diminishes in this sequence. The weaker the N–Cl bond and the stronger the nucleophile that reacts at chlorine, the less the need for proton transfer to nitrogen in order to have Cl^+ transfer to the nucleophile. Sulfite is a stronger nucleophile than iodide, as is reflected in its Brønsted base strength and in its much more positive reduction potential (eqs 32 and 33). Sulfite also would

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \qquad E^\circ = 0.936\ \text{V} \qquad (32)$$

$$I^- + 2OH^- \rightarrow OI^- + H_2O + 2e^- \qquad E^\circ = -0.472\ \text{V} \qquad (33)$$

be expected to have a stronger attraction than iodide for a hard acid species such as Cl^+.[38] For the sequence in Chart I with other nucleophiles we can predict that the weaker the nucleophile, the more acid assistance will be needed, and conversely the stronger the nucleophilic attraction to Cl^+, the less acid assistance will be needed.

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Pressure Effect on the Kinetics of the Hexaaquairon(II/III) Self-Exchange Reaction in Aqueous Perchloric Acid

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The effect of pressure on the rates of the $Fe(H_2O)_6^{3+/2+}$ and the $Fe(H_2O)_5OH^{2+}/Fe(H_2O)_6^{2+}$ exchange reactions in homogeneous aqueous perchlorate solution can be represented by mean volumes of activation of −11.1 ± 0.4 and +0.8 ± 0.9 $cm^3\ mol^{-1}$, respectively, over the range 0–140 MPa at 2 °C and ionic strength 0.5 mol L^{-1}. These results can be accounted for essentially quantitatively on the basis of the Marcus–Hush theory, with minor modifications to accommodate the pressure dependences of the Fe–Fe separation and presumed anion–cation pairing, on the basis of an adiabatic outer-sphere mechanism for the $Fe(H_2O)_6^{3+/2+}$ exchange and a hydroxide-bridged inner-sphere mechanism for the $Fe(H_2O)_5OH^{2+}/Fe(H_2O)_6^{2+}$ reaction. For the $Fe(H_2O)_6^{3+/2+}$ self-exchange, the question of possible ligand interpenetration in the precursor complex is not unequivocally resolved, but neither aqua-bridged inner-sphere nor markedly nonadiabatic outer-sphere mechanisms are consistent with these measurements.

Silverman and Dodson[5] presented a definitive experimental study of the rate of the hexaaquairon(III/II) self-exchange reaction in homogeneous acidic aqueous solution as long as 1952, but since 1980, the kinetics and mechanism of this reaction have become the subject of extensive theoretical investigations and controversy.[6-18]

In noncomplexing (e.g., perchlorate) media, the reaction occurs by two parallel pathways, one involving $Fe(H_2O)_6^{3+}$ as the oxidant

$$Fe(H_2O)_6^{3+} + {}^*Fe(H_2O)_6^{2+} \overset{k_1}{\rightleftharpoons} Fe(H_2O)_6^{2+} + {}^*Fe(H_2O)_6^{3+} \qquad (1)$$

and the other its conjugate base $Fe(H_2O)_5OH^{2+}$[5,9]

$$Fe(H_2O)_6^{3+} \overset{K_a}{\rightleftharpoons} Fe(H_2O)_5OH^{2+} + H^+ \qquad (2)$$

$$Fe(H_2O)_5OH^{2+} + {}^*Fe(H_2O)_6^{2+} \overset{k_2}{\rightleftharpoons} {}^*Fe(H_2O)_5OH^{2+} + Fe(H_2O)_6^{2+} \qquad (3)$$

The latter path, like those occurring in the presence of complexing anions such as chloride[5] or sulfate,[19] may be expected to be of the inner-sphere (ligand-bridged) type. The mechanism of pathway 1, however, is less readily assigned. An outer-sphere mechanism is usually assumed, but $Fe(H_2O)_6^{3+}$[20,21] and especially $Fe(H_2O)_6^{2+}$[22] are substitutionally labile on the time scale of electron transfer, and an inner-sphere mechanism, presumably involving a bridging aqua ligand, has been proposed by Hupp and Weaver[15] and Bernhard et al.[18] to account for what has been perceived as the anomalously rapid self-exchange of hexaaquairon(II) and -(III) in homogeneous solution. In particular, Hupp and Weaver's electrochemical estimation of the $Fe(H_2O)_6^{3+/2+}$ self-exchange rate[15] gave a result at least 4 orders of magnitude slower than the rate determined directly for homogeneous solution by Silverman and Dodson[5] but in agreement with the self-exchange rate calculated by the Marcus cross-relation from the rates of redox reactions of $Fe(H_2O)_6^{3+}$ or $Fe(H_2O)_6^{2+}$ with other reagents.

Sutin and co-workers,[9] however, have redetermined the homogeneous $Fe^{III/II}(aq)$ exchange rate, and their results are in good agreement with those of Silverman and Dodson[5] and with the

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predictions of the updated Marcus theory of outer-sphere self-exchange rates;[6-14] thus, Sutin considers that "there is no reason to invoke an inner-sphere mechanism for the $Fe(H_2O)_6^{3+/2+}$ exchange reaction".[9] Nevertheless, the possibility remains[12,23] that the mechanism might be better represented as a nonadiabatic electron-transfer process, i.e., one in which the Fe^{II}–Fe^{III} electronic coupling in the encounter complex is so weak that the electronic transmission coefficient κ_{el} becomes $\ll 1$. Ab initio electronic coupling calculations[7,8,10,13] suggest that reaction 1 is indeed nonadiabatic at normal primary hydration envelope contact distances (Fe–Fe separation $\sigma \simeq 680$ pm) but can achieve near adiabaticity ($\kappa \simeq 1$) through interpenetration of the aqua ligands in the $Fe(H_2O)_6^{3+}/Fe(H_2O)_6^{2+}$ encounter complex ($\sigma \simeq 525$ pm). On the other hand, the experimental rate is equally well reproduced by a fully adiabatic model with $\sigma \simeq 650$ pm.[12]

Indeed, the question of nonadiabaticity may be the key to understanding the kinetics of redox reactions involving hexaaquairon(II) and -(III) ions. As Fürholz and Haim[16] have suggested, following Taube et al.[23] and Sutin and co-workers,[24] anomalies in the kinetics of cross-reactions involving $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ vis-à-vis the $Fe(H_2O)_6^{3+/2+}$ self-exchange rate may be attributed to a closer approach to adiabaticity in the self-exchange than in the cross-reactions. One of the objectives of the present paper is to show that the effect of pressure on the rate of the $Fe(H_2O)_6^{3+/2+}$ exchange is consistent with essentially full adiabaticity in this particular reaction. In addition, we provide further confirmation of the Silverman–Dodson results[5] and follow up our preliminary reports[25,26] that the effects of pressure are consistent with an outer-sphere mechanism for the $Fe(H_2O)_6^{3+/2+}$ exchange but inner sphere for the $Fe(H_2O)_5OH^{2+}/Fe(H_2O)_6^{2+}$ electron transfer.

Experimental Section

Separate stock solutions in dilute $HClO_4$ were prepared from $Fe(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith, recrystallized from aqueous $HClO_4$) and $Fe(ClO_4)_3 \cdot 9H_2O$ (Fluka, purum) and analyzed for Fe spectrophotometrically. The iron(II) solution contained some iron(III) (10% of total Fe), but this did not matter since the order of reaction with respect to Fe^{II} and Fe^{III} was known[5] and only the total Fe content was required. Solutions for the exchange experiments were made by mixing aliquots of the Fe^{II} and Fe^{III} stock solutions in molar ratio about 4:1 and adjusting the ionic strength I to 0.50 mol L^{-1} [27] with $HClO_4$ and $NaClO_4$. Iron(III) perchlorate labeled with ^{59}Fe (γ, 1.1 and 1.3 MeV, half-life 45 days) was made by fuming $^{59}FeCl_3$ (The Radiochemical Centre, Amersham, U.K.; initially 590 MBq mg^{-1}) to dryness in a Pt crucible with concentrated $HClO_4$ containing a few drops H_2O_2 and then dissolved in sufficient $HClO_4$ (1.0 mol L^{-1}) to give a specific activity suitable for labeling the exchange solutions.

The exchange reactions were carried out in a Perspex (poly(methyl methacrylate)) syringe in a thermostated pressure assembly described elsewhere;[28] the capillary through which samples were withdrawn under pressure was of Pt/Ir alloy. Because the exchange reaction was fairly rapid on the time scale of the high-pressure sampling technique, it was necessary to measure the exchange rate at as low a temperature as was practicable (2.0 °C). Furthermore, in the case of runs at elevated pressures, a small correction (maximum 7% for the initial rate at 68.9 MPa and 14% for that at 137.9 MPa—details given elsewhere[29]) was applied to each rate measurement throughout a run to allow for the temperature differential between the sample and the thermostat bath that arose from heating by the initial compression and then decayed exponentially at a known rate.

Reaction mixtures were thermally equilibrated in the pressure vessel to 2.0 ± 0.1 °C (1.5 h); then, a run was initiated by quickly removing the syringe, introducing a single drop of the ^{59}Fe-labeled tracer through the outlet, shaking to mix, and reassembling the apparatus—this took 30–45 s and caused a temperature perturbation of less than +0.3 °C. At selected times, the "holdup" (1.5 mL) was run out and rejected, and then an aliquot (1.0 mL) was discharged into the quenching solution (1.0 mL of 0.04 mol L^{-1} 2,2′-bipyridine in ethanol and 2.0 mL of an aqueous solution containing 0.2 mol L^{-1} of $Al(ClO_4)_3$ and 2.0 mol L^{-1} sodium acetate; pH 5, 2 °C; these conditions differ somewhat from those of Silverman and Dodson[5]) and the pressure was promptly restored without net change in temperature. Aqueous ammonia was then added immediately to precipitate the iron(III) along with the $Al(OH)_3$ coprecipitant. The sample was centrifuged, and an aliquot of the supernatant solution containing the Fe^{II} fraction was assayed with a scintillation counter.

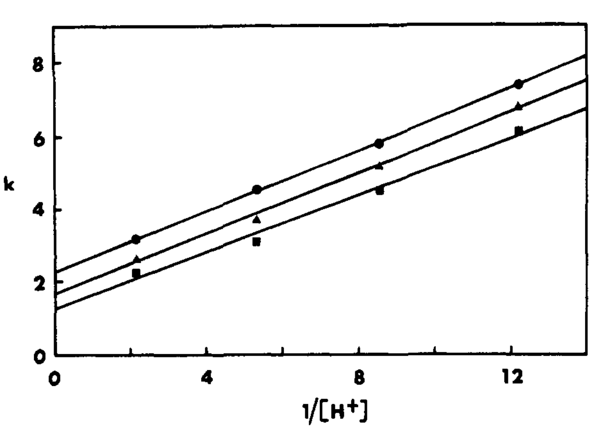

Figure 1. Dependence of the observed rate constant k/L mol^{-1} s^{-1} for the iron(III/II) exchange on $[H^+]^{-1}$/L mol^{-1} at 2 °C and ionic strength 0.5 mol L^{-1} ($HClO_4/NaClO_4$) ($[Fe^{II}] + [Fe^{III}] = 3.48 \times 10^{-5}$ mol L^{-1}): squares, 0.1 MPa; triangles, 68.9 MPa; circles, 137.9 MPa.

Table I. Pressure Dependence of the Rate Constants k_1 for Reaction 1 and k_2' for Reactions 2 and 3 Combined[a]

pressure/MPa	k_1/L mol^{-1} s^{-1}	k_2'/s^{-1}
0.1	1.17 ± 0.17	0.410 ± 0.015
68.9	1.67 ± 0.13	0.423 ± 0.012
137.9	2.28 ± 0.12	0.420 ± 0.010

[a] 2 °C; $[Fe^{III}] + [Fe^{II}] = 3.48 \times 10^{-5}$ mol L^{-1}; $I = 0.5$ mol L^{-1}.

Results

Runs at all pressures gave accurately linear McKay plots with a zero-time exchange of 10–20% for reactions carried out in the pressure assembly or 3–4% in preliminary runs carried out at ambient pressure in a glass vessel (cf. 35% zero-time exchange reported by Silverman and Dodson,[5] who assayed the Fe^{III} rather than the Fe^{II} fraction). Rates measured in the pressurizable assembly, however, were the same as the corresponding ones obtained in glassware. Thus, the zero-time exchange was almost entirely due to the sampling and separation procedure, which, however, was precisely the same for all experiments carried out with the pressurizable assembly.

The rates of exchange R obtained from the McKay plots gave rate constants $k = R/[Fe^{III}][Fe^{II}]$,[5] which were linearly dependent upon $[H^+]^{-1}$, as shown in Figure 1.

$$k = k_1 + k_2'[H^+]^{-1} \qquad (4)$$

Values of the rate constants k_1 for pathway 1, and $k_2' = k_2K_a$ for the combined reactions 2 and 3, are listed in Table I. For $I = 0.5$ mol L^{-1} at 2 °C and 0.1 MPa, it can be estimated[21,29,30] that $K_a \simeq 3.6 \times 10^{-4}$ mol L^{-1}, and so $k_2^0 \simeq 1.14 \times 10^3$ L mol^{-1} s^{-1} (superscripts denote the pressure in MPa). This and the k_1^0 value of Table I are in good agreement with the results of Silverman and Dodson at essentially the same ionic strength, interpolated to 2 °C, and are consistent with those of Brunschwig and co-workers[9] at $I = 0.1$ mol L^{-1}.

The pressure dependence of $\ln k_1$ and $\ln k_2'$ can be represented by $\overline{\Delta V_1}^* = -11.1 \pm 0.4$ and $\overline{\Delta V_2}^* = -0.4 \pm 0.4$ cm^3 mol^{-1}, re-

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spectively, on the assumption that the relationships are linear; this may not be the case (vide infra), and consequently these values are to be regarded as *averages* over the 0–140 MPa range.

Discussion

The currently preferred version[12] of the Marcus–Hush theory of adiabatic outer-sphere electron self–exchange rates can be presented as follows for SI units.

$$k_1 = (4000\pi N\sigma^3\kappa_{el}\nu_n/3)\exp[-(\Delta G_{IR}{}^* + \Delta G_{SR}{}^* + \Delta G_{COUL}{}^* + \Delta G_{DH}{}^*)/RT] \quad (5)$$

$$\Delta G_{SR}{}^* = (Ne^2/16\pi\epsilon_0)(1/2r_1 + 1/2r_2 - 1/\sigma)(n^{-2} - D^{-1}) \quad (6)$$

$$\Delta G_{COUL}{}^* = (Nz_1z_2e^2/4\pi\epsilon_0)/D\sigma \quad (7)$$

$$\Delta G_{DH}{}^* = -2RTz_1z_2CI^{1/2}/(1 + BaI^{1/2}) \quad (8)$$

Here, σ is the Fe–Fe separation associated with the highest probability of electron transfer; κ_{el} is the electronic transmission coefficient (=1 for adiabatic electron transfer, by definition); ν_n is the nuclear frequency; r_1 and r_2 are the effective primary hydration envelope radii of the reactants, which have charge numbers z_1 and z_2; n and D are respectively the refractive index and relative permittivity (static dielectric constant) of the solvent; a, B, and C are the Debye–Hückel parameters, of which B and C are pressure dependent; the subscripts IR, SR, COUL, and DH refer to the contributions to the free energy of activation ΔG^* from internal (ligand) reorganization, solvent reorganization, the coulombic work of bringing the reactants together, and the effect of ionic strength I (Debye–Hückel), respectively; and the other symbols have their usual meanings.

For reaction 1, $r_1 \simeq r_2 \simeq 340$ pm and the anion–cation closest approach parameter $a \simeq 620$ pm; σ is taken to be dependent on pressure P but with a zero-pressure value of $r_1 + r_2$. It is stressed that pressure dependence of σ is invoked because electron transfer is considered to occur over a *range* of Fe–Fe separations[12] and because interpenetration of the aqua ligands is still possible (indeed, probable)[10] at the nominal contact distance $(r_1 + r_2)$ of the primary hydration envelopes. There is no implication that the aqua complexes themselves are significantly compressible (they are not[25]); rather, the sum $(r_1 + r_2)$ represents a likely zero-pressure value for σ, and the calculated *pressure effects* on k are not very sensitive to this choice.

For self-exchange reactions in *nonaqueous* systems, depletion of the pool of charged reactants by anion–cation pairing can have a significant effect on k,[32–34] which is counteracted by applied pressure and which can be allowed for approximately by incorporation of ion-pair formation constants K_{IP} calculated from the Fuoss equation[35] for each reactant:

$$K_{IP} = (4000\pi Na^3/3)\exp(|z_+z_-|e^2/4\pi\epsilon_0k_BTaD) \quad (9)$$

$$[\text{free reactant 1}] = [\text{paired reactant 1}]/\{K_{IP(1)}([\text{total counterion}] - [\text{paired reactants 1 and 2}])\} \quad (10)$$

For *aqueous* solutions at low T and moderate I, such reactant pool depletion by ion pairing is of lesser importance but will substantially offset the increase in k with rising I predicted from the extended Debye–Hückel theory. Thus, in the present experiments, eq 9 indicates that 56.8% of Fe^{II} and 45.3% of Fe^{III} remain unpaired at 0.1 MPa, so that k is predicted to be only 27% of the value calculated without allowance for ion pairing; this is equivalent to a reduction of 11 J K^{-1} mol^{-1} in ΔS^*. This compensatory effect of ion pairing and Debye–Hückel interactions explains semiquantitatively the lack of marked dependence of the rates of several self-exchange reactions upon I in the ionic strength regime 0.1–1.0 mol L^{-1} noted by several authors.[10,33,36–38] Tembe et al.[10] offer effective alternative approaches to the persistent problem of ionic strength effects on electron-transfer rates, but we choose to retain the more familiar Debye–Hückel/ion association model. In this, pressure works against ion pairing, so that the calculated percentages of free Fe^{II} and Fe^{III} at 140 MPa rise to 58.1 and 47.2%, respectively, thus contributing a 7% acceleration of reaction 1 from this cause, 0–140 MPa, at $I = 0.5$ mol L^{-1}. (Brunschwig et al.[9] reported that k_1 for reaction 1 was not significantly affected by varying [ClO$_4^-$] at constant I, but their observation referred to $I = 0.1$ rather than 0.5 mol L^{-1}).

Table II. Observed and Predicted Relative Rates and Mean Volumes of Activation for the Acid-Independent Pathway of the $Fe(H_2O)_6{}^{3+/2+}$ Self-Exchange Reaction in Water[a]

	$\ln(k_1{}^{68.9}/k_1{}^0)$	$\ln(k_1{}^{137.9}/k_1{}^0)$	$\overline{\Delta V^*{}_1}$ (0–140 MPa)/ cm^3 mol^{-1}
obsd	0.357 ± 0.077	0.671 ± 0.050	−11.1 ± 0.4
adiabatic			
free, 680	0.298	0.545	−9.0
free, 525	0.309	0.567	−9.5
paired, 680	0.333	0.609	−10.1
paired, 525	0.343	0.631	−10.4
nonadiabatic			
free, 680	0.441	0.802	−13.2
free, 525	0.418	0.766	−12.7
paired, 680	0.475	0.867	−14.3
paired, 525	0.453	0.830	−13.7

[a] Rate constants at 68.9 and 137.9 MPa relative to 0.1 MPa; 2 °C; ionic strength 0.5 mol L^{-1}; $r_1 = r_2 = 340$ pm; $a = 620$ pm; $\alpha = 10$ nm^{-1}; "paired" and "free" denote models with and without Fuoss ion pairing, respectively; "525" denotes models with ligand interpenetration to $\sigma = 525$ pm; "680" indicates normal first hydration envelope contact at $\sigma = r_1 + r_2 = 680$ pm.

Beyond some critical Fe–Fe separation d, electronic coupling will become too weak, in the Marcus–Hush sense, and the electron transfer at this range will be nonadiabatic; thus, for $\sigma > d$, κ_{el} will be <1 and will depend on σ in a manner that can be conveniently approximated by the equation

$$\kappa_{el} \propto H_{AB}{}^2 = (H_{AB}{}^0)^2\exp[-2\alpha(\sigma - d)] \quad (11)$$

in which H_{AB} is the electronic coupling matrix element and α is a nonadiabaticity scaling factor, which, for reaction 1, has been estimated to about 10 nm^{-1}.[10,12,13] The pressure dependence of σ can be represented by[39,40]

$$\sigma = \sigma_0(\rho_0/\rho)^{1/3} \quad (12)$$

where ρ is the solvent density and the subscripts indicate ambient ("zero") pressure. Thus, in the event that reaction 1 is nonadiabatic, this will be reflected in a significant additional acceleration, over and above that expected from the pressure dependence of eqs 5–10 with κ_{el} set to 1.

We may therefore consider eight alternative models, summarized in Table II, representing combinations of the following assumptions: (a) adiabatic vs nonadiabatic electron transfer; (b) depletion of the reactant pools by Fuoss ion pairing vs no depletion; (c) electron transfer at the Fe–Fe separation $\sigma = 680$ pm (primary hydration envelope contact) vs at $\sigma \simeq 525$ pm (corresponding to substantial interpenetration of the first coordination spheres). Although the absolute calculation of k_1 for these models of various pressures from eqs 5–12 is unlikely to reproduce k_1 very precisely, the *relative* rate $k_1{}^P/k_1{}^0$ (superscripts indicate the pressure) should be fairly accurately predictable if a model is appropriate, since

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factors comprising only pressure-independent parameters such as H_{AB}^0 will cancel out.[39,40] The question, then, is which of the alternative models generates values of k_1^P/k_1^0 closest to those observed experimentally?

Table II gives the results of calculations of ln (k_1^P/k_1^0) on the basis of eqs 5–12 and the properties of water under pressure as given by Grigull et al.[41,42] and Owen et al.[43] (cf. ref 40). The pressure dependence of ΔG_{IR}^* ($=\Delta V_{IR}^* = +0.47$ cm^3 mol^{-1}), which is slight, was calculated as in ref 25. Clearly, only the adiabatic model that allows for ion pairing and ligand interpenetration fits the observed data within the stated limits, which are standard errors (s)—these limits, however, are of limited statistical validity in view of the paucity of data. The adiabatic model allowing for ion pairing but without interpenetration of the ligands comes within the 95% confidence limits (1.96s) of ln (k_1^P/k_1^0), as does the nonadiabatic model with ligand interpenetration but no ion pairing, and these should not be excluded. The results of the adiabatic models are not very sensitive to the choice of σ, even though that corresponding to ligand interpenetration comes closest to the experimental data, but it seems that the nonadiabatic models *without* ligand interpenetration can be discounted. Thus, the high-pressure data support Newton's contention[7,10,13] that ligand interpenetration occurs to bring about essentially adiabatic electron transfer. Alternatively, the simplest interpretation, without reference to theoretical estimates of the Fe–Fe electronic coupling, is that reaction 1 is fully adiabatic at ordinary ion–ion contact distances. In either case, a small contribution to the pressure effect from pairing between the reactants and the counterion should be acknowledged.

The volume of activation $\Delta V_1^* = -RT(\partial \ln k_1/\partial P)_T$ and the compressibility coefficient of activation $\Delta\beta_1^* = -(\partial \Delta V_1^*/\partial P)_T$ can be predicted for any pressure P by calculating ln (k_1^P/k_1^0) over a very small pressure interval $P \pm \delta P$.[40] Such calculations, however, show clearly that neither ΔV_1^* nor $\Delta\beta_1^*$ can be regarded as constant over an extended pressure range, although the variability is less dramatic than that predicted for self-exchange in nonaqueous solvents.[32] For example, for the preferred model (adiabatic electron transfer at 525 pm with allowance for ion pairing), the calculated ΔV_1^* ranges smoothly but nonlinearly from −12.2 cm^3 mol^{-1} at 0 MPa to −8.4 cm^3 mol^{-1} at 140 MPa; for $\Delta\beta_1^*$, the corresponding data are −0.024 and −0.046 cm^3 mol^{-1} MPa^{-1}. Accordingly, only *average* values of the calculated ΔV_1^* over the working pressure range (0–140 MPa in 10-MPa intervals) are reported in Table II. Only the preferred model comes within the 95% confidence limit.

An alternative approach[25,32,37-40] to the analysis of pressure effects on reaction 1 involves evaluating the components ΔV_{IR}^*, ΔV_{SR}^*, ΔV_{COUL}^*, ΔV_{DH}^*, and βRT (from the pressure dependence of the preexponential part of eq 5; β is the isothermal compressibility of the solvent) of ΔV^*, along with contributions from ion pairing (ΔV_{IP}^*, which varies with reactant concentrations) and nonadiabaticity (ΔV_{NA}^*) as required. This procedure has the defect, noted above, that all these components are themselves pressure dependent, but it is instructive to compare the magnitudes of the contributions (in cm^3 mol^{-1}) from various sources for, e.g., the preferred model at zero pressure; $\Delta V_{IR}^* = +0.5$, $\Delta V_{SR}^* = -11.4$, ΔV_{COUL}^* −5.3, $\Delta V_{DH}^* = +4.0$, $\beta RT = +1.1$ $\Delta V_{IP}^* = -1.2$. The near cancellation of the last four terms is typical of calculations for ion–ion self-exchange reactions in aqueous solution at I on the order of 0.1–1.0 mol L^{-1}, with the result that ΔV^* for such reactions is determined largely by the solvent reorganization term, unless electron exchange is nonadiabatic.[39,40]

For the conjugate-base pathway, the k_2' values of Table I give $\Delta V_2'^* = -0.4 \pm 0.4$ cm^3 mol^{-1} (0–140 MPa) for the combined reactions 2 and 3. The value of $\Delta V_a = -1.2 \pm 0.5$ cm^3 mol^{-1} obtained by Vanderhoek[31] under our experimental conditions for the hydrolysis equilibrium (reaction 2) then gives an experimental value of $\Delta V_2^* = +0.8 \pm 0.9$ cm^3 mol^{-1} for reaction 3 alone. Calculations of a theoretical ΔV_2^* for reaction 3 on the basis of outer-sphere mechanisms as above give completely incompatible results (e.g., −11.4 cm^3 mol^{-1} at $P = 0$ for the preferred model). For an inner-sphere, OH-bridged mechanism, however, a water molecule must be expelled from the first coordination sphere of $Fe(H_2O)_6^{2+}$ to form $(H_2O)_5Fe{-}OH{-}Fe(H_2O)_5^{4+}$, and a semiempirical relationship can be used to estimate a volume change of +13.1 ± 1.6 cm^3 mol^{-1} at ambient pressure and $I = 0$ for this process.[26] This may be combined with a volume of activation for electron transfer of −11.3 cm^3 mol^{-1}, calculated as above for $\sigma \simeq 415$ pm (the approximate Fe–O–Fe distance in the inner-sphere precursor complex) at $P = 0$, to give a predicted ΔV_2^* of +1.8 ± 1.6 cm^3 mol^{-1} at zero pressure for reaction 2, in good agreement with experiment. Thus, pressure effects indicate an inner-sphere mechanism for reaction 3 and, by the same token, make an aqua-bridged mechanism[15,18] highly unlikely for reaction 1.

Conclusions

Pressure effects indicate that the direct self-exchange of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{2+}$ in aqueous solution is an adiabatic outer-sphere process, although they do not in themselves distinguish between full adiabaticity at normal ion–ion contact distances and adiabaticity gained by interpenetration of the aqua ligands in the precursor complex. Adiabaticity may therefore be marginal for the homogeneous $Fe(H_2O)_6^{3+/2+}$ self-exchange reaction, as has been suggested,[6-14] but both marked outer-sphere nonadiabaticity and inner-sphere electron transfer involving a bridging aqua ligand appear to be inconsistent with the experimental results. The aberrations noted for the $Fe(H_2O)_6^{3+/2+}$ self-exchange at electrode surfaces[15] (where the distance to the electrode surface and back again almost certainly exceeds the 525–680 pm considered here) and in cross-reactions involving $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{2+}$ [15,16,23,24] are very likely due to nonadiabatic electron transfer. The Marcus–Hush theory, with minor modifications to allow for the presumed pressure dependences of the Fe–Fe separation σ and anion–cation pairing, accounts satisfactorily for the effect of pressure on the rates of both the direct $Fe(H_2O)_6^{3+/2+}$ self-exchange and, if the volume change due to the loss of an aqua ligand is allowed for, the inner-sphere $Fe(H_2O)_5OH^{2+}/Fe(H_2O)_6^{2+}$ exchange.

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Registry No. $Fe(H_2O)_6^{3+}$, 15377-81-8; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Fe(H_2O)_5OH^{2+}$, 15696-19-2.

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