Electrochemical and Homogeneous Exchange Kinetics for Transition-Metal Aquo Couples: Anomalous Behavior of Hexaaquoiron(III/II)

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Rate data for electrochemical and homogeneous redox reactions involving Ru$_{aq}^{3+/2+}$, V$_{aq}^{3+/2+}$, Fe$_{aq}^{3+/2+}$, Eu$_{aq}^{3+/2+}$, and Cr$_{aq}^{3+/2+}$ redox couples (where *aq* represents aquo ligands) have been analyzed and compared by using the rate relations due to Marcus in order to ascertain how the kinetics of outer-sphere electron exchange are dependent upon the metal redox center. The work-corrected rate constants for electrochemical exchange at mercury electrodes, $k_{ex}^e$, were found to be in uniformly good agreement with the rate constants for homogeneous self-exchange, $k_{ex}^h$, extracted from cross-reaction data involving outer-sphere coreactants, yielding the reactivity sequence Ru$_{aq}^{3+/2+}$ $>$ V$_{aq}^{3+/2+}$ $>$ Fe$_{aq}^{3+/2+}$ $>$ Cr$_{aq}^{3+/2+}$ $>$ Eu$_{aq}^{3+/2+}$. However, the measured rate constant for Fe$_{aq}^{3+/2+}$ self-exchange is not consistent with this sequence, being at least 10$^4$-fold larger than the values of $k_{ex}^h$ extracted from both the homogeneous cross-reaction and electrochemical data. The latter values of $k_{ex}^h$ and also $k_{ex}^e$ are in harmony with the relative inner-shell barriers for Fe$_{aq}^{3+/2+}$ and Ru$_{aq}^{3+/2+}$ calculated from crystallographic structural data. The above reactivity sequence is also consistent with the relative structural changes accompanying electron transfer as monitored by the corresponding reaction entropies.

Recent developments in the theory of outer-sphere electron transfer have focused attention on the contribution of inner-shell reorganization, $\Delta G_{is*}$, to the intrinsic free energy barrier for electron exchange $\Delta G_{ex*}$. Transition-metal redox couples containing only aquo ligands, of the type $M_{aq}^{3+} + e^- \rightarrow M_{aq}^{n+}$ where $M = Ru, Fe, Co, V, and Eu$, form an especially interesting series in which to compare the theoretical predictions with experiment since they exhibit large differences in redox reactivity that are likely to be due primarily to the influences of the metal electronic structure upon $\Delta G_{ex*}$. Some of these reactions exhibit remarkably small exchange rates.

Experimental estimates of $\Delta G_{ex*}$ can be obtained from the rates of homogeneous self-exchange or electrochemical exchange or, less directly, from the kinetics of suitable homogeneous cross-reactions with other redox couples having self-exchange kinetics that are known or can be estimated. Relationships between the kinetics of these reactions are given by the well-known equations derived from an adiabatic electron-transfer model:

$$k_{ex}^h / A_h \leq (k_{ex}^h / A_h)^{1/2}$$  (1)

and

$$k_{ex}^h = 2^{1/2} (k_{ex}^h / k_{ex}^{h2} K_{i2})^{1/2}$$  (2a)

where

$$\log f = (\log K_{i2})^2/[4 \log (k_{ex}^h k_{ex}^{h2} / A_h)]$$  (2b)

In eq 1, $k_{ex}^h$ and $k_{ex}^h$ are the corresponding rate constants for electrochemical exchange and homogeneous self-exchange for a given redox couple and $A_h$ and $A_h$ are the electrochemical and homogeneous frequency factors, respectively. In eq 2, $k_{ex}^h$ and $k_{ex}^{h2}$ are the rate constants for the parent self-exchange reactions corresponding to the homogeneous cross-reaction having a rate constant $k_{ex}^{h2}$ and equilibrium constant $K_{i2}$. All these rate constants are presumed to be corrected for work terms. A given rate constant for homogeneous self-exchange $k_{ex}^h$ can be related to the corresponding intrinsic barrier $\Delta G_{ex*}$ by:

$$k_{ex}^h = \kappa A_h \exp(-\Delta G_{ex*}^* / RT)$$  (3)

where $\kappa$ is an electronic transmission coefficient. The rate constant for electrochemical exchange $k_{ex}^e$ can also be related to $\Delta G_{ex*}$ by:

$$k_{ex}^e = \kappa A_e \exp(-\Delta G_{ex*}^e / RT)$$  (4a)

$$k_{ex}^e = \kappa A_e \exp(-\Delta G_{ex*}^e + C / 2RT)$$  (4b)

where $\Delta G_{ex*}^e$ is the intrinsic electrochemical barrier. The factor 2 arises in eq 4b because only one reactant is required to be activated in the electrochemical reaction, rather than a pair of reactants as in the homogeneous case. The contributions to $\Delta G_{ex*}^e$ and $\Delta G_{ex*}^e$ arising from inner-shell (i.e., metal–ligand) reorganization, $\Delta G_{is*}^e$ and $\Delta G_{is*}^e$, respectively, are therefore related by $\Delta G_{is*}^e = 2 \Delta G_{is*}^e$. The relationship between the components of $\Delta G_{ex*}^e$ and $\Delta G_{ex*}^e$ due to outer-shell (i.e., solvent) reorganization, $\Delta G_{os*}^e$ and $\Delta G_{os*}^e$, is somewhat less straightforward. According to a dielectric continuum treatment, these quantities are given by:

$$\Delta G_{os*}^e = \frac{e^2}{4} \left( \frac{1}{a - R_h} \right) \left( \frac{1}{e_{op} - e_i} \right)$$  (5a)

$$\Delta G_{os*}^e = \frac{e^2}{8} \left( \frac{1}{a - R_e} \right) \left( \frac{1}{e_{op} - e_i} \right)$$  (5b)

where $e$ is the electronic charge, $a$ is the (average) reactant radius, $e_{op}$ and $e_i$ are the optical and static dielectric constants, $R_h$ is the close contact distance between the homogeneous redox centers, and $R_e$ is twice the distance between the reactant and the electrode surface. It is generally expected for outer-sphere reactions that $R_e > R_h$; therefore, $\Delta G_{ex*} < 2 \Delta G_{os*}$. The quantity $C$ in eq 4b accounts for this inequality, which is also the origin of the inequality sign in eq 1; from eq 4 and 5

$$C = \frac{e^2}{4} \left( \frac{1}{R_h - \frac{1}{R_e}} \right) \left( \frac{1}{e_{op} - e_i} \right)$$  (6)

Equation 1 can therefore be written in the more general form

$$2 \log (k_{ex}^e / A_h) = \log (k_{ex}^e / A_h) - C / 2.303RT$$  (7)
For a series of reactants having similar sizes and structures, as for the present aquo couples, $R_a$ and $R_c$ and hence $C$ should remain approximately constant.

It is desirable to obtain a self-consistent set of experimental values of $k_{ex}^{app}$ or $k_{ec}$ for comparison with theoretical predictions obtained from calculated values of $\Delta G_{ex}^*$ by using eq 3 and 4. This task is less straightforward than is commonly presumed for two reasons. First, the experimental values of $k_{ex}^{app}$ or $k_{ec}$ may not refer to outer-sphere pathways since (except for $Ru_{aq}^{3+/2+}$) at least one of the aquo reaction partners is substitutionally labile so that more facile inner-sphere pathways may provide the dominant mechanism. Second, values of $k_{ex}^{app}$ derived by using eq 2 from rate constants for appropriate outer-sphere cross-reactions not only rely on the availability of values of $k_{ex}^{app}$ for the correacting redox couple along with values of $K_1$, but also depend on the applicability of this relation 10,11. The resulting estimates of $k_{ex}^{app}$ for different redox couples are often difficult to compare since large systematic errors can be introduced by the use of cross-reaction data involving structurally different coreactants, inappropriate electrode potential data, etc.

In spite of their direct relationship to the desired intrinsic barriers, electrochemical exchange rate data have seldom been utilized for this purpose. One reason is that these data have commonly been gathered at ill-defined solid surfaces where the work terms arising from double-layer effects are large and unknown, precluding quantitative intercomparison of the results. However, we have determined accurate electrochemical rate data for $V_{aq}^{3+/2+}$, $Cr_{aq}^{3+/2+}$, $Eu_{aq}^{3+/2+}$, $Ru_{aq}^{3+/2+}$, and $Fe_{aq}^{3+/2+}$ at the mercury–aqueous interface under conditions where the work terms are small and can be estimated with confidence 12-14. The interactions between the reactant and the metal surface are likely to be weak and nonspecific, so that the electrode can be viewed as providing an inert electron source or sink that does not influence the electron-transfer barrier. This allows information on the electron-transfer barrier to be gathered for individual redox couples as a function of the thermodynamic driving force. Such information is largely inaccessible from the kinetics of homogeneous electron transfer.15

The in the present paper, suitable rate data for electrochemical and homogeneous reactions involving aquo redox couples are analyzed and compared with use of eq 2 and 7 in order to ascertain in unambiguously as possible how the kinetics of outer-sphere electron exchange depend on the metal redox center.

### Rate Constants for Electrochemical Exchange

Table I contains a summary of rate parameters for the electrochemical exchange of $Ru_{aq}^{3+/2+}$, $V_{aq}^{3+/2+}$, $Fe_{aq}^{3+/2+}$, $Eu_{aq}^{3+/2+}$, and $Cr_{aq}^{3+/2+}$ at the mercury–aqueous interface, using potassium hexafluorophosphate and lanthanum perchlorate supporting electrolytes. These experimental conditions minimized the extent of the electrostatic double-layer effect upon the apparent rate constants for electrochemical exchange, $k_{ex}^{app}$ (i.e., the “standard” rate constants measured at the formal potential $E_f$ for the redox couple concerned), enabling values of the work-corrected rate constants, $k_{ex}^{app}$, to be evaluated with confidence by using 16

$$\ln k_{ex}^{app} = \ln k_{ex}^{app} + \frac{F}{RT}(Z_f - \alpha_{cor})\phi_d$$

| redox couple | electrolyte | $E_f^{1b}$ (mV vs. SCE) | $k_{ex}^{app}$ (cm s$^{-1}$) | $\varphi_d$ (mV) | $k_{ex}^{app}$ (cm s$^{-1}$)
---|---|---|---|---|---
$Ru_{aq}^{3+/2+}$ | 0.4 M KPF$_6$ | -20 | 5 x 10$^{-3}$ | 10 | 2 x 10$^{-2}$
$V_{aq}^{3+/2+}$ | 0.2 M KPF$_6$ | 472 | 1.5 x 10$^{-5}$ | 5 | 1 x 10$^{-3}$
$Fe_{aq}^{3+/2+}$ | 0.4 M KPF$_6$ | 495 | 2 x 10$^{-5}$ | 51 | 1 x 10$^{-3}$
$Eu_{aq}^{3+/2+}$ | 0.4 M KPF$_6$ | 625 | 6 x 10$^{-4}$ | 20 | 8 x 10$^{-4}$
$Cr_{aq}^{3+/2+}$ | 0.4 M KPF$_6$ | -655 | 2 x 10$^{-5}$ | 25 | 2 x 10$^{-4}$
$La(ClO$_4$_)$_3$ | 0.2 M KPF$_6$ | 495 | 2 x 10$^{-5}$ | 5 | 1 x 10$^{-3}$

1 Electrocataly contained sufficient (>300-100 mM) acid to suppress significant deprotonation of MOH$_2^+$; b. Formal potential for $Fe_{aq}^{3+/2+}$ in stated electrolyte at 25°C. Values taken from ref 20 and supplemented by unpublished data from this laboratory. c. Measured (apparent) rate constant at mercury electrode in stated electrolyte at formal potential; obtained from ref 12-14. d. Approximate potential across diffuse layer at $E_f$ in given electrolyte; obtained or estimated from ref 12-14. e. Work-corrected rate constant for electrochemical exchange; obtained from $k_{ex}^{app}$ and $\varphi_d$ by using eq 8. f. Estimated as indicated in the text.

where $Z_r$ is the reactant charge number, $\alpha_{cor}$ is the work-corrected cathodic transfer coefficient, and $\varphi_d$ is the potential drop across the diffuse layer. Details of this procedure are given in ref 12–14. The KPF$_6$ electrolyte provides an especially suitable medium for this purpose. This is because $\varphi_d$ is small over a wide potential range positive of the potential of zero charge (~440 mV vs. SCE) since the positive electronic charge density at the electrode is matched approximately by the charge density due to specifically adsorbed PF$_6^-$ anions.13,16 The rate data in Table I all refer to acid-independent pathways. In contrast to homogeneous reactions between aquo cations, the rates of most of these reactions are independent of pH at values (≤pH 2.5) below which the formation of hydroxo complexes is unimportant. The single exception is $V_{aq}^{3+/2+}$, which exhibits a significant inverse acid-dependent pathway at pH ≥3.17

The formal potential for $Fe_{aq}^{3+/2+}$ is too positive (495 mV vs. SCE in 0.4 M KPF$_6$) to allow rate measurements in the vicinity of $E_f$ to be made at mercury since anodic dissolution of the electrode occurs beyond about 375 mV. However, the electroreduction of $Fe_{aq}^{3+}$ was found to be sufficiently irreversible so that the cathodic and normal-pulse polarograms were obtained over the potential range 300–0 mV, yielding values of $k_{ex}$ in 0.4 M KPF$_6$ of $4 \times 10^{-4}$ cm$^{-1}$ at 300 mV and 0.1 cm$^{-1}$ at 0 mV vs. SCE. Extrapolation of the cathodic Tafel plots (i.e., in $k_{ex}$ vs. $E$, where $k_{ex}$ is the apparent cathodic rate constant) was therefore required in order to extract $k_{ex}^{app}$ (app). However, this procedure can be applied with confidence: the work-corrected cathodic transfer coefficients, $\alpha_{cor}$, for several other aquo couples are close to 0.50 (±0.02) over a wide range of cathodic equilibrium potentials.13 The value of the observed transfer coefficient $\alpha_{cor}$ (0.48) for $Fe_{aq}^{3+/2+}$ reduction in 0.4 M KPF$_6$ indicates that the potential dependence of the double-layer effects is likely to be small, as expected. Consequently, the resulting value of $k_{ex}^{app}$ (~2 x 10$^{-5}$ cm$^{-1}$), is likely to be within a factor of 2- to 5-fold of $k_{ex}^{app}$ we have therefore set an upper limit of 1 x 10$^{-4}$ cm$^{-1}$ for $k_{ex}^{app}$ in Table I.

These values of $k_{ex}^{app}$ and $k_{ec}$ are smaller than those commonly reported for Fe$_{aq}^{3+/2+}$ at platinum and gold elec-
trodes.18 However, cathodic voltammograms that are highly irreversible (half-wave potential $E_{1/2} \approx 0$ mV vs. SCE), yielding similarly small values of $k_{ex}^{app}$ ($\approx 10^{-5}$ cm s$^{-1}$), have recently been obtained at platinum and gold in perchlorate media from which halide impurities have been rigorously excluded.18 The larger values of $k_{ex}^{app}$ are therefore due to the presence of halide-catalyzed, possibly inner-sphere, pathways.19 Rate measurements at dropping mercury electrodes are not susceptible to such difficulties since the surface is continuously renewed and adsors most anions much more weakly than do noble metals.

The electrochemical reactivities of Fe$_{aq}^{3+/2+}$ and Ru$_{aq}^{3+/2+}$ provide an interesting comparison. At the formal potential for Ru$_{aq}^{3+/2+}$ in 0.4 M KPF$_6$ = -20 mV vs. SCE, the observed rate constant for electroreduction of Fe$_{aq}^{3+}$ is 0.15 (±0.05) cm s$^{-1}$. This value is only moderately (30-fold) larger than that for Ru$_{aq}^{3+}$ reduction at the same potential, 5 (±2) $\times$ 10$^{-3}$ cm s$^{-1}$, despite the enormous cathodic overpotential (515 mV, corresponding to an equilibrium constant of 5 x 10$^8$) for the former reaction. Since these rate constants were obtained under the same conditions and the reactants are of very similar structure, the work terms will be essentially identical. Any reasonable driving force correction for Fe$_{aq}^{3+}$ reduction therefore must yield a value of $k_{ex}$ ca. 10$^{-2}$-fold smaller than for Ru$_{aq}^{3+}$ reduction, irrespective of the work term corrections upon the individual rate constants. From eq 7, this results in a corresponding estimate of $k_{ex}$ that is ca. 10$^{-2}$-fold smaller for the former reaction (vide infra).

**Rate Constants for Electron Exchange from Homogeneous Cross-Reaction Kinetics**

Table II summarizes pertinent rate and equilibrium data for the acid-independent pathways for cross-reactions Fe$_{aq}^{3+/2+}$, Ru$_{aq}^{3+/2+}$, V$_{aq}^{3+/2+}$, Eu$_{aq}^{3+/2+}$, and Cr$_{aq}^{3+/2+}$, together with the values of $k_{ex}$ for these couples resulting from the application of eq 2. The rate constants for the cross-reactions, $k_{ex}$, and for self-exchange of the various co-reactants, $k_{ex}^{app}$, listed in Table II are taken from literature data; they are corrected for Debye–Hückel work terms as described in ref 11 (see the footnotes to Table II and ref 11 for the data sources). The measured values of $k_{ex}^{app}$, are also

listed, with the ionic strength at which they were determined in parentheses. The equilibrium constants $K_{12}$ given in Table II were obtained from measurements of formal potentials for the appropriate redox couples at ionic strengths comparable (0.1 ≤ μ ≤ 1) to those at which the kinetic data were gathered. (Most of these formal potentials were obtained in our laboratory by using cyclic voltammetry. The uniform use of these data avoids the substantial errors that can arise if literature electrode potential values gathered under disparate conditions are employed to calculate $K_{12}$, as is commonly done.) Although values of $k_{ex}$ for some of the polypyridine redox couples utilized in Table II [Fe(bpy)$_3$]$_{3/2}^+$, Fe(phen)$_3$]$_{3/2}^+$, Os(bpy)$_3]_{3/2}^+$, and Cr(bpy)$_3]_{3/2}^+$ (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline)] have not been determined, they are assumed to be comparable to that obtained for Ru(phen)$_3]_{3/2}^+$; ca. $1 \times 10^4$ M$^{-1}$ s$^{-1}$. The inner-shell reorganization energies for all these couples are likely to be close to zero since they uniformly involve the transfer of a delocalized $t_{2g}$ electron.

Detailed inspection of Table II reveals that work-corrected values of $k_{ex}$ are obtained for each aquo redox couple that are reasonably constant (mostly within ca. 10-fold of each other), at least for cross-reactions having relatively small driving forces (e.g., $K_{12} < 1 \times 10^3$, $f \gtrsim 0.2$). There are good reasons to prefer such weakly exergonic cross-reactions for extracting values of $k_{ex}$ by using eq 2. The assumptions made in deriving eq 2, that the reactions are adiabatic ($\kappa = 1$), the work terms are non-specific, and the reactant and product free energy profiles are harmonic, are questionable, especially for reactions involving aquo cations. However, these factors have only a minor influence upon its applicability to reactions having small driving forces providing that the work terms and $\kappa$ are comparable for the corresponding self-exchange reactions and cross-reactions. Indeed, progressively smaller estimates of $k_{ex}$ are generally determined by using eq 2 from cross-reactions having increasingly large driving forces. These discrepancies have been attributed to the influence of unfavorable specific work terms, anharmonicity, and nonadiabaticity.

The extraction of relative values of $k_{ex}$ for $V_{aq}^{3+/2+}$, $E_{aq}^{3+/2+}$, and $C_{aq}^{3+/2+}$ is facilitated by the proximity of the formal potentials for these couples (~472, ~625, and ~655 mV vs. SCE; $\mu = 0.5$; Table I). Thus, especially reliable values of $k_{ex}$ can be determined from cross-reactions with similarly small driving forces involving common reactants having known self-exchange kinetics. Suitable oxidants for this purpose are Co(phen)$_{3}^{3+/2+}$, Ru(NH$_3$)$_{6}^{3+/2+}$, and V$_5$V$_{aq}^{3+/2+}$. Careful inspection of Table II yields average values of $k_{ex}$ for $V_{aq}^{3+/2+}$, $E_{aq}^{3+/2+}$, and $C_{aq}^{3+/2+}$ of ca. 5 (±4.2) × 10$^{-2}$, 2 (±1.5) × 10$^{-4}$, and ~2 × 10$^{-6}$ M$^{-1}$ s$^{-1}$, respectively.

The estimation of $k_{ex}$ for Ru$_{aq}^{3+/2+}$ self-exchange in the same manner is slightly less straightforward because of the more positive formal potential for this couple (~20 mV vs. SCE; $\mu = 0.4$; Table I). Values of $k_{ex}$ obtained from suitable cross-reactions ($f > 0.2$), involving $V_{aq}^{3+/2+}$, Ru(NH$_3$)$_{6}^{2+/3+}$, Co(phen)$_{3}^{3+/2+}$, Ru(NH$_3$)$_{6}^{2+/3+}$, and Ru(NH$_3$)$_{6}^{3+/4+}$ as reactants, vary by a factor of almost 200 (Table II). However, the relatively low value (0.4 M$^{-1}$ s$^{-1}$) obtained with Co(phen)$_{3}^{3+/2+}$ is also characteristic of cross-reactions involving this oxidant with $V_{aq}^{3+/2+}$, $E_{aq}^{3+/2+}$, and $C_{aq}^{3+/2+}$ (Table II). Also, the estimate $k_{ex}$ for Ru$_{aq}^{3+/2+}$ self-exchange is likely to be too small since the free energy barrier for $V_{aq}^{3+/2+}$ oxidation appears to respond to changes in driving force to a noticeably smaller extent than predicted from eq 2.15 The remaining cross-reactions yield a reasonably consistent estimate of $k_{ex}$ for Ru$_{aq}^{3+/2+}$ of ca. 50 (±20) M$^{-1}$ s$^{-1}$. (A somewhat larger estimate of $k_{ex}$ for ca. 200 M$^{-1}$ s$^{-1}$ was obtained at a previous related argument but involved extrapolation of values of $k_{ex}$ obtained from cross-reactions having highly varying driving forces.)

The "observed" value of $k_{ex}$ for $V_{aq}^{3+/2+}$, 3 × 10$^{-2}$ M$^{-1}$ s$^{-1}$ (i.e., that obtained directly from the observed self-exchange kinetics), is close to the estimates obtained from cross-reactions with Co(phen)$_{3}^{3+/2+}$ and Ru(NH$_3$)$_{6}^{3+/4+}$. In contrast, the "observed" value of $k_{ex}$ for Fe$_{aq}^{3+/2+}$, 15 M$^{-1}$ s$^{-1}$, is considerably (10$^{-2}$ to 10$^{-4}$-fold) larger than those derived from cross-reactions having suitably small driving forces ($f > 0.2$; Table II). Equation 2 can be rewritten as

$$
\log k_{12} = 0.5(\log k_{11} + \log k_{22}) + 0.5 \log K_{12} +
\frac{8 \log (k_{11}k_{22}/A^2)}{(9)}
$$

The estimate of $k_{11}$, 60 M$^{-1}$ s$^{-1}$, for Ru$_{aq}^{3+/2+}$ given in ref 15 refers to an ionic strength of 1 M and is therefore uncorrected for work terms. Application of this correction yields $k_{11} = 200$ M$^{-1}$ s$^{-1}$.$^{11}$

Under these conditions it is likely that any residual work terms will affect each value of $k_{12}$ to an essentially equal extent. In addition, the predominant reaction channel for cross-reactions having similarly small driving forces will involve transition-state structures that closely resemble those for the parent self-exchange reactions.$^{15}$

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Suitably small driving forces inevitably involve different co-
applicability of eq 2 could occur. These errors could vitiate
constant being presumed to reflect a "normal" outer-sphere
considered to be falsely small, the observed self-exchange rate
pathway.1°

Therefore, a plot of (2 log $k_{12} - 2$ log $k_{22}$) vs. $[log K_{12} + (log K_{12}/[4 log (k_{11}k_{22}/Z_{13})])]$ should yield a straight line of
slope 1.0 with an intercept equal to log $k_{11}$. Figure 1 shows
such a plot for 32 reactions involving Feaq,2+/3+2/3+,
formally expressed as Feaq3+ oxidations. (The data sources are indicated
by footnote citations; $A_b$ is assumed to equal $1 \times 10^5$ M$^{-1}$ s$^{-1}$.
The value of $k_{11}$ in the last term in eq 9 was obtained by
iteration; for most reactions choosing any reasonable value of
$k_{11}$ in the range $10^{-4}$ to $10^{-12}$ M$^{-1}$ s$^{-1}$ led to essentially identical
results.) The straight line of slope 1.0 in Figure 1 provides the
best fit to the solid points, which refer to the cross-
reactions. The intercept, which equals log $k_{ex}$ for Feaq,3+/2/+,
corresponds to $k_{ex} = 7 \times 10^{-4}$ M$^{-1}$ s$^{-1}$. The open point, which refers to the "observed" value of $k_{ex}$ (15 M$^{-1}$ s$^{-1}$).
The open point, which refers to the "observed" value of $k_{ex}$ (15 M$^{-1}$ s$^{-1}$),
is clearly at variance with the other points, yielding a
discrepancy of over 10-fold in $k_{ex}$. Figure 2 shows a similar
plot for cross-reactions involving Vaq,3+/2+. Although the data
points are less numerous, the open point for Vaq,3+/2+ self-
exchange ($k_{ex} = 3 \times 10^{-2}$ M$^{-1}$ s$^{-1}$) is consistent with the
remaining entries. Admittedly, the slope (0.9) of the best fit
line in Figure 2 differs somewhat from unity; possible causes
are discussed elsewhere.15

Such a behavioral difference between Vaq,3+/2+ and Feaq,3+/2+
has been noted previously.10 The striking discrepancies with
eq 2 for Feaq,3+/2+ were ascribed in part to especially facile
reaction pathways for self-exchange of the cross-reaction partners
that contain pyridine-type ligands arising from
interpenetration of the pyridine rings. Since such interactions
will be absent for the Feaq,3+/2+ cross-reactions, the resulting estimates of $k_{ex}$ for Feaq,3+/2+ (ca. $10^{-4}$ to $10^{-3}$ M$^{-1}$ s$^{-1}$) were
considered to be falsly small, the observed self-exchange rate
constant being presumed to reflect a "normal" outer-sphere
pathway.10

A difficulty in comparing data for cross-reactions involving Feaq,3+/2/+ with the other aquo couples is that the formal potential for Feaq,3+/2+ is substantially more positive of those for the
remaining aquo couples. Therefore, cross-reactions having
suitably small driving forces inevitably involve different co-
reactants with the likelihood that systematic errors in the
applicability of eq 2 could occur. These errors could vitiate its
use for obtaining even relative values of the self-exchange kinetics of Feaq,3+/2+ with respect to the other couples. However,
the comparison of the kinetics of the Os(bpy)$_3$3+-Feaq,2+,

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**Table III. Summary of Rate Constants for Electron Exchange at 25 °C and Comparison with Theoretical Predictions**

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>$k_{ex}^{a}$ cm s$^{-1}$</th>
<th>$k_{ex}^{b}$ M$^{-1}$ s$^{-1}$</th>
<th>$k_{ex}^{eq}$ (eq 7),c</th>
<th>$k_{ex}^{calcd}$,d M$^{-1}$ s$^{-1}$</th>
<th>$\Delta G_{Fe}^{e}$ cal deg$^{-1}$ Fe mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_{aq}$3+/2+</td>
<td>2.0 x 10$^{-3}$</td>
<td>50</td>
<td>25</td>
<td>2.5 x 10$^{-3}$</td>
<td>36</td>
</tr>
<tr>
<td>Va$_{aq}$3+/2+</td>
<td>1.1 x 10$^{-3}$</td>
<td>3 x 10$^{-3}$, [3 x 10$^{-3}$]</td>
<td>6 x 10$^{-3}$</td>
<td>2.5 x 10$^{-3}$</td>
<td>37</td>
</tr>
<tr>
<td>Fe$_{aq}$3+/2+</td>
<td>$\leq$ 1 x 10$^{-4}$</td>
<td>$\leq$ 6 x 10$^{-4}$</td>
<td>90</td>
<td>(3.5 x 10$^{-4}$)</td>
<td>43</td>
</tr>
<tr>
<td>Cu$_{aq}$3+/2+</td>
<td>8.0 x 10$^{-1}$</td>
<td>4 x 10$^{-3}$</td>
<td>4 x 10$^{-3}$</td>
<td>4 x 10$^{-3}$</td>
<td>48</td>
</tr>
<tr>
<td>Cr$_{aq}$3+/2+</td>
<td>2.0 x 10$^{-4}$</td>
<td>2.5 x 10$^{-1}$</td>
<td>1 x 10$^{-4}$</td>
<td>(4 x 10$^{-10}$)</td>
<td>49</td>
</tr>
</tbody>
</table>

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Figure 2. As for Figure 1 but for cross-reactions involving Vaq,3+/2+, expressed as Vaq,3+ oxidations. $k_{ex}$ refers to $k_{ex}$ and $k_{ex}$ self-exchange.

Data sources are from Table II or ref 11 unless indicated otherwise.

Key to oxidants: (1) U$_{4+}^{4+}$; (2) Ru$_{aq}$3+/2+; (3) Ru(NH$_3$)$_3^{2+}$; (4) Ru(NH$_3$)$_2$py$_3^{2+}$; (5) Co(en)$_3^{3+}$; (6) Co(bpy)$_3^{3+}$; (7) Ru(NH$_3$)$_3$jm$_3^{2+}$; (8) Co(phen)$_3^{3+}$; (9) Vaq,3+/2+.

and Vaq,3+-Cr(bpy)$_3^{3+}$ cross-reactions provides a way of
circumventing this problem. Both these reactions have suitably
small driving forces [equilibrium constants of 80 and 1.2,
respectively (Table II)], and the coreacting redox couples,
Os(bpy)$_3^{3+}$/2+ and Cr(bpy)$_3^{3+}$/2+, not only have the same
ligand composition but also are likely to have similarly small
barriers to electron exchange since they both involve electron
acceptance into a delocalized tzs orbital. Therefore, on the
assumptions that the rate constants for Os(bpy)$_3^{3+}$/2+ and
Cr(bpy)$_3^{3+}$/2+ self-exchange, $k_{ex}$ and $k_{ex}$ are equal and that
the $f$ terms are essentially unity, the ratio of the rate constants
for Feaq,3+/2+ and Vaq,3+/2+ self-exchange, $k_{ex}$, can be found from the kinetics and thermodynamic data for
the corresponding cross-reaction by using (eq 2)

\[
k_{ex}^{Fe}/k_{ex}^{Va} (=k_{11}/k_{33}) = k_{22}^{Fe}k_{44}^{Va}/k_{22}^{Va}k_{44}^{Fe}
\]

Inserting the experimental values $k_{11} = 3 \times 10^{3}$, $k_{34} = 1 \times 10^{3}$ M$^{-1}$ s$^{-1}$, $K_{12} = 80$, and $K_{34} = 1.2$ (Table II) into eq 10
yields $k_{ex}^{Fe}/k_{ex}^{Va} = 0.14$. Taking $k_{ex}^{Fe}$ to be $5 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ (vide supra) yields the result $k_{ex}^{Va} = 7 \times 10^{-3}$ M$^{-1}$ s$^{-1}$.24
Ah for the present aquo couples into these expressions yields range of encounter distances ("reaction zone thickness") within Ah and 

between log zone thickness close to the electrode surface, and redox centers in the transition state, 6rh is the approximate of the "best fit" values of estimates of measured self-exchange kinetics. The straight line is the relationship (33) Although a frequency factor formulation based on the simple gas-phase (31) R. A. Marcus, 4rNrh2(6rh)vn/1O3 and in parentheses are ratios of preequilibrium model' using the expressions Ah and (30) B. S. Brunschwig, C. Creutz, D. H. Macartney, Admittedly, the self-exchange rates for Os(bpy)33+/2+ and Cr(bpy)33+'2+ have faster self-exchange kinetics as a result of greater delocalization of the transferred electron, which would yield an even smaller value of 3.5 and Rh greater than that obtained from the self-exchange kinetics.

Comparison between Electrochemical and Homogeneous Exchange Kinetics

Strong evidence supporting the validity of such smaller estimates of khex,aFe is obtained from the rate constants for electrochemical exchange, khex. Table III contains a summary of the "best fit" values of khex and khex,a for each redox couple, along with estimates of khex,a obtained from eq 7, obtained from the corresponding values of khex by using eq 7. The values given in parentheses are ratios of khex,a for each couple, with respect to those for Ruq3+/2+ (khex,a/Ruq3+/2+). The frequency factors A and B required in eq 7 were estimated from an "encounter equilibrium" model11,29-33 using the expressions A = 4πnr2(6n)νp/103 and B = (6n)νp where N is Avogadro's number, r is the average distance between the homogeneous redox centers in the transition state, 6n is the approximate range of encounter distances ("reaction zone thickness") within which electron transfer occurs, 6n is the corresponding reaction zone thickness close to the electrode surface, and 6n is the effective activation electron transfer occurs. Inserting the anticipated values of 6n = 3 Å, 6n = 6n = 1 Å,30,32 and 6n = 1 Å,30,32 for the present aquo couples into these expressions yields A = 3.5 × 1013 M-1 s-1 and A = 1 × 1012 cm s-1. The value of C in eq 7 was estimated to be 3.0 kcal mol-1 by inserting the values R = 7 Å and R = 13 Å into eq 6. (Note that, although there is some uncertainty in the appropriate absolute values of both R and R, this partially cancels in eq 6.)

The absolute as well as relative values of khex,a (eq 7) are seen to be uniformly in good agreement with those values of khex,a (eq 7) obtained from homogeneous cross reactions. This is also illustrated in Figure 3 as a plot of log khex,a against log khex. The straight line represents the correlation predicted from eq 7. The solid points refer to values of khex,a obtained from cross reactions, and the open circles represent the values of khex,a for Veq3+/2+ and Feaq3+/2+ obtained from the self-exchange kinetics. Although all the other entries are consistent with this correlation, that obtained from the Feaq3+/2+ self-exchange kinetics is again about 104-fold larger than expected.

Correlation of Intrinsic Barriers with Reactant Structure

As noted above, it is instructive to compare the variations in the experimental values of khex,a and khex with the structural properties of the redox couples. To a certain extent, the observed reactivity sequence Ruq3+/2+ > Veq3+/2+ > Feaq3+/2+ ≥ Euq3+/2+ > Craq3+/2+ is consistent with structural expectations; the three most reactive couples all involve the acceptance of the transferring electron into a t2g orbital for which the required distortions of the metal–ligand geometry, and hence ΔGis*, are anticipated to be relatively small.3

The calculation of ΔGis* and hence khex,a or khex from electron-transfer theory requires quantitative information on the changes in the metal–ligand bond distances, Δδ, accompanying electron transfer.1,3 Although sufficiently reliable determinations of Δδ are sparse, recent X-ray diffraction measurements have established values for Ru(OH2)63+/2+ and Fe(OH2)63+/2+ of 0.09 Å and 0.14 Å, respectively. An effective value of Δδ for Cr(OH2)63+/2+, equal to 0.20 Å, has also been determined from solution EXAFS measurements.10 The relation

\[ \Delta G_{is}^* = n f_s f_d (\Delta \delta)^2 / 2 (f_2 + f_3) \] (11)

where n is the number of metal–ligand bonds involved (6) and f2 and f3 are the metal–ligand force constants in the divalent and trivalent oxidation states, with the corresponding metal–oxygen stretching frequencies assumed to be 390 and 490 cm-1, respectively.1 yields values of ΔGis* of 3.5, 8.4, and 17.2 kcal mol-1 for Ruq3+/2+, Feaq3+/2+, and Craq3+/2+, respectively. Errors in these values may arise both from anharmonicity of the potential energy surfaces as well as from uncertainties in the appropriate force constants. The effective values of ΔGis* are slightly smaller as a result of nuclear tunneling;1 the nuclear tunneling factors, f, of 1.5, 2, and 6 for Ruq3+/2+, Feaq3+/2+, and Craq3+/2+, respectively.1,3,10 yield effective values of ΔGis* equal to 3.25, 8.0, and 16.1 kcal mol-1, respectively.

The outer-shell contribution to ΔGis*, ΔGis*, can be estimated from eq 5a; again, using the values 6n = 3 Å and R = 7 Å yields ΔGis* = 6.5 kcal mol-1. Inserting the resulting estimates of ΔGis* into eq 3 along with the above estimate of A = 3.5 × 1012 M-1 s-1, and assuming that f = 1 yield the calculated values of khex,a, khex,calcd, listed in Table III. Ratios of khex,calcd with respect to that for Ruq3+/2+, (khex,a/Ruq3+/2+)calcd are also listed in parentheses in Table III alongside the corresponding experimental rate ratios.

(28) Admittedly, the self-exchange rates for Os(bpy)33+/2+ and Cr(bpy)33+/2+ may differ somewhat. However, if anything, the former reaction should have faster self-exchange kinetics as a result of greater delocalization of the transferred electron, which would yield an even smaller value of khex,a from eq 7.


(33) Although a frequency factor formulation based on the simple gas-phase collision model has conventionally been employed to estimate A and A, the use of an "encounter equilibrium" model where activation is considered to occur chiefly via unimolecular activation within a statistical distribution of encounter complexes appears to be physically more appropriate for both homogeneous and electrochemical electron-transfer processes.

(34) Since it is likely that the outer-sphere transition state for electrochemical reactions is separated from the electrode by a layer of water molecules,12 R is estimated to be twice the sum of the reactant radius (∼3.5 Å) and the effective diameter of a water molecule (3 Å).


Electrochemical and Homogeneous Exchange Kinetics

For all three couples it is seen that $k_{c}^{*} < k_{ex}^{*}$ (calcd), the calculated values being about 3-4 orders of magnitude larger than both $k_{ex}$ and $k_{c}$ (calcd). The "observed" value of $k_{ex}$ for $Fe^{3+/2+}$ self-exchange, $k_{ex,Fe}$, is substantially closer to $k_{ex}^{*}$ (calcd), which might be viewed as evidence that this value corresponds more closely to the "true" intrinsic barrier for $Fe^{3+/2+}$. However, the overriding evidence suggests otherwise. Thus, the calculated rate ratio, $(k_{ex,Fe}^{*}/k_{ex,Ru})$, for the $Fe^{3+/2+}$ vs. $Ru^{3+/2+}$ couples $(3.5 \times 10^{6})$ is roughly comparable to the corresponding experimental rate ratio obtained from cross-reactions ($\sim 2 \times 10^{6}$) and electrochemical reactivities ($\sim 3 \times 10^{5}$) but substantially smaller than that obtained by using the "observed" value of $k_{ex}^{*}$ (0.3) (Table III).

Recent calculations suggest that the $Fe^{3+/2+}$ self-exchange reaction is significantly nonadiabatic ($\kappa \approx 0.01$) at the normal ion–ion "contact" distance of 6.9 Å, although some overlap of the reactant cospHERES seems feasible. Since the values of $\kappa$ will depend upon the extent of electronic coupling with the coreactants, and hence upon the electronic and ligand structures, such nonadiabaticity ($\kappa \ll 1$) may account for some disparities in $k_{ex}$ obtained with different coreactants, for example, the low values obtained here by using Co(phen)$_{3}^{3+/2+}$ (vide supra). Nevertheless, although nonadiabatic effects could account in part for the discrepancies between $k_{ex}$ and $k_{ex}^{*}$ (calcd), their inclusion is unlikely to increase the ratio $(k_{ex,Fe}^{*}/k_{ex,Ru})^{calcd}$ since the 4d ruthenium orbitals are more likely to couple effectively than the more compact 3d iron orbitals, thereby yielding larger $\kappa$ values for the $Ru^{3+/2+}$ reactions. Consequently, the rate ratio $k_{ex,Fe}^{*}/k_{ex,Ru}^{*}$ (0.3) obtained from the $Fe^{3+/2+}$ self-exchange kinetics is not consistent with these theoretical expectations.

It might be argued that the discrepancies $k_{ex}^{*}$ (eq 7) $< k_{ex}^{*}$ (calcd) arise at least in part from nonadiabaticity of the electrochemical reactions, especially since current physical models of the double layer suggest that the reactant–electrode distance at the plane of closest approach may be approximately the same as the distance separating the reacting pair in homogeneous outer-sphere reactions. Although such reactions may be marginally nonadiabatic, it is unlikely that they are especially so. Thus, the frequency factors determined from the temperature dependence of rate constants at mercury are not especially anomalous. The $Cr_{aq}^{3+/2+}$ electrochemical exchange reaction at mercury has been ascertained to be only marginally nonadiabatic, $\kappa \approx 0.2-0.5$, from a comparison with the rates of closely related inner-sphere electrode reactions. Even if the electrochemical as well as the homogeneous reactions are indeed nonadiabatic, the $\kappa$ values would appear to be very small (to within, e.g., a factor of 10) independent of a reaction environment for each redox couple in order to account for the consistently good agreement with the predictions of eq 2 and 7. Since $\kappa$ is expected to be sensitive to the nature of the donor and acceptor orbitals in each reactant pair, this implies that $\kappa$ is unlikely to lie below ca. $10^{-3}$, especially in view of the variety of orbital symmetries $(\tau_{sp}, \tau_{sp})$ involved in the present systems.

A major reason for the observed discrepancies between $k_{ex}$ and $k_{ex}^{*}$ (calcd) could arise from a deficiency in the theoretical models used to calculate $\Delta G_{e}^{*}$ and/or the work terms. In addition to the possible errors in the calculated values of $\Delta G_{e}^{*}$ noted above, the outer-shell barrier $\Delta G_{e}^{*}$ could be larger than calculated from eq 5 in both homogeneous and electrochemical environments as a result of alterations in short-range solvent polarization that are known to accompany electron transfer.

Finally, it is instructive to compare the relative values of $k_{ex}$ and $k_{ex}^{*}$ with the reaction entropies $\Delta S_{o}^{*}$ for the redox couples (Table III). The latter values provide a monitor of the changes in solvent polarization that accompany formation of $M_{aq}^{2+}$ from $M_{aq}^{3+}$. The magnitude of $\Delta S_{o}^{*}$ might be expected to parallel $\Delta G^{*}$ and hence $\Delta S_{ex}^{*}$, larger values of $\Delta S_{o}^{*}$ should yield greater alterations in the electron density of the aquo hydroxides and hence more extensive changes in the extent of ligand–solvent hydrogen bonding induced by electron transfer. Indeed, the observed sequence of $\Delta S_{o}^{*}$ values $Ru_{aq}^{3+/2+} < V_{aq}^{3+/2+} < Fe_{aq}^{3+/2+} < Eu_{aq}^{3+/2+} < Cr_{aq}^{3+/2+}$ uniformly parallels the observed reaction sequence (Table III) although yet again the values of $k_{ex}^{*}$ for $Fe_{aq}^{3+/2+}$ obtained from self-exchange data is not consistent with this trend.

Conclusions and Mechanistic Implications

Taken together, the above results provide strong support to the suspicions noted previously that the intrinsic barrier to outer-sphere electron exchange for $Fe^{3+/2+}$ is significantly greater than anticipated from the measured self-exchange kinetics. Persuasive evidence is provided by the observation that the electrochemical reactivity of $Fe^{3+/2+}$ is noticeably smaller than that of $Ru^{3+/2+}$ and even $V_{aq}^{3+/2+}$ under the same or comparable conditions at the mercury–aqueous interface and by the uniformly good agreement between $k_{ex}^{*}$ (eq 7) and the values of $k_{ex}^{*}$ extracted from homogeneous cross-reactions having suitably small driving forces and structurally similar coreactants. On this basis, the reported self-exchange rate constant for $Fe_{aq}^{3+/2+}$ may well be at least $10^{3}$-fold larger than that corresponding to the "normal" outer-sphere intrinsic barrier for this couple in other homogeneous and also electrochemical environments.

It remains to consider physical reasons for the enhanced reactivity of the $Fe_{aq}^{3+/2+}$ couple when undergoing self-exchange. One possibility is that the "observed" value of $k_{ex}^{*}$ refers to a "normal" outer-sphere pathway, the electrochemical and homogeneous cross-reaction data corresponding to "abnormal", for example strongly nonadiabatic, pathways that are all less favorable by about $10^{3}$- to $10^{5}$-fold in $k_{ex}$ while not beyond the bounds of possibility. However, the weight of evidence presented above would seem to strongly favor this explanation. A more likely possibility is that the self-exchange reaction proceeds via a more facile inner-sphere pathway. Although the presence of an acid-independent pathway for $Fe_{aq}^{3+/2+}$ self-exchange has recently been confirmed by using mixed LiClO$_{4}$–HClO$_{4}$ electrolytes, this result by no means eliminates the possibility that the observed pathway involves a water-bridged inner-sphere transition state. The observed acid-independent rate constant for $Co_{aq}^{3+/2+}$ self-exchange has recently been demonstrated to be ca. $10^{3}$-fold larger than that obtained from cross-reaction data and attributed to the presence of a water-bridged pathway. It was suggested that the dominant presence of such pathways may be confined to redox couples such as $Co_{aq}^{3+/2+}$ with extremely positive standard potentials on the basis of a model where the inner-sphere reaction coordinate involves metal-bridging ligand homolysis. Such a pathway would, all other factors being
equal, be less favorable for Feeq⁴⁺/²⁺ self-exchange since Feeq¹⁺ is a considerably less strong oxidant than Coeq³⁺. However, this could easily be offset by the manifold other factors that control the relative rates of competing inner- and outer-sphere pathways. In any case, on this basis water bridging is more likely for Feeq³⁺/²⁺ self-exchange than for the other aquo complexes considered here; aside from Ru eq³⁺/²⁺, which is constrained to follow outer-sphere pathways, all the other couples considered here are ca. 1 V less strongly oxidizing than Feeq³⁺/²⁺. Such pathways are clearly unavailable for cross-reactions involving substitutionally inert coreactants such as those in Table II, so that the Feeq³⁺/²⁺ reactivity within these environments should reflect that for a “normal” outer-sphere pathway. Water- or hydroxo-bridged pathways are also unlikely within electrochemical redox environments, especially at mercury electrodes in view of the weak interaction between water molecules and this surface.51

Regardless of the detailed reasons for the anomalous behavior of Feeq³⁺/²⁺ self-exchange it can be concluded that this couple is in some respects a nonideal choice for the detailed comparisons between experimental rate parameters and the predictions of contemporary theory. Nevertheless, the required structural information is becoming available for a number of other redox couples,50 enabling such comparisons to be made not only for self-exchange reactions50 but also for a variety of cross-reactions and electrochemical processes.43

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Registry No. Ru, 7440-18-8; V, 7440-62-2; Fe, 7439-89-6; Eu, 7440-53-1; Cr, 7440-47-3.


(50) It was asserted49 that the Coeq³⁺—Feeq⁴⁺ reaction follows an outer-sphere pathway on the basis of the agreement with the rates of other cross-reactions involving Coeq³⁺ and outer-sphere reductants calculated by using eq 2 and the measured value of k⁴⁻⁴⁻. However, using the present estimate of k⁴⁻⁴⁻ for outer-sphere Feeq³⁺/²⁺ self-exchange instead yields a Coeq³⁺—Feeq⁴⁺ reaction rate ca. 10⁻³-fold larger than predicted from eq 2, indicative of a water-bridged pathway for this reaction as well.

(49) Footnote 54 of ref 26.

Activation Volume as Evidence for a Dissociative-Interchange Mechanism of Nickel(II) Ion Complexation with Isoquinoline in Water, N,N-Dimethylformamide, Acetonitrile, Methanol, and Ethanol

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Activation volumes for the complexation of nickel(II) ion with isoquinoline in various solvents were determined by a high-pressure stopped-flow technique. Values of activation volume for formation and dissociation of the (isoquinoline)nickel(II) complex are respectively 7.4 ± 1.3 and 8.9 ± 0.8 cm³ mol⁻¹ in water, 9.3 ± 0.3 and 12.2 ± 0.3 cm³ mol⁻¹ in N,N-dimethylformamide, 12.8 ± 0.6 and 9.9 ± 0.5 cm³ mol⁻¹ in methanol, and 12.6 ± 0.5 and 15.7 ± 1.1 cm³ mol⁻¹ in ethanol. The activation volume of the complex formation in acetoneitrile is 9.4 ± 0.1 cm³ mol⁻¹. All the positive values of the activation volume strongly indicate that the ligand substitution reactions on nickel(II) ion proceed via a dissociative-interchange mechanism in these solvents.

Introduction

Activation volumes for solvent exchange on metal ions including transition metals and typical elements in various solvents have been extensively measured by a high-pressure NMR method,1,2 while for complex formation there are not as many data of activation volumes.3 Caldin and Greenwood have recently reported volumes of activation for the complexation of nickel(II) ion in nonaqueous solvents by using a high-pressure laser-flash temperature-jump technique.36

We have studied the mechanism of iron(III) ion complexation on the basis of activation volume obtained by a high-pressure stopped-flow apparatus.4,5 The sign of activation volume for complexation will reflect the character of a metal ion. Thus the high-pressure stopped-flow technique is a powerful and reliable tool for the mechanistic investigation of complex formation. We present a high-pressure study on the complex formation of nickel(II) ion with isoquinoline in various solvents. This paper will provide a unified aspect of the mechanism of nickel(II) ion complexation.

Experimental Section

Solvents. Nonaqueous solvents purchased from Wakojunyaku (Osaka, Japan) were purified just before use. Distilled water was redistilled in the presence of alkaline potassium permanganate. Reagent grade acetoneitrile was fractionally distilled twice from a packed column at high reflux ratio over diposphorous pentoxide (2 g/dm³) and calcium hydride (4 g/dm³). The reflux was performed for 1 h prior to each distillation. Reagent grade methanol was dried over 3Å molecular sieves for a few days and then twice distilled.

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