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Kinetics of Thiocyanate Binding to Vanadium(II) and -(III)

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Formation and dissociation rate constants (k_f and k_d) for the binding of thiocyanate to $V(H_2O)_6^{2+}$ and $V(H_2O)_6^{3+}$ have been determined by means of the temperature-jump method. In the case of V(II), $k_f = 15 \pm 2\ M^{-1}\ sec^{-1}$ and $k_d = 1.4 \pm 0.2\ sec^{-1}$ at 24° and $\mu = 1\ M$. The corresponding rate constants for V(III) are $104 \pm 10\ M^{-1}\ sec^{-1}$ and $0.7 \pm 0.1\ sec^{-1}$ at 23° and $\mu = 1\ M$. The results are discussed in terms of electronic effects on the substitution labilities of octahedral complexes. Also considered is the possibility of distinguishing between outer-sphere and inner-sphere reductions from an estimate of the vanadium(II)–water exchange rate. Unlike substitution reactions of other trivalent hexaaquo complexes, no evidence was found for a catalytic path involving the hydroxy form of V(III).

Introduction

Although a great deal of data is now available on the kinetics of metal complex formation, little published work exists on vanadium species. Particularly needed are the rates of replacement of coordinated water in $V(H_2O)_6^{2+}$ and $V(H_2O)_6^{3+}$. These complexes play an important role in electron-transfer studies and their labilities pertain directly to the problem of differentiating between "outer" and "inner-sphere" oxidation–reduction reactions. A related subject is the effect of electron configuration on octahedral substitution rates. Comparing V(II) and V(III) anation rates with those of other (first row) bi- and tripositive aquo cations, respectively, would be a means of assessing the importance of electronic effects in these two series.

Using the temperature-jump method we have measured the formation and dissociation rate constants for the 1:1 thiocyanate complexes of V(II) and V(III).[3,4] Thiocyanate was chosen as ligand because it forms fairly stable complexes with the vanadium species in question and is free of complications arising from hydrolysis. Also, since thiocyanate has often been employed in other anation studies, its binding rate leads directly to relative reactivities between a number of aquo complexes.

Experimental Section

$VOSO_4$ and NaSCN were reagent grade. NaSCN was recrystallized twice from water and its stock solutions were analyzed by titration with $AgNO_3$. All other chemicals were analytical grade and were used without further purification.

V(II) and V(III) are easily oxidized and must be handled in the absence of oxygen. In preparing a reaction solution, vanadium stock of known concentration was added to a stoppered serum bottle containing a nitrogen-purged mixture of NaSCN, $NaClO_4$, and $HClO_4$. Prior to receiving the reaction solution, the temperature-jump cell was also purged with nitrogen. Solutions were transferred by means of glass syringes equipped with stainless steel needles.

Vanadium(II) perchlorate was prepared by electrolytic reduction of VO^{2+} in $HClO_4$, the vanadyl perchlorate being prepared by mixing equivalent amounts of $Ba(ClO_4)_2$ and $VOSO_4$ solutions. The reduction was carried out under an atmosphere of nitrogen. V(II) solutions are unstable with respect to the slow reduction of perchlorate, resulting in V(III) accumulation.[5] Since replacing perchlorate with chloride had no appreciable effect on the kinetics, most reaction mixtures were therefore made from vanadium(II) chloride (even at relatively low concentrations V(III) could interfere spectrophotometrically with the V(II) kinetic measurements and, in principle, could lead to catalytic aquation *via* $VNCS^+$–V(III) electron transfer). The vanadium(II) chloride was prepared by electrolyzing a known amount of NH_4VO_3 in HCl medium. The extent of reduction was estimated from the optical density at 400 mμ. At this wavelength $\epsilon_{V(III)}/\epsilon_{V(II)} = 10$ and the OD thus serves as a sensitive measure of [V(III)].[6] On this basis no more than 3% of the vanadium existed as V(III).

To prepare stock vanadium(III) perchlorate, a slight excess (usually 5 mole %) of vanadium(II) perchlorate was added to an acidic solution of vanadyl perchlorate. These solutions were used before any significant oxidation of V(III) could take place by perchlorate.[5]

The V(II) and V(III) spectra were in very good agreement with those reported in the literature.[6]

The temperature-jump apparatus was of double-beam design. Discharging a 0.05-μF capacitor loaded to 40,000 V effected a temperature rise of 6 ± 1°. Since platinum catalyzes the evolution of hydrogen from V(II) solutions, gold-plated electrodes were employed in the temperature-jump cell. The reciprocal relaxation time,[9] τ^{-1}, was calculated from a plot of $-\log \Delta C$ *vs.* time, where ΔC is proportional to the deviation of (M–NCS) from its equilibrium position. At least five oscillograms were averaged per run. The deviation from the mean was usually less than 5%.

Results

The V(II) reaction was followed at 520 mμ. At this wavelength only negligible absorption is expected from trace amounts of V(III) and $VNCS^{2+}$.[6-8] τ^{-1}, plotted as a function of the equilibrium concentrations (Figure 1), conforms to the behavior expected for a substitution process first order in ligand and metal[9] (eq 1–3).

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[3] The same systems have recently been the subject of a stopped-flow investigation. For a preliminary report see B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

[4] The present results supersede the preliminary findings of W. K.[13,24]

[5] W. R. King and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

[6] G. Gordon and P. H. Tewari, *ibid.*, **70**, 200 (1966).

[7] $\epsilon_{VNCS^+} \sim 23$ and $\epsilon_{VNCS^{2+}} \sim 13$ at 520 mμ. Taken together with $\epsilon_{V(II)}$, $\epsilon_{V(III)}$, and the stability constants for SCN^- binding, we calculate that trivalent vanadium contributes no more than 5% to the total OD of any reaction solution.

[8] For reasons presented elsewhere[3] it is assumed that SCN^- is bound to vanadium through the nitrogen atom.

[9] M. Eigen and L. de Maeyer in "Technique of Organic Chemistry," A. Weissberger, Ed., Vol. VIII, part 2, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1963.

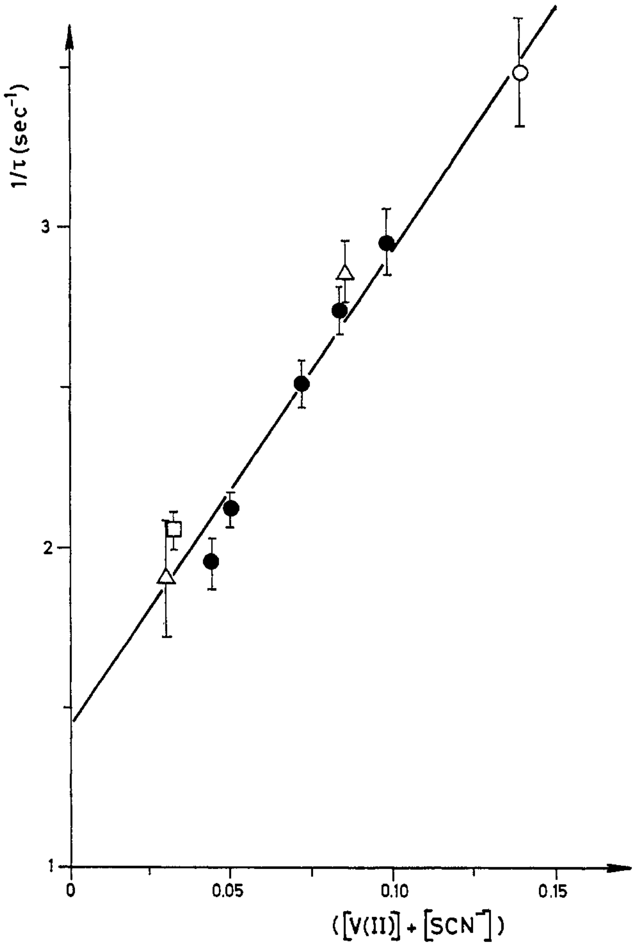

Figure 1.—Concentration dependence of the reciprocal relaxation times of the vanadium(II) reaction at 24° and in Cl^-–ClO_4^- medium of $\mu = 1$ *M*: ●, 0.2 *M* H^+; △, ClO_4^- medium, 0.2 *M* H^+; □, 0.1 *M* H^+; ○, 0.4 *M* H^+.

$$M + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} ML \qquad (1)$$

$$\tau^{-1} = k_f([M] + [L]) + k_d \qquad (2)$$

$$K = k_f/k_d \qquad (3)$$

Equilibrium concentrations were calculated using 14 M^{-1} for the stability constant, *K*. This figure was obtained by spectrophotometric titration (23° and $\mu = 0.4$ *M*) but, owing to the formation of more than one complex at high [SCN^-], can only be considered a first approximation.[10] To prevent higher complexes from interfering in the kinetic runs, the total vanadium concentration was always kept at least threefold larger than the total thiocyanate concentration. Equilibrium concentrations ranged from 0.13 to 0.023 *M* in the case of V(II) and from 0.014 to 0.0040 *M* in the case of SCN^-. Considering the differences in temperature and ionic strength, the formation and dissociation rate constants calculated from the slope and intercept of Figure 1 give a stability constant (Table I) in satisfactory agreement with the one estimated spectrophotometrically.

Although Cl^- was present in most V(II) reaction mixtures, it had no appreciable effect on either the V(II) spectrum (we find the spectrum in 1 *M* Cl^- identical with that in 1 *M* ClO_4^-) or the substitution kinetics (see Figure 1). In addition, trace amounts of trivalent vanadium can be tolerated; at ([V(II)] + [SCN^-]) = 0.084 *M* the total concentration of trivalent vanadium was made 0.01 *M*, but no significant change occurred in τ. The kinetics were also independent of [H^+] in the range 0.1–0.4 *M*.

TABLE I

RATES OF FORMATION AND DISSOCIATION OF THE $V^{II}NCS$ AND $V^{III}NCS$ COMPLEXES AND ESTIMATED RATES OF CATION–SOLVENT WATER EXCHANGE

M	k_f, M^{-1} sec⁻¹	k_d, sec⁻¹	K,[a] M^{-1}	k_{ex},[b] sec⁻¹
V(II)[c]	15 ± 2	1.4 ± 0.2	11	∼75
V(III)[d]	104 ± 10	0.7 ± 0.1	153	(∼3 × 10³)

[a] $K = k_f/k_d$. [b] The rate of exchange of a particular water in the hexaaquo complex. [c] At 24° and $\mu = 1$ *M* (mixed Cl^-–ClO_4^- medium). [d] At 23° and $\mu = 1$ *M* (ClO_4^- medium).

The V(III) reaction was followed at 400 mμ. Ratios of $[V(III)]_{total}/[SCN^-]_{total}$ were always greater than 3 and equilibrium concentrations varied from 2.9×10^{-2} to 5.0×10^{-3} *M* for [V(III)] and from 3.0×10^{-3} to 6.5×10^{-4} *M* for [SCN^-]. In addition to the relatively slow complex formation, a very fast ($\tau < 15$ μsec) reaction was observed, the amplitude of the relaxation effect increasing as the acidity was decreased. From a consideration of relative extinction coefficients,[6,7,11] concentrations, and ΔH values,[11,12] the effect can be attributed to the hydrolysis equilibrium $VOH_2^{3+} \rightleftharpoons VOH^{2+} + H^+$.

Using 100 M^{-1} as a first approximation to the stability constant,[12] an initial plot of τ^{-1} *vs.* ([V(III)] + [SCN^-]) was made. The slope:intercept ratio of the resulting straight line gave a second approximation (150 M^{-1}) and this new value was used to plot the graph appearing in Figure 2. The two plots gave essentially the same rate constants.

Varying [H^+] from 0.04 to 0.5 *M* had no appreciable effect on τ. At the lower acidity, $[VOH^{2+}]/[VOH_2^{3+}] = 0.05$.

Discussion

The V(II) Reaction.—The wealth of experimental evidence to date indicates that the bipositive aquo ions of the first transition series undergo ligand substitution *via* rapid ion-pair formation followed by rate-determining loss of coordinated water[13,14]

$$M(H_2O)_6^{2+} + L^n \overset{K_0}{\rightleftharpoons} M(H_2O)_6^{2+}\cdot L^n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(H_2O)_5L^{+2+n} + H_2O \qquad (4)$$

$$k_f = K_0k_1 \approx K_0k_{ex} \qquad (5)$$

$$k_d = k_{-1} \qquad (6)$$

For a particular metal, formation rate constants, k_f, are generally independent of the nature of the ligand.

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[10] In the kinetic studies, the condition [V(II)] >> [SCN^-] was always satisfied. Therefore the calculated concentration sum of eq 2 is relatively insensitive to errors in *K*. The same holds for the V(III) reaction.

(11) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

(12) S. C. Furman and C. S. Garner, *ibid.*, **73**, 4528 (1951).

(13) M. Eigen and R. G. Wilkins in "Mechanisms of Inorganic Reactions," R. K. Murmann, Ed., Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

(14) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

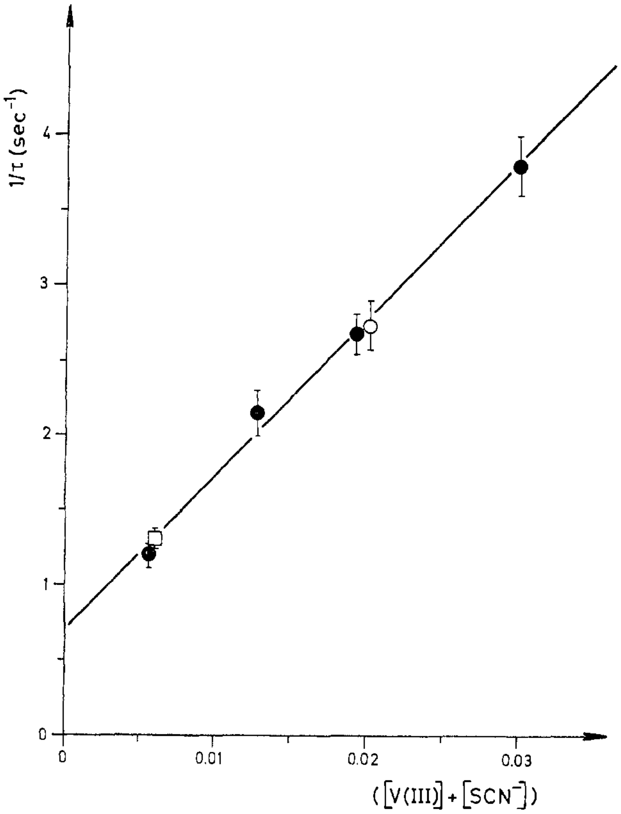

Figure 2.—Concentration dependence of the reciprocal relaxation times of the vanadium(III) reaction at 23° and in perchlorate medium of $\mu = 1\ M$: ●, 0.5 M H$^+$; □, 0.04 M H$^+$; ○, 0.1 M H$^+$.

Differences are observed for ligands of different charge, but these can be attributed to variations in K_0, the outer-sphere association constants. Values of K_0 have been obtained both experimentally[15] and estimated from the Bjerrum formulation for ion pairs.[16] They indicate that k_1 is not far from k_{ex}, the rate constant for metal–solvent water exchange.[17]

Apparently V(II) is no exception to this general behavior. Although no anation rate constants are available for comparison with the SCN$^-$ results, some recent electron-transfer studies by Price and Taube[18] suggest that V(II) substitution rates are relatively independent of the nature of the ligand. It seems significant that recently published values for the V(II) inner-sphere reductions of CrSCN^{2+} and *cis*-Co(en)$_2$(N$_3$)$_2$$^+$ are comparable[19,20] to what Price and Taube found for Co(NH$_3$)$_5$O$_2$CCOX^{2+} and Co(NH$_3$)$_5$C$_2$O$_4$$^+$, respectively. Therefore, in common with so many other bivalent cations, V(II) appears to undergo substitution at a rate primarily controlled by the loss of a coordinated water.

From eq 5 it is seen that an estimate of the V(II) water-exchange rate constant can be made from the relation[14]

$$k_{ex,V(II)} = \frac{k_{f,V(II)}}{k_{f,Ni(II)}} k_{ex,Ni(II)} \qquad (7)$$

where $k_{ex,Ni(II)}$ refers to the known rate of water exchange[17] of Ni(II) and $k_{f,Ni(II)}$ is the rate constant for formation of NiNCS$^+$.[21] Judging from the existing agreement between water-exchange and ligand-substitution data,[13] $k_{ex,V(II)}$ obtained in this way (Table I) is probably valid to within a factor of 3. When comparing the labilities of aquo complexes and when considering rates of substitution *vs.* rates of electron transfer for a particular metal, one is often dealing with rate constants differing by more than an order of magnitude; in these cases the error in the present estimate is of little consequence.

Compared to other bipositive aquo complexes, V(II) is strikingly inert. Even Ni(II) is considerably more reactive, indicating a wider range of exchange rates than found previously. In the transition series, k_{ex} varies from ~75 sec^{-1} (V(II)) to 2×10^8 sec^{-1} (Cu(II)) at 25°. The inertness of V(II) can be rationalized in terms of either valence bond[22] or crystal field[23] theory applied to a d^3 electron configuration. The latter approach is an attempt to quantitatively predict relative rates from estimated "crystal field activation energies" (CFAE) and finds experimental support in an apparent relationship between aquo ion labilities and crystal field stabilization energies (CFSE).[24] A comparison of the SCN$^-$ anation rates of Ni(II) and V(II) should be a particularly straightforward application of the theory. The hexaaquo cations are identical in charge and very similar in size and thermodynamic affinity for SCN$^-$. Furthermore, they both possess the large CFSE of 12*Dq*[23] and, for an S$_N$1 mechanism, would be assigned identical crystal field activation energies of 2.0*Dq*.[23] Any difference in rates should then be accounted for solely by the difference in *Dq* between Ni(II) and V(II). Using spectroscopic *Dq* values[25] and a CFAE of 2.0*Dq*, we calculate $k_{f,Ni(II)}/k_{f,V(II)} = 40$ (25°). However, it can be argued that the mechanism is better described as a "ligand-assisted dissociation."[26,27] In this case the CFAE of 2.0*Dq* would be replaced by 1.8*Dq*[26,28] giving $k_{f,Ni(II)}/k_{f,V(II)} = 25$. These ratios are to be compared with the experimental ratio of 300. The theory predicts correctly that Ni(II) is the more reactive complex and is of value in making a semiquantitative estimate of the relative rates. At the same time the results indicate that either a refinement of the theory or a consideration of parameters other than crystal field stabilization energies is

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(15) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

(16) See, *e.g.*: (a) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4629 (1962); (b) F. P. Cavisino, *J. Phys. Chem.*, **69**, 4380 (1965); (c) R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964); (d) D. B. Rorabacher, *ibid.*, **5**, 1891 (1966).

(17) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(18) H. Price and H. Taube, to be published.

(19) The V(II) inner-sphere reduction of Cr(H$_2$O)$_5$SCN^{2+} has a rate constant of 7.1 M^{-1} sec^{-1} at 25° and $\mu = 1\ M$.[3]

(20) The V(II) inner-sphere reduction of *cis*-Co(en)$_2$(N$_3$)$_2$$^+$ has a rate constant of 33 M^{-1} sec^{-1} at 25° and $\mu = 1\ M$: J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 1276 (1967).

(21) A. G. Davies and W. M. Smith, *Proc. Chem. Soc.*, 380 (1961).

(22) H. Taube, *Chem. Rev.*, **50**, 69 (1952).

(23) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(24) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(25) See ref 23, p 44.

(26) R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964).

(27) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(28) N. S. Hush, *Australian J. Chem.*, **15**, 378 (1962).

necessary for correlations of a more quantitative nature.[29]

V(II) is often employed as a reducing agent in electron-transfer reactions. The important question as to whether it reacts by way of an "outer-" or "inner-sphere" mechanism has been the subject of a number of studies.[14] For reductions occurring at a rate slower than V(II)–solvent exchange, this point is not easily settled. On the other hand, a reduction proceeding at a rate faster than interpenetration of the V(II) coordination shell can be unambiguously assigned as outer sphere (assuming, of course, the oxidizing agent is substitution inert). In principle, one should then be able to predict a *maximum* value for an inner-sphere rate constant (k_I^{max}) from a knowledge of the parameters which control simple substitution reactions. k_I^{max} corresponds to the rate constant for formation of the

$$M^{III}\text{–}L + V^{II}\text{–}OH_2 \xrightarrow{k_I^{max}} M^{III}\text{–}L\text{–}V^{II} + H_2O \qquad (8)$$

bridged intermediate and becomes the rate constant for the over-all reaction when electron transfer is rapid relative to substitution. According to eq 4 and 5, formation of the bridged intermediate must wait upon loss of coordinated water and k_I^{max} should therefore be related to $k_{ex,V(II)}$ by

$$k_I^{max} \approx K_0 k_{ex,V(II)} \qquad (9)$$

It is obvious that an estimate of k_I^{max} cannot be more accurate than the value chosen for K_0, the stability constant for the outer-sphere association between the oxidizing agent and V(II). In the absence of experimental stability constants, it has become customary to estimate K_0 from[16a–c,30]

$$K_0 = \frac{4\pi N a^3}{3000} e^{-U(a)/kT} \qquad (10)$$

$$U(a) = Z_1 Z_2 e^2 / Da(1 + \kappa a) \qquad (11)$$

where the symbols have their usual significance. Despite the many assumptions involved in deriving (10), association constants calculated in this way are believed to be valid to within a factor of 2–3.[16a] Note that oxidizing agents of the same size and charge should, in the limit of rapid electron exchange, undergo inner-sphere reductions at similar rates.

Price and Taube[18] find formation of the bridged intermediate to be the rate-determining step in the inner-sphere reductions of some cobalt(III) pentaammines. It is therefore of interest to calculate k_I^{max} for these reactions, based on outer-sphere association constants estimated from eq 10 and setting $k_{ex,V(II)} = 75$ sec^{-1} (Table I). The distance of closest approach, a, is taken as 7 Å—the center-to-center distance between a V^{2+} and Co^{3+} ion separated by one water and one ammonia molecule.[31] At an ionic strength of 1 M and a temperature of 25°, the calculated K_0 values are 0.45 and 0.26 M^{-1}, for a monopositive and a bipositive amine, respectively. Substitution in eq 9 gives rate constants of 34 and 19 M^{-1} sec^{-1}, to be compared with experimental values[18] of about 45 and 11 M^{-1} sec^{-1}. In the same way k_I^{max} has been calculated for the inner-sphere reductions of $Co(en)_2(N_3)_2^+$ (a = 8 Å[32]) and $Cr(H_2O)_5SCN^{2+}$ (a = 7 Å[33]). The predicted k_I^{max} values of 55 and 19 M^{-1} sec^{-1} are not far from the observed rate constants[19,20] of 33 and 7.1 M^{-1} sec^{-1}.

This correlation between electron transfer and thiocyanate anation rates corroborates the view that the over-all rate of an inner-sphere reduction is limited by the rate at which (in this case) the reducing agent normally undergoes ligand replacement.[34] However, considering the difficulties in calculating an accurate K_0—particularly regarding the somewhat arbitrary choice of a, the unsymmetrical nature of the oxidizing agents, and the existence of interactions other than simple electrostatic repulsions—the good agreement between the predicted rate constants and those found experimentally may be in part fortuitous.

Owing to the similarity in second-order rate constants for both processes, the assumption that mechanism 4 obtains in both simple substitution reactions and inner-sphere reductions leads to the conclusion that the extent of outer-sphere association between two cations can become comparable to that between a cation and an anion. Such a possibility is, however, entirely compatible with eq 10. At high μ (*i.e.*, large κ) K_0 becomes relatively insensitive to charge type. In addition, an increase in a can compensate for electrostatic repulsions—an important consideration in the present case. The distance of closest approach has been taken as approximately 4–5 Å when the ion-pair partners are believed to be separated by only a single water molecule,[16a–c] whereas for the inner-sphere reductions a distance of 7–8 Å seems appropriate. In addition, specific effects not accounted for in (10), such as dipole–dipole attractions and hydrogen bonding, may also compensate for Coulombic repulsions. It is believed[35] that specific interactions of the hydrogen-bonding type are in part responsible for the substantial outer-sphere association between $C_2O_4^{2-}$ (and $HC_2O_4^-$) and $Cr(C_2O_4)_2(H_2O)_2^-$.

The V(III) Reaction.—The available kinetic data on the substitution reactions of tripositive hexaaquo complexes are not as comprehensive as for the bipositive ions.[13] Furthermore, the acidity of these complexes introduces an ambiguity regarding the nature of the reactants; in the case of basic ligands, the reactants may be regarded as either MOH_2^{3+} and L^- or MOH^{2+}

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[29] An order of magnitude discrepancy between theory and experiment becomes especially significant when one considers that Co(II), with *no* CFSE, is only about 30 times more labile than the highly stabilized Ni(II).[13,17]

[30] E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).

[31] Calculated using the crystallographic radii cited in ref 23, pp 48, 49, 66, 67.

[32] Assuming the metal ion centers to be separated by a water and ethylenediamine molecule.

[33] Assuming the metal ion centers to be separated by two water molecules.

[34] This is not a trivial point, since there is at least one way in which the binding of an oxidizing agent to V(II) could differ fundamentally from the binding of a simple ligand. It involves attack on the face of V(II) by the oxidizing agent, resulting in expansion of the V(II) coordination shell. The driving force for such a process has been discussed in terms of orbital symmetries. See H. Taube in "Topics in Modern Inorganic Chemistry," W. O. Milligan, Ed., Welch Foundation Conference on Chemical Research, 1963, p 7.

[35] H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 706 (1967).

and HL. The ligand dependency observed in Fe(III) anations has been reduced by invoking the latter formulation,[36] and it has been suggested that here again substitution rates are controlled primarily by loss of coordinated water.[36]

The available rate constants for the formation of mono complexes between trivalent aquo ions and *weakly* basic anions are listed in Table II, together with some first-order water-exchange constants. The Cr(III)-Br^- and Cr(III)-Cl^- data have been calculated from hydrolysis rates and stability constants. Note that both Fe(III) and Cr(III) anations appear to be ligand dependent with respect to SCN^- and, moreover, show little relationship to eq 5. K_0 for these reactions[37,38] is close to 1, leading to k_1/k_{ex} ratios as small as 0.0007. To be consistent with eq 5, k_1/k_{ex} should not be far from unity.[39] The uncertainties in relating k_f to k_{ex} in the trivalent series, together with the possibility of an SN2 displacement on V(III) (see below), make an estimate of $k_{ex,V(III)}$ rather tenuous. However, in the absence of any direct measurements of the V(III)-exchange rate, even a rough approximation is of interest. An entry for $k_{ex,V(III)}$ has therefore been included in Table I, based on the analog of eq 7 and the appropriate Fe(III) rate constants. The Cr(III) data give a similar value of 1×10^3 sec^{-1}.

TABLE II

SECOND-ORDER ANATION RATE CONSTANTS (M^{-1} SEC^{-1}), FIRST-ORDER WATER-EXCHANGE RATE CONSTANTS (SEC^{-1}), AND THE RELATIVE REACTIVITIES OF THE AQUO AND HYDROXO FORMS OF VARIOUS TRIVALENT HEXAAQUO COMPLEXES. UNLESS OTHERWISE NOTED, ENTRIES ARE FOR 25°

M	pK_a[a]	L	k_f	$k_f^{HO^-}/k_f$[b]	Ref
V(III)[c]	2.7	SCN^-	104	$\leqslant 2$[d]	This work
Cr(III)	4.0	SCN^-	180×10^{-8}	30	*e*
		Cl^-	2×10^{-8}	1×10^3	*f, g*
		Br^-	1×10^{-8}	2×10^3	*h, g*
		H_2O[m]	25×10^{-7}	$\leqslant 20$[d]	*i*
Fe(III)	2.8	SCN^-	127	80	*j*
		Cl^-	9	1×10^3	*j*
		Br^-[k]	20	1×10^2	*j*
		H_2O[m]	3.3×10^3 10^3	$\sim 1 \times 10^2$	*j*
Co(III)	0.7[l]	Cl^-	$\leqslant 2$	$\geqslant 1 \times 10^2$	*l*
Rh(III)	3.2[n]	H_2O[m]	2×10^{-5}	2×10^2	*n*

[a] Taken from ref 35 unless otherwise noted. Most values refer to ionic strengths of 1–3 *M*. [b] $k_f^{HO^-}$ defined as: $k_f^{HO^-}$ = rate/[MOH^{2+}][L]. [c] At 23°. [d] Calculated from the aquo ion pK_a and the lowest acidity studied. [e] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955). [f] R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964). [g] T. H. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). [h] J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960). [i] J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954). [j] Ref 36. [k] At 22 ± 2°. [l] T. J. Conocchioli, *et al.*, *Inorg. Chem.*, **5**, 1 (1965). [m] The exchange rate constant for a particular water in the hexaaquo complex. [n] W. Plumb and G. M. Harris, *Inorg. Chem.*, **3**, 542 (1964); data refer to 64°.

Qualitatively, the V(III) results are also consistent with crystal field theory and illustrate the kinetic stability of the d^3 configuration in the trivalent series. Cr(III) (d^3) and V(III) (d^2) are of the same charge and quite similar with respect to size and affinity for SCN^-, yet V(III)—which enjoys considerably less crystal field stabilization energy[23]—is 10^8 more reactive. The importance of crystal field effects is also suggested by the fact that the SCN^- rate constant is nearly the same for V(III) and Fe(III) and is of the same order of magnitude as that found for Ti(III).[39] The CFAE for all three ions is predicted to contribute very little to the total activation energy,[23] and therefore the rates are expected to be of nearly the same order of magnitude. These conclusions are reached for either an SN1 or an SN2 mechanism.

The labilities of V(III) and Ti(III) relative to Cr(III) are also predicted by valence bond theory.[22] Of the hexaaquo transition complexes, V(III) and Ti(III) alone possess unoccupied nonbonding d orbitals. This could have important consequences regarding promotion of ligand–metal bond formation in the activated complex. That the V(III) reaction proceeds through an SN2-type mechanism is, in fact, suggested by its acid independence. Tripositive cations generally undergo substitution more rapidly as the acidity is decreased, presumably due to an enhancement in the rate of SN1 loss of inner-sphere water.[40] The apparent uniqueness of V(III) in this respect is illustrated in Table II. The difference between Rh(III), Co(III), Fe(III), and Cr(III) on the one hand and V(III) on the other may arise from a ligand-assisted anation in the latter case. In such a mechanism the hydroxo form must not necessarily be more reactive than the aquo species. This interpretation is corroborated by the observation[39] that $k_f^{OH^-}/k_f$ for the SCN^- anation of Ti(III) is not larger than 1. Also noteworthy is the complete absence of a base-catalyzed path in the muroxide–scandium(III) reaction.[41,42]

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(36) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

(37) Outer-sphere association constants of 1.5 and ~1 (25°, μ = 1 *M*) have been reported for Cr(III)·Cl^- and Cr(III)·SCN^-, respectively,[38] and presumably similar values apply to Fe(III).

(38) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(39) H. Diebler, private communication.

(40) Refer to the discussion at the end of ref 13 for some views on this subject.

(41) G. Geier, *Ber. Bunsenges. Physik. Chem.*, **69**, 617 (1965).

(42) After submitting this article for publication we were notified of the work by B. R. Baker, N. Sutin, and T. J. Welch on the temperature dependence of the V(III)–SCN^- reaction (*Inorg. Chem.*, **6**, 1948 (1967)), in which further evidence in favor of a ligand-assisted mechanism has been deduced from the magnitude of the activation parameters. Using a flow technique, these workers find k_f = 103 ± 10 M^{-1} sec^{-1} and k_d = 0.89 ± 0.06 sec^{-1} at 23.0° and μ = 1 *M*, in satisfactory agreement with our results. We thank Dr. Sutin and associates for communicating this information prior to its publication.