Kinetics of Reactions of Aqueous Iron(III) Ions with Azide and Thiocyanate at High Pressures

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A high-pressure stopped-flow study of the reaction of $Fe^{III}(aq)$ with HN_3/N_3^- at 25 °C and ionic strength 1.0 mol kg^{-1} showed that two pathways predominated: (a) the previously unreported pathway involving $Fe(H_2O)_5OH^{2+}$ and N_3^- (rate constant $k_{bb} = 3.8 \times 10^5$ kg mol^{-1} s^{-1}, volume of activation $\Delta V_{bb}^* = +12.9 \pm 1.5$ cm^3 mol^{-1}) and (b) the reaction of $Fe(H_2O)_5OH^{2+}$ with HN_3 ($k_{ba} = 5.0 \times 10^3$ kg mol^{-1} s^{-1}, $\Delta V_{ba}^* = +6.8 \pm 0.5$ cm^3 mol^{-1}). A third pathway involving $Fe(H_2O)_6^{3+}$ and HN_3 was barely detectable. The isomeric alternative to pathway b, in which $Fe(H_2O)_6^{3+}$ would react directly with N_3^-, can be ruled out by consideration of these kinetic data relative to those for reactions of $Fe^{III}(aq)$ with other nucleophiles, notably NCS^-. In this context, the latter reaction has been reexamined by stopped-flow spectrophotometry at pressures up to 200 MPa to resolve serious discrepancies existing in the literature; for $Fe(H_2O)_6^{3+} + NCS^-$, $\Delta V_{ab}'^* = -5.7 \pm 0.3$ cm^3 mol^{-1} and the equilibrium molar volume change is $+11.8 \pm 0.3$ cm^3 mol^{-1}, while for $Fe(H_2O)_5OH^{2+} + NCS^-$, $\Delta V_{bb}'^* = +9.0 \pm 0.4$ cm^3 mol^{-1}, agreeing with the stopped-flow results of Funahashi et al. (*Inorg. Chem.* **1983**, *22*, 2070) but contradicting the results obtained by several groups using temperature- or pressure-jump methods. Possible sources of these discrepancies are considered. The mechanisms of these reactions of $Fe(H_2O)_5OH^{2+}$ may be described as I_d, and those of $Fe(H_2O)_6^{3+}$ as I_a, within the limitations of this classification.

Introduction

The study reported here grew out of our long-standing interest in the kinetics and mechanism of ligand substitution by azide ion in solution, on the one hand,[1-4] and in the kinetic effects of high pressure, on the other. Although there exists a substantial body of high-pressure kinetic data on the substitution of water in $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ by a variety of nucleophiles X^{n-},[5-17] the case of $X^{n-} = N_3^-$ or HN_3 is conspicuously absent, despite the relative ease of monitoring the formation of red $Fe(H_2O)_5N_3^{2+}$ (molar absorbance 3680 L mol^{-1} cm^{-1} at 460 nm)[18] through stopped-flow spectrophotometry in the visible region[19] (cf. $Fe(H_2O)_5NCS^{2+}$, the formation of which is widely used in testing fast-reaction devices).

Unlike Cl^-, NCS^-, etc., azide ion is the anion of a rather weak Brønsted acid ($pK_A = 4.42$ at 25 °C, ionic strength $I = 1.0$ mol L^{-1}); relative to this, $Fe(H_2O)_6^{3+}$ is quite acidic ($pK_A = 2.69$ under the same conditions).[20] Consequently, in moderately acidic solutions, the predominant form of the azide in the iron(III)–azide reaction is HN_3 rather than N_3^-, and a substantial fraction

of the Fe^{III} will be present as $Fe(H_2O)_5OH^{2+}$. It is not possible, on the basis of the rate equation alone, to distinguish pathway 1 (which would be directly comparable with those for the

$$Fe(H_2O)_6^{3+} + N_3^- \xrightarrow{k_{ab}} Fe(H_2O)_5N_3^{2+} + H_2O \qquad (1)$$
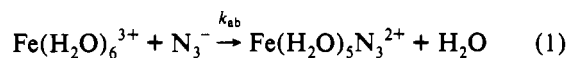
corresponding reactions of $Fe(H_2O)_6^{3+}$ with Cl^-, NCS^-, etc.) from pathway 2, which has an isomeric transition state.

$$Fe(H_2O)_5OH^{2+} + HN_3 \xrightarrow{k_{ba}} Fe(H_2O)_5N_3^{2+} + H_2O \qquad (2)$$
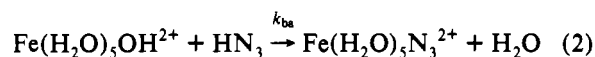
We use the subscripts a and b to rate constants k to designate pathways in which the reactants are the (conjugate) acid and (conjugate) base forms of $Fe^{III}(aq)$ and the nucleophile, respectively.

Seewald and Sutin, in their kinetic study of the aqueous iron(III)–azide reaction,[19] pointed out that the rate constant k_{ba} calculated on the basis of pathway 2 was of the order expected from experience with other reactions of $Fe(H_2O)_5OH^{2+}$, which is typically some 10^3-fold more labile than $Fe(H_2O)_6^{3+}$[21] and shows much less selectivity toward nucleophiles.[22] If, on the other hand, the calculation is based on pathway 1, the rate constant k_{ab} turns out to be 1000-fold larger for $X^- = N_3^-$ than that for $X^- = NCS^-$, so that, if pathway 1 were dominant, one would have to accept that azide ion is either an unusually strong nucleophile toward $Fe^{III}(aq)$ or abnormally strongly preassociated with it—or both. These latter possibilities cannot be dismissed lightly; $Fe(H_2O)_6^{3+}$, like $Cr(H_2O)_6^{3+}$,[22,23] does display significant selectivity toward nucleophiles, and it is known[4] that N_3^- is about 4 times more strongly ion paired, and 25 times more reactive within the ion pair, than NCS^- with $Cr(DMF)_6^{3+}$ at 71 °C in the aprotic solvent DMF (DMF = N,N-dimethylformamide)—that is, in a system where there can be no analogue of pathway 2.

It has been argued[1-3,23] that the incursion of conjugate acid/conjugate base (CACB) pathways such as (2) in the reactions of Brønsted bases with complexes having acidic protons on ligand donor atoms may be manifested through anomalously positive

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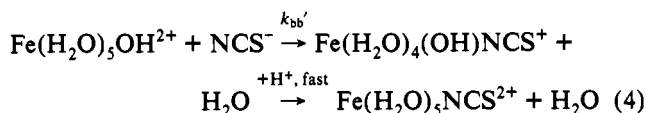(20) Martinez, P.; van Eldik, R.; Kelm, H. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 81.

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entropies of activation $\Delta S^{\ddagger}$ (this applies to both the forward and reverse reactions, since we are considering only alternative pathways between the same stoichiometric reactants and products). It may therefore be expected that the corresponding volumes of activation $\Delta V^{\ddagger}$ $(=-RT(\partial \ln k/\partial P)_T)$, which tend to be loosely correlated with $\Delta S^{\ddagger}$,[24] will also be more positive than otherwise expected if CACB pathways are dominant.[3] If, for the aqueous iron(III)–azide reaction, pathway 2 dominates and $\Delta V_{ba}^{\ddagger}$ is calculated on the assumption that the reacting species are $Fe(H_2O)_5OH^{2+}$ and HN_3, $\Delta V_{ba}^{\ddagger}$ should be markedly more positive than found for substitutions of $Fe(H_2O)_6^{3+}$ by nonbasic X^{n-}. At the same time, calculation of $\Delta V_{ab}^{\ddagger}$ on the supposition that the reactants are as in pathway 1 should give a value that is far too positive if in fact (2) is dominant, since the volumes of ionization ΔV_A of uncharged aqueous acids H_nX are invariably quite strongly negative[25,26] while ΔV_A for the acid ionization ("hydrolysis") of metal aqua ions is typically close to zero.[10,25,27] Thus, pressure effects are potentially effective criteria of the operation (or otherwise) of CACB pathways, so long as the corresponding data for "normal" reference reactions are available.

The most appropriate reference reaction for the $Fe^{3+}(aq)$–azide case is that of $Fe^{3+}(aq)$ with NCS^-. However, the reported $\Delta V_{ab}^{\prime\ddagger}$ values for reaction 3 range from +7.1 to –6.1 cm^3

$$Fe(H_2O)_6^{3+} + NCS^- \xrightarrow{k_{ab}'} Fe(H_2O)_5NCS^{2+} + H_2O \quad (3)$$
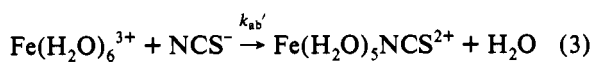
mol^{-1},[5,6,9,11,13,15] and there is a smaller but still unacceptable spread in $\Delta V_{bb}^{\prime\ddagger}$ for the analogous reaction of $Fe(H_2O)_5OH^{2+}$ (primes designate reaction of $Fe^{III}(aq)$ with thiocyanate):

$$Fe(H_2O)_5OH^{2+} + NCS^- \xrightarrow{k_{bb}'} Fe(H_2O)_4(OH)NCS^+ +$$
$$H_2O \xrightarrow{+H^+, fast} Fe(H_2O)_5NCS^{2+} + H_2O \quad (4)$$

We have therefore also reinvestigated the kinetics of the $Fe^{III}(aq)/NCS^-$ reaction at high pressure in detail.

Experimental Section

Materials. Solutions of iron(III) perchlorate (Fluka AG) were standardized by Ce^{IV} titration after passage through a Jones reductor[28] or by spectrophotometry as $Fe(phen)_3^{2+}$ in chloride media after removal of interfering perchlorate on a Dowex 1–X4 anion-exchange column.[29] Sodium azide (BDH, AR grade) solutions were standardized by Ce^{IV} titration. Sodium thiocyanate (Baker and Adamson) was recrystallized twice from water and standardized gravimetrically as AgNCS. Stock acid solutions were prepared from 69.9% $HClO_4$ (Baker Analyzed) and standardized against NaOH. Sodium perchlorate, prepared from $HClO_4$ and Na_2CO_3, was used to adjust the ionic strength I to 1.0 mol L^{-1}.

Kinetic Measurements. All reaction transients were recorded at 25.0 ± 0.2 °C on a Hi-Tech HPSF-56 high-pressure stopped-flow spectrophotometer interfaced with an Apple IIe microcomputer. The Hi-Tech data analysis software was modified to convert the photomultiplier output to absolute absorbance units. Typically, two or three runs were recorded at each of seven pressures P (1–200 MPa) after a 45-min thermal equilibration period and were signal-averaged. Molar concentrations valid at ambient temperature and pressure were converted to the pressure-independent molal (mol kg^{-1}) scale, and molar absorbances at elevated pressures were corrected using the appropriate compression data.[30]

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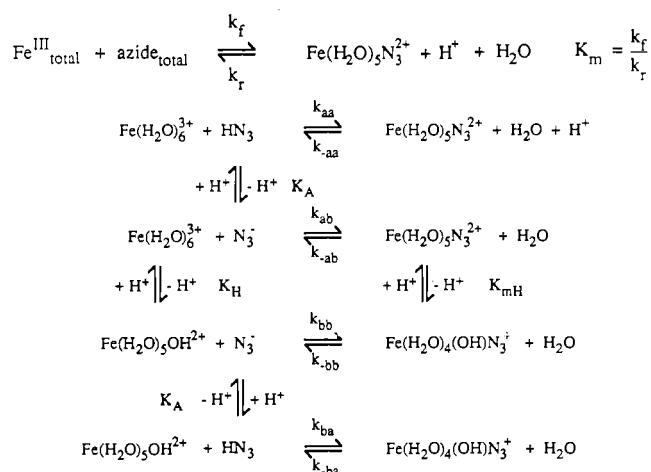(26) Hamann, S. D. *Div. Appl. Chem. Tech. Pap. (Aust., C.S.I.R.O.)* **1972**, No. 3.
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Scheme I

Second-order forward rate constants k_f or k_f' were evaluated using the expressions for reversible reactions given by Espenson.[31] "Infinite-time" absorbances were determined iteratively from the kinetic measurements but were occasionally verified by measuring the final absorbance on a Cary 219 spectrophotometer (agreement was within 2%).

Results

Uncertainties given in this paper are standard deviations σ. Full listings of all rate and equilibrium constants and reaction conditions are available as supplementary material.

The Iron(III)–Azide Reaction. The formation of $Fe(H_2O)_5N_3^{2+}$ at 25.0 °C and $I = 1.0$ mol kg^{-1} was followed at 460 nm[18] over the concentration ranges $[Fe^{III}] = 0.46–11.0$ mmol L^{-1}, $[azide]_{tot} = 4.1–20.0$ mmol L^{-1}, and $[H^+] = 0.0073–0.93$ mol L^{-1},[32] to obtain second-order forward rate constants k_f and overall equilibrium constants K_m for each pressure P and $[H^+]$.

$$K_m = [FeN_3^{2+}][H^+]/\{[Fe^{III}] - [FeN_3^{2+}]\}\{[azide]_{tot} - [FeN_3^{2+}]\} \quad (5)$$

The acid dependence of k_f at each pressure was first fitted by nonlinear least-squares regression to the three-term rate expression (6), weighting the k_f values as σ^{-2}. The three terms on the right-

$$k_f = \{k_{aa}/(1 + K_H/[H^+])(1 + K_A/[H^+])\} + \{k_{ba}/(1 + [H^+]/K_H)(1 + K_A/[H^+])\} + \{k_{bb}/(1 + [H^+]/K_H)(1 + [H^+]/K_A)\} \quad (6)$$

hand side of eq 6 represent three concurrent reactions, shown in Scheme I, if pathway 2 is active to the exclusion of pathway 1: (i) $Fe(H_2O)_6^{3+}$ with HN_3 (rate constant k_{aa}); (ii) $Fe(H_2O)_5OH^{2+}$ with HN_3 (k_{ba}); and (iii) $Fe(H_2O)_5OH^{2+}$ with N_3^- (k_{bb}). K_A and K_H are the acid dissociation constants of HN_3 and $Fe(H_2O)_6^{3+}$, respectively. Values of K_A for HN_3 at the various pressures P were calculated from the volume of ionization $\Delta V_A = -7.6$ cm^3 mol^{-1}, measured dilatometrically by Shalders and Tregloan,[33] and $K_A = 3.76 \times 10^{-5}$ L mol^{-1} at 0.1 MPa,[34] for 25.0 °C and $I = 1.0$ mol L^{-1}. Values of K_H were interpolated from a linear regression of the ln K_H data of Martinez et al.[20] on P; use of quadratic regression led to changes of no more than 0.1 cm^3 mol^{-1} in the volumes of activation reported below.

Next, the data were fitted to eq 7, which is equivalent to eq 6 except that pathway 1 (k_{ab}) replaces pathway 2; the calculated values of k_{aa} and k_{bb} were the same as before.

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$$k_f = \{k_{aa}/(1 + K_H/[H^+])(1 + K_A/[H^+])\} + \{k_{ab}/(1 +$$
$$K_H/[H^+])(1 + [H^+]/K_A)\} + \{k_{bb}/(1 + [H^+]/K_H)(1 +$$
$$[H^+]/K_A)\} \quad (7)$$

The results are summarized in Table I, which shows that k_{aa} ($\approx 2 \pm 3$ kg mol^{-1} s^{-1}, with no discernible pressure dependence; cf. 4 L mol^{-1} s^{-1} estimated by Seewald and Sutin[19]) was negligibly small and indeed not significant relative to σ. The regressions were therefore repeated after dropping the first terms on the right-hand sides of eqs 6 and 7 to gain a small improvement in σ, but the values of k_{ba} and k_{bb} so obtained at each pressure were not significantly different from those listed in Table I, which may therefore be taken as definitive.

It was found that ln k_{ab}, ln k_{ba}, and ln k_{bb} can be represented as linear functions of P, within the experimental uncertainty. The extrapolated values of k_{ab}, k_{ba}, and k_{bb} at atmospheric pressure were $(2.74 \pm 0.05) \times 10^5$, $(5.03 \pm 0.09) \times 10^3$, and (3.81 ± 0.19) $\times 10^5$ kg mol^{-1} s^{-1}, respectively; the first two are in reasonable agreement with those of Seewald and Sutin,[19] who did not report a value for k_{bb}. The corresponding pressure-independent volumes of activation are $\Delta V_{ab}^* = +16.5 \pm 0.5$, $\Delta V_{ba}^* = +6.8 \pm 0.5$, and $\Delta V_{bb}^* = +12.9 \pm 1.5$ cm^3 mol^{-1} (Table II).

The Iron(III)–Thiocyanate Reaction. The formation of Fe(H$_2$O)$_5$NCS^{2+} at 25.0 °C and $I = 1.0$ mol kg^{-1} was followed at 460 nm (molar absorbance 4680 L mol^{-1} cm^{-1})[35] over the following concentration ranges:[32] [Fe^{III}] = 1.2–11.0 mmol L^{-1}; [NCS$^-$] = 0.070–0.65 mmol L^{-1}; [H$^+$] = 0.057–0.91 mol L^{-1}. Reaction conditions were chosen so that formation of Fe-(H$_2$O)$_4$(NCS)$_2^+$ was negligible. From these measurements, overall second-order forward rate constants k_f' and equilibrium constants K_m' were derived for the formation of Fe(H$_2$O)$_5$NCS^{2+} at each pressure and [H$^+$].

$$K_m' = [FeNCS^{2+}]/\{[Fe^{III}] - [FeNCS^{2+}]\}\{[NCS]_{tot} - [FeNCS^{2+}]\} \quad (8)$$

Nonlinear least-squares regression confirmed that the rate data conformed to the two-term rate equation (9) corresponding to reaction of NCS$^-$ with Fe(H$_2$O)$_6^{3+}$ (k_{ab}') and with Fe(H$_2$O)$_5$-OH^{2+} (k_{bb}'), as summarized in Scheme II.

$$k_f' = \{k_{ab}'/(1 + K_H'/[H^+])\} + \{k_{bb}'/(1 + [H^+]/K_H')\} \quad (9)$$

Values of k_{ab}' and k_{bb}' at 25.0 °C, $I = 1.0$ mol kg^{-1}, and various pressures are listed in Table III. Plots of ln k_{ab}' and ln k_{bb}' vs P, weighted according to σ^{-2}, were linear within the experimental uncertainty, giving $k_{ab}' = 93.8 \pm 1.4$ kg mol^{-1} s^{-1} and $k_{bb}' = (7.15 \pm 0.09) \times 10^3$ kg mol^{-1} s^{-1} at zero pressure, with $\Delta V_{ab}'^* = -5.7 \pm 0.3$ and $\Delta V_{bb}'^* = +9.0 \pm 0.4$ cm^3 mol^{-1} (Table II). Finally, since we find the equilibrium molar volume change $\Delta V_{ab}'$ for the formation of Fe(H$_2$O)$_5$NCS^{2+} from Fe(H$_2$O)$_6^{3+}$ and NCS$^-$ to be $+11.8 \pm 0.3$ cm^3 mol^{-1}, it follows that the volume of activation $\Delta V_{-ab}'^*$ for the *reverse* reaction (aquation of Fe(H$_2$O)$_5$NCS^{2+}) is -17.5 ± 0.4 cm^3 mol^{-1}.

These volumes of activation are in excellent agreement with those obtained in stopped-flow experiments by Funahashi et al.;[13] the small differences in the rate constants are attributable to the effect of ionic strength. Whereas, in the present work, iron(III) was maintained in excess over NCS$^-$ to obviate formation of significant amounts of Fe(H$_2$O)$_4$(NCS)$_2^+$, Funahashi and co-workers[13] used relatively high thiocyanate concentrations and interpreted the stopped-flow observations on the basis that formation of the mono(thiocyanato) complex was rate-determining; our results, and our reevaluation of their supplementary

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Table I. Pressure Dependence of Second-Order Rate Constants for the Reaction of Fe^{III}(aq) with Azide/Hydrazoic Acid[a]

P/MPa	k_{aa}^b	$k_{ab}^b/10^5$	$k_{ba}^b/10^3$	$k_{bb}^b/10^5$
1.4	2.4 ± 3.0	2.74 ± 0.05	5.06 ± 0.10	3.65 ± 0.21
35.9	3.2 ± 5.4	2.10 ± 0.08	4.45 ± 0.18	3.59 ± 0.37
70.8	0.1 ± 4.6	1.76 ± 0.07	4.26 ± 0.16	2.56 ± 0.29
100.9	2.1 ± 1.8	1.38 ± 0.02	3.76 ± 0.06	2.32 ± 0.10
140.2	0.9 ± 4.0	1.09 ± 0.05	3.46 ± 0.15	1.76 ± 0.21
170.3	0.2 ± 4.3	0.942 ± 0.045	3.35 ± 0.16	1.19 ± 0.21
200.2	3.5 ± 7.2	0.709 ± 0.069	2.82 ± 0.28	1.45 ± 0.33

[a] At 25.0 °C and $I = 1.0$ mol kg^{-1} (HClO$_4$/NaClO$_4$). [b] Units are kg mol^{-1} s^{-1}.

Table II. Volumes of Activation ΔV^* and of Reaction ΔV for the Substitution of Coordinated Water in Fe^{III}(aq) by X^{n-}

X^{n-}	Fe^{III}	I/ mol kg^{-1}	ΔV^*/ cm^3 mol^{-1}	ΔV/ cm^3 mol^{-1}	method[a]
H$_2$O	Fe(H$_2$O)$_6^{3+}$	6.0	−5.4 ± 0.4	0.0	NMR[b]
	Fe(H$_2$O)$_5$OH^{2+}		+7.0 ± 0.3	0.0	NMR[b]
NCS$^-$	Fe(H$_2$O)$_6^{3+}$	1.0	−5.7 ± 0.3	11.8 ± 0.3	SF[c]
	Fe(H$_2$O)$_5$OH^{2+}		+9.0 ± 0.4		SF[c]
	Fe(H$_2$O)$_6^{3+}$		+4.3 ± 0.6	7.6 ± 0.3	TJ[d]
	Fe(H$_2$O)$_5$OH^{2+}		+15.6 ± 1.3		TJ[d]
	Fe(H$_2$O)$_5$OH^{2+}	0.1–1.5	+5.4 to +16.5		TJ[d]
	Fe(H$_2$O)$_6^{3+}$	0.2	−4.9 to +4.4	8.9 ± 0.5	TJ[e]
	Fe(H$_2$O)$_5$OH^{2+}		+7.1 ± 1.0		TJ[e]
	Fe(H$_2$O)$_6^{3+}$	0.8	+5 to +6	17.5 ± 0.6	PJ[f]
	Fe(H$_2$O)$_6^{3+}$	1.0		8.9 ± 0.2	dil[g]
	Fe(H$_2$O)$_6^{3+}$	1.5	−6.1 ± 1.0		SF[h]
	Fe(H$_2$O)$_5$OH^{2+}		+8.5 ± 1.2		SF[h]
HN$_3$	Fe(H$_2$O)$_6^{3+}$	1.0		3.8 ± 0.8	SF[c]
	Fe(H$_2$O)$_5$OH^{2+}		(+6.8 ± 0.5)[i]		SF[c]
N$_3^-$	Fe(H$_2$O)$_6^{3+}$		(+16.5 ± 0.5)[i]		SF[c]
	Fe(H$_2$O)$_5$OH^{2+}		+12.9 + 1.5		SF[c]
Cl$^-$	Fe(H$_2$O)$_6^{3+}$	1.5	−4.5 ± 1.1		TJ[j]
	Fe(H$_2$O)$_5$OH^{2+}		+7.8 ± 1.0		TJ[j]
Br$^-$	Fe(H$_2$O)$_6^{3+}$	2.0	−8 ± 4		TJ[k]
Hipt	Fe(H$_2$O)$_6^{3+}$	1.0	−8.7 ± 0.8		SF[h,l]
	Fe(H$_2$O)$_5$OH^{2+}		+4.1 ± 0.6		SF[h,l]
Hahx	Fe(H$_2$O)$_6^{3+}$	1.0	−10.0 ± 1.4		SF[h,m]
	Fe(H$_2$O)$_5$OH^{2+}		+7.7 ± 0.6		SF[h,m]

[a] NMR = nuclear magnetic resonance line broadening; SF = stopped-flow spectrophotometry; TJ = temperature jump; PJ = pressure jump; dil = dilatometry. [b] Reference 10. [c] This work. [d] Reference 15. [e] Reference 6. [f] Reference 5. [g] Reference 36. [h] Reference 13. [i] See text. [j] Reference 7. [k] Reference 8. [l] Hipt = 4-isopropyltropolone. [m] Hahx = acetohydroxamic acid.

Scheme II

Fe^{III}$_{total}$ + thiocyanate$_{total}$ $\overset{k_f'}{\underset{k_r'}{\rightleftharpoons}}$ Fe(H$_2$O)$_5$SCN^{2+} + H$_2$O $K_m' = \dfrac{k_f'}{k_r'}$

Fe(H$_2$O)$_6^{3+}$ + SCN$^-$ $\overset{k_{ab}}{\underset{k_{-ab}}{\rightleftharpoons}}$ Fe(H$_2$O)$_5$SCN^{2+} + H$_2$O

+H$^+$ ⇂↑ -H$^+$ K_H +H$^+$ ⇂↑ -H$^+$ K_{mH}'

Fe(H$_2$O)$_5$OH^{2+} + SCN$^-$ $\overset{k_{bb}}{\underset{k_{-bb}}{\rightleftharpoons}}$ Fe(H$_2$O)$_4$(OH)SCN$^+$ + H$_2$O
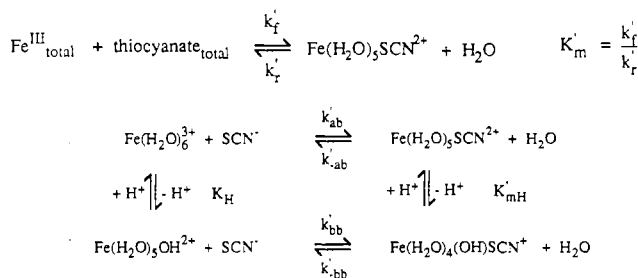
data, vindicate this approach. However, the $\Delta V_{ab}'^*$ value, in particular, differs significantly from some of the results of temperature- or pressure-jump studies (Table II). While the early studies of Brower[5] and Jost[6] were clearly imprecise and can probably be discounted, the discrepancy between our results and those of Martinez et al.[15] requires closer consideration.

One possible source of disagreement might be that we have adopted Lister and Rivington's[35] acid dissociation constant of 7 $\times 10^{-5}$ mol L^{-1} for Fe(H$_2$O)$_5$NCS^{2+}, which implies that no detectable amounts of Fe(H$_2$O)$_4$(OH)NCS$^+$ could survive in the pH range we used, and hence the only absorbing species absorbing at 460 nm would be Fe(H$_2$O)$_5$NCS^{2+} (our analysis of the Fe^{III}–

Table III. Pressure Dependence of Second-Order Rate Constants for the Reaction of $Fe^{III}(aq)$ with NCS^- [a]

P/MPa	k_{ab}'/kg mol^{-1} s^{-1}	k_{bb}'/10^3 kg mol^{-1} s^{-1}	K_m'/kg mol^{-1}
1.4	95.1 ± 1.9	7.06 ± 0.10	123.1 ± 3.3
35.9	102.3 ± 2.8	6.31 ± 0.15	96.8 ± 2.2
70.7	107.4 ± 2.2	5.65 ± 0.12	81.0 ± 1.3
100.9	119.5 ± 2.7	4.96 ± 0.15	70.3 ± 1.3
140.5	129.5 ± 2.3	4.23 ± 0.13	59.2 ± 1.2
170.4	138.3 ± 3.8	3.86 ± 0.22	52.0 ± 1.1
200.3	149.3 ± 3.4	3.31 ± 0.20	45.8 ± 1.0

[a] At 25.0 °C and I = 1.0 mol kg^{-1} (HClO$_4$/NaClO$_4$).

azide data involves a similar assumption). Martinez et al.,[15,37] on the other hand, have claimed an acid dissociation constant of 6.2×10^{-2} mol L^{-1} for this species; this seems highly improbable on any reasonable theoretical grounds, as the corresponding parameter for $Fe(H_2O)_6^{3+}$ is only 2×10^{-3} mol L^{-1} under the same conditions. In any event, recalculation of our results with the value proposed by Martinez et al.[15] gives $\Delta V_{ab}'^{\ddagger}$ = −8.6 and $\Delta V_{bb}'^{\ddagger}$ = +11.3 cm^3 mol^{-1}; i.e., $\Delta V_{ab}'^{\ddagger}$ becomes even more negative, whereas Martinez et al.[15] report +4.3 cm^3 mol^{-1}. If, on the other hand, the data of Martinez et al.[15] are recalculated with the Lister and Rivington[35] acidity constant for Fe-$(H_2O)_5NCS^{2+}$, the curvature shown in the plots of τ^{-1}/X vs Y/X in ref 15 disappears. This curvature had led Martinez et al. to analyze only the data at high [H$^+$] to obtain k_{ab}' (which would otherwise appear to be a highly uncertain *negative* quantity), whereas use of the Lister and Rivington value gives k_{ab}' = 189 ± 7 L mol^{-1} s^{-1}—a result twice as large as ours, but feasible. The corresponding value of $\Delta V_{ab}'^{\ddagger}$, however, is then +8.6 cm^3 mol^{-1}, which is even less compatible with our results and those of Funahashi et al.[13] In addition, the extraordinarily strong apparent dependence of $\Delta V_{ab}'^{\ddagger}$ on ionic strength reported by Martinez et al.[15] (Table II) further undermines confidence in the high-pressure temperature-jump data but again provides no clue as to the source of disagreement between the results of the stopped-flow and jump methods.

The discrepancies probably originate in the nature of the temperature-jump technique: the highly acidic $Fe^{III}(aq)/NCS^-$ solution is subjected to a very high electrical current for a short period (with attendant risks of electrolysis) to raise the temperature and so produce a relatively *small* perturbation of the preexisting equilibrium. Thus, the fractional changes in the measured absorbances are necessarily small and sensitive to experimental error—particularly when several parameters describing different reaction rates and equilibria must be extracted from the raw data. It is a matter of common experience in high-pressure chemistry that errors generally increase with the pressure; thus, the volumes of activation are especially prone to large systematic uncertainties that may not be evident in the statistical goodness-of-fit parameters. Our reanalyses of the data of Martinez et al.[15] confirmed that rate constants and volumes of activation extracted from their absorbance measurements are indeed very sensitive to both possible systematic errors and to the inevitable assumptions made in the calculations, and we consider the stopped-flow method, in which the absorbance changes can be large and neither the temperature nor the electrochemistry of the reacting solutions is perturbed significantly, to provide the definitive results.

Discussion

The rate constant for the reaction of $Fe(H_2O)_5OH^{2+}$ with N_3^- (k_{bb} = 3.8 × 10^5 kg mol^{-1} s^{-1} at 25 °C and I = 1.0 mol kg^{-1}), reported here for the first time, is 10–100 times larger than is typical for reactions of $Fe(H_2O)_5OH^{2+}$ with other singly charged anions X$^-$ under similar conditions[21] (cf. k_{bb}' = 7.1 × 10^3 kg mol^{-1} s^{-1} for X$^-$ = NCS$^-$, from this work). This observation

would seem to run counter to the view that a dissociative interchange (I$_d$) mechanism[38] is operating in this series or, equivalently, that $Fe(H_2O)_5OH^{2+}$ shows low selectivity in substitution reactions.[22] It is, however, close to that found for X^{n-} = SO$_4^{2-}$ (1.1 × 10^5 L mol^{-1} s^{-1}),[39] and it may be surmised that the mechanism of azide attack is indeed of the I$_d$ type but, like the sulfate case, is enhanced by strong preassociation of the reactants (presumably through hydrogen bonding of the aqua hydroxo complex to the basic azide ion). Other possibilities are that the nucleophilicity of N_3^- is unusually high, that a CACB mechanism is again involved (HN$_3$ with $Fe(H_2O)_4(OH)_2^+$), or that the reaction proceeds via transient reduction of the Fe^{III} to labile Fe^{II} by the azide ion; this last pathway may be discounted in view of the high standard electrode potential (+1.33 V) for the $N_3^\bullet/N_3^-$ couple.[40] The volume of activation for the reaction of $Fe(H_2O)_5OH^{2+}$ with N_3^- (Table II) is about 3 cm^3 mol^{-1} more positive than those for the reactions with NCS$^-$ and other X$^-$ (which average about +9 cm^3 mol^{-1}), and this is consistent with an I$_d$ mechanism in which preassociation (with attendant desolvation) is stronger than usual.

The rate constant for the other principal pathway in the reaction of azide with Fe^{III} lies within the range typical of $Fe(H_2O)_5OH^{2+}$ reactions with neutral nucleophiles[13,21] if it is calculated on the basis of the CACB pathway (2) (k_{ba} = 5.0 × 10^3 kg mol^{-1} s^{-1}). Furthermore, the volume of activation calculated on this basis ($\Delta V_{ba}^{\ddagger}$ = +6.8 ± 0.5 cm^3 mol^{-1}) is in effect the same as that for water exchange on $Fe(H_2O)_5OH^{2+}$,[10] whereas that calculated on the basis of $Fe(H_2O)_6^{3+}$ and N_3^- ($\Delta V_{ab}^{\ddagger}$ = +16.5 cm^3 mol^{-1}) is 22 cm^3 mol^{-1} more positive than the volume of activation for $Fe(H_2O)_6^{3+}$ and NCS$^-$, as reported here, and similarly exceeds those for reactions of $Fe(H_2O)_6^{3+}$ with other nonbasic X^{n-} including H$_2$O—all of which are negative (Table II). Thus, all the evidence favors the CACB mechanism (2) over pathway 1. The equilibrium molar volume of reaction for the formation of $Fe(H_2O)_5N_3^{2+}$ + H$^+$ from $Fe(H_2O)_6^{3+}$ + HN$_3$ (Table II), together with that for the hydrolysis of $Fe(H_2O)_6^{3+}$ and $\Delta V_{ba}^{\ddagger}$, lead to a volume of activation $\Delta V_{-ba}^{\ddagger}$ = +4 ± 1 cm^3 mol^{-1} for the acid-independent aquation of $Fe(H_2O)_5N_3^{2+}$ by the reverse of the CACB pathway (2). This is some 21 cm^3 mol^{-1} more positive than $\Delta V_{-ab}'^{\ddagger}$ for the acid-independent aquation of $Fe(H_2O)_5NCS^{2+}$, for which the CACB pathway is not available; interestingly, the volume of activation for the aquation of $Co(NH_3)_5N_3^{2+}$ exceeds that for $Co(NH_3)_5NCS^{2+}$ by 20 cm^3 mol^{-1}.[3]

The *negative* volumes of activation for the reactions of $Fe(H_2O)_6^{3+}$ with NCS$^-$, Cl$^-$, Br$^-$, H$_2$O, Hipt, and Hahx (Table II) are all indicative of a substantial associative component in the activation of this cation. Those for the anionic nucleophiles would presumably be somewhat more negative still, in the absence of desolvation due to charge cancellation in the encounter complex. The extent of the associative contribution to the volume of activation will vary from one X^{n-} to another (as is seen for the neutral X, for which desolvation is unimportant); thus, no special significance is to be attached to the close similarity between the volumes of activation for NCS$^-$ attack and for water exchange. The mechanism may be described as I$_a$, with due caution concerning the use of this term,[22] and this is consistent with the moderate selectivity in substitution kinetics displayed by $Fe(H_2O)_6^{3+}$. These results and conclusions have a close analogue in the reactions of $V(H_2O)_6^{3+}$ with X^{n-}, which show considerable selectivity;[41] there, $\Delta V^{\ddagger}$ is negative and essentially the same (−9 cm^3 mol^{-1}) for X^{n-} = H$_2$O and NCS$^-$, and an I$_a$ mechanism has

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been assigned.[42] Furthermore, the volumes of activation $\Delta V_{-ab}'^{*}$ found here for the aquation of $Fe(H_2O)_5NCS^{2+}$ (-17.5 ± 0.4 cm^3 mol^{-1}) is virtually identical with that for the aquation of $V(H_2O)_5NCS^{2+}$ (-17.9 cm^3 mol^{-1}),[42] which strengthens confidence in both these values, strikingly negative though they are by comparison with corresponding data for aquation of e.g. Co^{III} or Cr^{III} pentaammines,[3,43] and suggests a mechanistic similarity between the Fe^{III}(aq) and V^{III}(aq) systems.

Supplementary Material Available: Tables of rate and equilibrium constants and plots of their pressure dependences (15 pages). Ordering information is given on any current masthead page.

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