Ric. Sci.*, **35** (II-A), 1120 (1965).

(17) M. Eigen, *Ber. Bunsenges. Physik. Chem.*, **67**, 753 (1963).

(18) M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1965, p 55.

(19) J. I. Steinfeld and G. G. Hammes, *J. Phys. Chem.*, **67**, 928 (1963).

taining a more or less linear O-U-O axis with a roughly hexagonal equatorial plane at right angles to this axis.² It seems clear that f orbitals participate in the bonding, accounting for both the relatively strong U-O axial bonds, and the over-all geometric configuration.^{20,21} In one of the earlier papers concerned with the role of f orbitals in the bonding of uranium and the transuranic elements, Connick and Hugus consider charge distribution in the uranyl ion and its effect on the entropy of the ion.²² Their conclusion that "... a uranyl ion appears as a +3 ion to waters about its equator. ..." is in accord with the kinetic experiments reported on here.

There remains, then, the question of the ordering of the k_1 rate constants with regard to properties of the ligands studied. To effect a comparison, it is necessary to "normalize" the charge effect, so that the divalent sulfate can be compared with the univalent ions. Therefore, if we divide the rate constants for the univalent ions by $2 M^{-1}$ and the rate constant for sulfate ion by $10 M^{-1}$ (approximate values for the ion-pair formation constants at these temperatures and ionic strengths¹⁴), we obtain the order $\text{CH}_3\text{COO}^- > \text{SCN}^- > \text{ClCH}_2\text{COO}^- > \text{SO}_4^{2-}$. This series would correlate with decreasing pK, and hence basicity, were it not for thiocyanate. The same would be true for the correlation with the stability constant K_{ML} if it were normalized, again with the exception of SCN^- . What is really of importance here, however, is how strong a nucleophile the ligand is with regard to this cation. Since thiocyanate is known to form complexes rather frequently with most metal ions,²³ we feel justified in surmising that the above ligand order of decreasing rate of substitution is also consistent with decreasing nucleophilic character.

Whether or not there is an influence of ligand properties on the kinetics of substitution depends upon the mechanism. In particular, the formation of a transition state of reduced coordination number by a dissociation mechanism would be ligand independent, while formation of a transition state of expanded coordination number by a displacement mechanism should be ligand dependent.²⁴ An *a priori* choice between the two mechanisms would be difficult to make because the effectiveness of a ligand field in splitting electron levels for 5f electrons is not on the same order of magnitude as for 3d and 4d electrons;²⁵ consequently, a change in coordination number need not signify appreciable loss in crystal field stabilization energy. On the basis of the experimental evidence, however, we conclude that the displacement mechanism predominates.

In contrast to the uranyl studies, for which no other values were available, the vanadyl thiocyanate study may be compared to a previous investigation, namely, the pressure-jump study in which the kinetics of reaction between VO^{2+} and SO_4^{2-} were measured.⁵ For these ions, the recombination rate constant is about $10^4 M^{-1} \text{ sec}^{-1}$, while the SCN^- rate constant is $160 M^{-1} \text{ sec}^{-1}$. The pK of HSCN is less than 1 while the pK of HSO_4^- is 1.92.⁷ Therefore, a displacement type of mechanism with dependency on the ligand basicity seems to be indicated.

For both the VO^{2+} and the UO_2^{2+} kinetic studies with thiocyanate, the pH dependence was examined and within experimental accuracy none was found. A pH dependence was found for the SO_4^{2-} experiment. This kind of behavior would imply that the appearance of a pH dependence depends on whether or not the ligand has an appreciable pK value, that is, a value at least greater than unity, unless, of course, the effect is to be associated solely with hydroxyl ion catalysis.

As in the case of the uranyl ion, the structure of vanadyl complexes as exemplified by the acetylacetonate is known.² It has a square pyramidal structure with the vanadium atom above the center of the basal square of oxygens. Thus, an alternative explanation for the vanadyl results is possible.

It may well be that two different processes are being observed in these studies. Attack by the ligand at the open, basal side of the square pyramidal complex may have been observed in one system. In the other, substitution may have been initiated at the apical side of the complex. At this time it does not seem feasible to determine which of the two is the more rapid.

Indeed, it is possible that further fast reaction studies on these ions will disclose other relaxational processes in the range between 10 msec and the diffusion-controlled relaxation time for ion-pair formation of about 10 nanosec. Furthermore, the anisotropic structures of the oxo ions can give rise to many different interactions with the solvent, of which association between the negatively charged oxygen ends of the O-U-O axis and water is an interesting possibility.

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