Redox Kinetics of Metal Complexes in Non-Aqueous Solutions. XII. Effect of Non-Bridging Ligands on Intramolecular Electron Transfer in the $FeL_5^{3+}/Fe(Me_4phen)_3^{2+}$ Reaction in Acetonitrile

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In acetonitrile the reductions of a series of iron(III) solvates, FeL_6^{3+} (L = TMP, DMF, DEF (= diethyl formamide), AA (= acetamide), and DMSO), by Fe(tmphen)$_3^{2+}$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) proceed via formation of a kinetically-detectable intermediate. All evidence available suggests its form as L_5Fe(acetonitrile)Fe(tmphen)$_3^{5+}$ wherein acetonitrile features a bridge between phenanthroline and FeL_5^{3+} in that the C–N triple bond interacts with the π orbitals on the peripheries of the phenanthroline complex and the nitrile N coordinates to FeL_5^{3+}. The decomposition rate constant of that intermediate, signifying the rate of the actual electron transfer, has been measured in dependence of ligands and temperature. For the series of related reactions the isokinetic relationship holds. As the donor number of the ligands increases, the activation energy is decreased according to the increase in electronic coupling, over the wide range of 50 kJ mol^{-1}. At the same time the activation entropy shifts to more negative values, due to increased steric crowding in the successor complex, over an even wider range from −41 to the extremely negative value of −286 J K^{-1} mol^{-1}. Consequently the decrease in $\Delta S^{\neq}$ strongly overcompensates the favorable change in $\Delta H^{\neq}$: The reaction series is entropy-controlled, as is recognized by an isokinetic temperature which is below the experimental temperature range $T_{iso} \sim -70$ °C.

Introduction

Recently we have seen an ever-increasing awareness of measuring rates of electron transfer reactions in the intramolecular mode. The scheme became possible when an ingenious, although indirect, strategy for synthesizing high concentrations of precursor complexes was devised. The topic has been excellently reviewed latterly in a section lecture given by Haim during the XXIInd International Conference on Coordination Chemistry [1]. Accordingly, progress made during the past few years gives rise to the feeling that an understanding of fundamental aspects of the charge-transfer act itself seems to be just around the corner. Hitherto however changes in structure and composition, for comparative purposes, have been limited to the bridging group (all involving nitrogen heterocycles), an exception being the passing reference made by Zawacky and Taube [2] regarding the rate difference of electron transfer in the 4,4'-bipyridine bridged complex,

$$(L)(NH_3)_4Ru^{II}(BP)Co^{III}(NH_3)_5^{n+} \quad (1)$$

where L is H_2O or SO_3^{2-}. (The slower rate for the sulfito complex was explained in terms of this ligand being a π acid leading to a decreased electronic coupling between the metal centers.)

At this juncture, a systematical evaluation of non-bridging ligand effects on intramolecular electron transfer would enlarge the research horizons of the field. On the basis of the types of systems investigated thus far, however, the possibilities are severely limited, not least because water is used as solvent. One opportunity could be the extension of the variation in ligands at the Ru(II) moiety in the above system, on utilizing the preparative work featured by Bernhard *et al.* [3] and switching to non-aqueous and poorly coordinating solvents (so as to prevent ligand exchange reactions). We recently encountered a reaction system which opens up the possibility of studying non-bridging ligand effects: the redox reactions of iron phenanthroline complexes and iron solvates proceeding, in acetonitrile as solvent, via kinetically-detectable intermediates whose decomposition rates are in the stopped flow range [4, 5]. In particular we have in mind the oxidation of tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II), Fe(tmphen)$_3^{2+}$, by various iron(III) solvates, FeL_6^{3+}, L being H_2O, TMP, DMF, DEF (diethyl formamide), AA (acetamide), and DMSO. As these ligands can be ordered according to their Lewis basicities by making use of the donor numbers (DN) [6] we have a means of classifying their mode of action [4].

In this article we now extend our previous work by making a temperature-dependence study, the

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object being to observe the activation parameters in the light of the ligand donor strengths. At first, however, we must try to settle the question of the identity of the intermediate whose form has remained obscure, except that we can assume that acetonitrile is involved. This can be postulated because no intermediate at all could be detected in other solvents [7, 8]. For the sake of clarity let us briefly review the kinetics of the redox process under consideration. The reaction proceeds via parallel inner-sphere and outer-sphere pathways the basis of recognition being a slow (compared to the actual redox reaction) but appreciable equilibrium between less active hexa- and highly active penta-coordinated solvate species*,

$$\underset{(\mathrm{Fe_i^{3+}})}{\mathrm{FeL_6^{3+}}} \overset{k_{ia}}{\rightleftharpoons} \underset{(\mathrm{Fe_a^{3+}})}{\mathrm{FeL_5^{3+}}} + \mathrm{L} \qquad (1)$$

The reaction of $\mathrm{Fe_i^{3+}}$ with $\mathrm{Fe(tmphen)_3^{2+}}$ is simply second-order,

$$\mathrm{Fe_i^{3+}} + \mathrm{Fe(tmphen)_3^{2+}} \xrightarrow{k_i} \mathrm{Fe_i^{2+}} + \mathrm{Fe(tmphen)_3^{3+}} \qquad (2)$$

whereas, except for the hydrate [9], rate saturation occurs in the reduction of $\mathrm{Fe_a^{3+}}$ at each of high $[\mathrm{Fe_a^{3+}}]$ and $[\mathrm{Fe(tmphen)_3^{2+}}]$,

$$\mathrm{Fe_a^{3+}} + \mathrm{Fe(tmphen)_3^{2+}} \rightleftharpoons \mathrm{I} \xrightarrow{k_a} \mathrm{Fe_a^{2+}} + \mathrm{Fe(tmphen)_3^{3+}} \qquad (3)$$

Thus the form of I and a detailed study on k_a, especially the meaning of its decrease with increasing DN of the ligands at $\mathrm{Fe_a^{3+}}$, are the topics of the present paper.

Experimental

Materials

The preparation of the perchlorate salts of $\mathrm{FeL_6^{3+}}$ and of tetramethylferroin, and the purification of acetonitrile, were as described previously [4, 9].

Kinetic Studies

The stopped-flow measurements were done in an approved manner [4]. The thermostatting equipment employed has been described recently [10]. In evaluating the rate constants k_a and k_i of the steps noted in the introduction, the reactions of $\mathrm{Fe(tmphen)_3^{2+}}$ with $\mathrm{Fe_a^{3+}}$ and $\mathrm{Fe_i^{3+}}$ are so different in rate that for runs with about equimolar solutions or $\mathrm{Fe(tmphen)_3^{2+}}$ in excess, the $[\mathrm{Fe(tmphen)_3^{3+}}]$–t curves display two distinct stages which can be analyzed separately. With a certain excess (depending on the ligand [4]) of the iron(III) solvate, the slow stage (reaction of $\mathrm{Fe_i^{3+}}$) disappears and the rate now measured corresponds to the reaction of $\mathrm{Fe_a^{3+}}$. The pseudo-first-order rate constant, k_a', of this fast stage reveals saturation at high $[\mathrm{FeL_6^{3+}}]$. The double-reciprocal plot is linear and thus allows one to calculate k_a. Figure 1 shows the results for the TMP solvate. It should be mentioned, however, that in these plots the (unavailable) concentration of $\mathrm{Fe_a^{3+}}$ must be used instead of simply $[\mathrm{FeL_6^{3+}}]_0$. Nevertheless the plots are actually linear suggesting a linear trend between $[\mathrm{Fe_a^{3+}}]$ and $[\mathrm{FeL_6^{3+}}]_0$ in the concentration range employed. Of course, the Michaelis constant as the second quantity available from these plots cannot be evaluated without knowing the absolute values of $[\mathrm{Fe_a^{3+}}]$. Therefore,

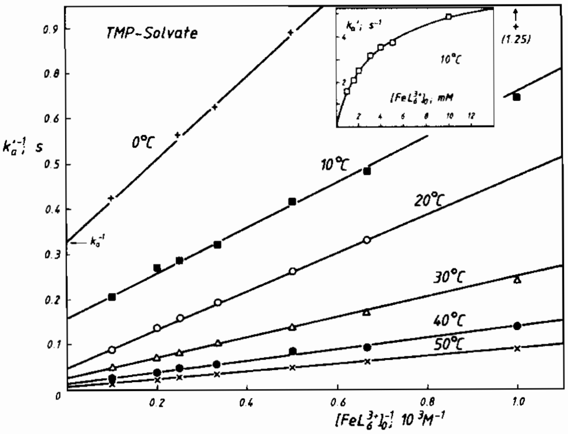

Fig. 1. Dependence of the first-stage pseudo-first-order rate constant on the concentration of $\mathrm{Fe(TMP)_6^{3+}}$ and temperature.

$$k_a' = \frac{k_a \cdot \mathrm{const} \cdot [\mathrm{FeL_6^{3+}}]_0}{1 + \mathrm{const} \cdot [\mathrm{FeL_6^{3+}}]_0} \qquad (4)$$

where const equals the Michaelis constant in the case that $[\mathrm{FeL_6^{3+}}]_0 = [\mathrm{Fe_a^{3+}}]$.

The alternative possibility for obtaining values of k_a is the double-reciprocal plot using $\mathrm{Fe(tmphen)_3^{2+}}$ in excess. Though in this method $[\mathrm{Fe_a^{3+}}]$ could be roughly estimated from the relative contribution of the first stage to the net deflection obtained on the

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*For the question of whether or not acetonitrile occupies the vacant site, no definite conclusion could hitherto be reached. Although we were biased formerly in favor of the latter, the involvement of an (unfavorable) equilibrium, $\mathrm{FeL_5^{3+}} + \mathrm{An} \rightleftharpoons \mathrm{FeL_5An^{3+}}$, cannot be excluded. Such an equilibrium would indeed be consistent with the form of the precursor we propose in this paper. In the context of this ambiguity however it is important to our interpretations to follow that, beyond equilibrium (1), the solvate complexes are stable entities in poorly coordinating solvents. The evidence is at least of three kinds: i) The solvate complexes can be recrystallized from acetonitrile. ii) There is a correlation between the rate constants k_a and k_i and the donor numbers of the ligands. iii) The An solutions of the solvate complexes are stable for kinetic measurements. Even having stood overnight (under dry nitrogen), reactant solutions yield identical results.

recording instrument, there are additional uncertainties owing to the poor solubility of the phenanthroline complex salt not allowing sufficient excess to be employed. Recently we noted [4] a principal agreement between k_a values obtained using both methods, indicating a correct procedure.

A plot of the pseudo-first-order rate constant k_i' *versus* excess $[\mathrm{Fe(tmphen)}_3^{2+}]$ yields a straight line which passes the origin as in Fig. 2, which is for the acetamide solvate,

$$k_i' = k_{ia} + k_i[\mathrm{Fe(tmphen)}_3^{2+}] \qquad (5)$$

Therefore the slope of these plots yields k_i. The TMP runs were complicated by the appearance of a third stage when the phenanthroline complex was in more than about sixfold excess, thus troubling the evaluation of k_i. Therefore the constant was determined under second-order conditions. The same method was also applied to the DMF runs.

No further determinations of the temperature-dependence of k_{ia}, *i.e.*, the intercepts of the above plots, were made because of the inaccuracy of the $[\mathrm{Fe}_a^{3+}]$ values available (which are in turn dependent on temperature). In order to obtain k_{ia}, values of k_i' must be plotted versus the residual concentration of the phen complex after the first stage instead of the total concentration.

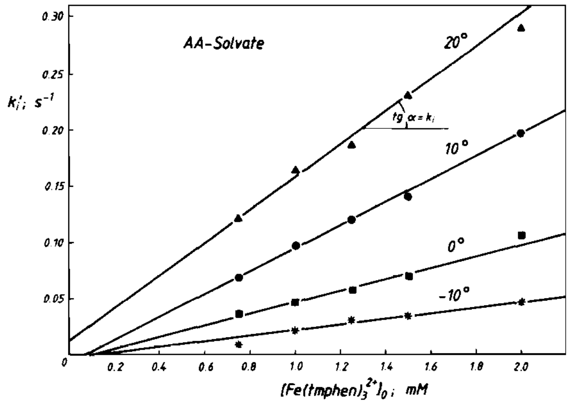


Fig. 2. Dependence of the second-stage pseudo-first-order rate constant on the concentration of $\mathrm{Fe(tmphen)}_3^{2+}$ for the iron(III) acetamide solvate.

TABLE I. Temperature and Concentration Dependence of the Pseudo-First-Order Rate Constant k_a' ($[\mathrm{Fe(tmphen)}_3^{2+}]_0 = 0.2$ mM).

Solvate	$[\mathrm{FeL}_6^{3+}]_0$ mM	k_a' (10^{-2} s^{-1})[a] T (°C)			
		20.0	30.0	40.0	50.0
$\mathrm{Fe(AA)}_6^{3+}$	1.5	38			
	2.0	47	75		
	3.0	70	110	435	526
	4.0	85		488	690
	5.0	111	182	556	909
	10.0		225	800	1250
$\mathrm{Fe(DMF)}_6^{3+}$	1.0	1.98[b]			
	1.5		5.85[c]		13.9
	2.0	3.86[b]	7.58[c]	11.9	20.0
	3.0	5.56[b]	14.1[c]		
	4.0	8.26[b]		23.3	35.7
	5.0	9.17[b]	16.9[c]	30.3	43.5
	10.0	14.9[b]	25.6[c]	52.6	76.9
$\mathrm{Fe(DEF)}_6^{3+}$	2.0	3.64	4.67	7.52	13.9
	3.0	5.10	6.45	11.2	20.0
	4.0		8.77	14.3	25.6
	5.0	7.35	11.0	19.6	30.3
	10.0	11.5	17.0	32.3	62.5
$\mathrm{Fe(DMSO)}_6^{3+}$	1.0		0.197	0.242	0.250
	1.5	0.164[d]	0.215		0.288
	2.0	0.189[d]	0.233	0.293	
	2.5	0.204[d]	0.262	0.303	0.307
	3.0	0.217[d]	0.271	0.325	0.338
$\mathrm{Fe(TMP)}_6^{3+}$	see Fig. 1				

[a] Each rate constant is accurate to within 5%. [b] At 20.2 °C. [c] At 30.2 °C. [d] At 22.0 °C.

TABLE II. Temperature and Concentration Dependence of k_i' ($[FeL_6^{3+}]_0$ = 0.2 mM).

Solvate	$[Fe(tmphen)_3^{2+}]$ mM	k_i' (10^{-2} s^{-1})^a T (°C)				
		−10.0	0.0	10.0	20.0	30.0
$Fe(H_2O)_6^{3+}$	0.80	29	97	124	220	
	1.05			199	294	
	1.30	40	111	242	359	
	1.80	60	160	315	490	
$Fe(TMP)_6^{3+b}$	0.25	2.30	4.13	8.3	15.0	28.2
	0.30	2.70	5.10	10.0	17.8	33.5
	0.40		6.64	13.4	23.7	43.5
	0.50	4.29				
	0.60	5.25	9.75	20.1		
	0.70	6.34				
	0.80	7.13	13.5	26.6	48.0	88.0
$Fe(DMF)_6^{3+\,b}$	0.30	0.23	0.32	0.65	0.94	
	0.40	0.32	0.45	0.85	1.28	2.50
	0.50	0.39			1.56	3.10
	0.60	0.48	0.57	1.22	1.86	3.96
	0.70	0.53				
	0.80	0.62	0.87	1.80		5.00
$Fe(AA)_6^{3+}$	see Fig. 2					

[a] Each rate constant is accurate to within 8%. [b] Values are determined from second-order-conditions and converted into pseudo-first-order constants.

Results

The pseudo-first-order rate constant k_a' and k_i' for the various iron(III) solvates, reactant concentrations and temperatures are summarized in Tables I and II and Figs. 1 and 2. From these data derived values of k_a and k_i may be seen from Table III and Fig. 3.

TABLE III. Temperature Dependence of the Second-Order-Rate-Constant k_i.

Solvate	ln k_i^{a} T (°C)				
	−10.0	0.0	10.0	20.0	30.0
$Fe(H_2O)_6^{3+}$	5.74	6.75	7.43	7.89	
$Fe(TMP)_6^{3+}$	4.49	5.12	5.81	6.35	7.01
$Fe(AA)_6^{3+}$	3.24	3.93	4.63	5.00	
$Fe(DMF)_6^{3+}$	2.03	2.35	3.06	3.45	4.13

[a] k_i in M^{-1} s^{-1}. The estimated experimental error in ln k_i is ±0.12 ln units.

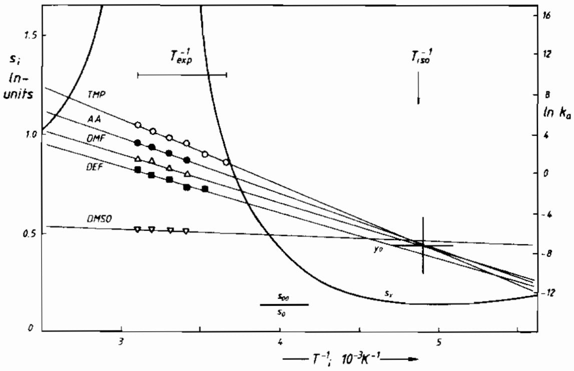


Fig. 3. Arrhenius plot of the first-stage rate constant involving various ligands L at FeL_5^{3+}, in Exner's terms. The full line is the function s_x (constrained standard deviation from the regression lines) of x (= 1/T). The estimated experimental error in ln k_a (k_a in s^{-1}) is ±0.1 ln units.

The Arrhenius plots for the k_a and k_i rate constants for each solvate are linear. For testing whether the isokinetic relationship (IKR) holds and for evaluating the isokinetic temperature (T_{iso}), we used the statistical method developed by Exner [11, 12]. The way of proceeding was the same as previously reported [13, 14]. Figure 3 displays the Arrhenius plot for k_a in Exner's terms. Since the isokinetic standard deviations from the regression lines are smaller than the unconstrained ones ($s_o < s_{oo}$), the IKR is to be accepted. The isokinetic temperature is below the experimental temperature range, $T_{iso} \sim -70$ °C. A similar plot, not shown here, is obtained for the

TABLE IV. Activation Parameters[a,b] of the k_a and k_i Reactions.

Iron(III) Solvate	k_a reaction		k_i reaction	
	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}
H_2O			44 (47)	−30 (−16)
TMP	53 (54)	−41 (−38)	39 (39)	−57 (−57)
AA	44 (46)	−84 (−79)	36 (38)	−74 (−73)
DMF	38 (38)	−114 (−116)	33 (33)	−104 (−103)
DEF	37 (32)	−130 (−144)		
DMSO	2 (6)	−286 (−274)		

[a] Calculated from the unconstrained regression lines of the Arrhenius plot using the equations $\Delta H^‡ = E_a - R\bar{T}$ and $\Delta S^‡ = 2.303\ R\ (\lg A - \lg\bar{T} - 10.75)$, where $\bar{T}$ is the mean experimental temperature. [b] Isokinetic (*i.e.* with the constraint of a common point of intersection) values in parentheses.

k_i constants ($s_o = 0.103 < s_{oo} = 0.111$, $T_{iso} \sim -130$ °C, the logarithm of the rate constant at T_{iso}, $y_o = -10.89$). The activation parameters for the steps pertinent to k_a and k_i are collected in Table IV.

In turning to the temperature variation of the ligand effect on k_a, a decrease is observed in the order

TMP > AA > DMF > DEF > DMSO

which is the order of increasing donor number [4]. Recently, in discussing the relations between the Arrhenius and the Hammett plots, we have pointed out [13], that a temperature variation of a simple LFER might result in a set of straight lines all intersecting at a single point which reveals the isokinetic substituent (ligand, solvent), *i.e.*, whose introduction would cause the specific rate to become insensitive to temperature. In the present instance however it is impossible to draw an exact correlation diagram owing to the fact that for two of the five ligands (AA and DEF) exact donor numbers have not been measured. Nevertheless when making reasonable estimates [4] and when taking the DN_B value for DMF instead of the basic DN[15, 16] as calculated from a linear relationship between DN and the Lewis basicity parameter B, the correlation represented in Fig. 4 is obtained. Though this plot cannot be taken as established at this time because the donor numbers have been chosen so as to obtain straight-line relationships, it would agree well with the (exact) Arrhenius plot in Fig. 3. The common point of intersection in either plot occurs at the same specific rate. This is to be expected from a logical point of view in that the specific rate at the isokinetic temperature is insensitive to ligand variation and thus also includes the isokinetic ligand and vice versa. Hitherto such an agreement between the specific rate at the isokinetic temperature and that for the isokinetic substituent has been suggested for isoentropic reaction series only [13]. The common point of intersection in the LFER is close to the point for DMSO. This is in line with the Arrhenius plot, as for the DMSO ligand the activation energy is near zero indicating the isokinetic ligand for the reaction series.

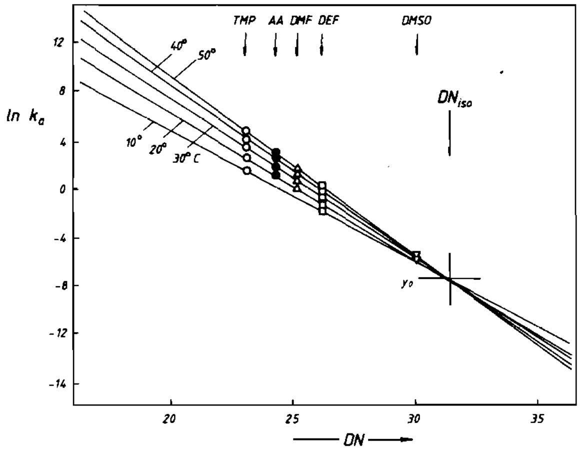


Fig. 4. Temperature-variation of the LFER for the same reaction series as in Fig. 3.

Discussion

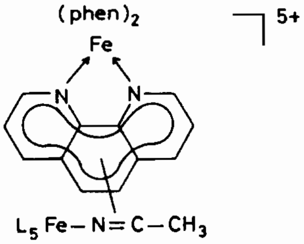
Form of the Precursor

Since a mechanism involving a ligand bridge between 'normal' coordination positions of both reacting ions can be ruled out, and since the phenanthroline complex is substitution-inert on the time scale for electron transfer, the occurrence of an intermediate in the title redox reaction must be interpreted to mean that acetonitrile forms a link between phenanthroline and Fe_a^{3+} and thereby provides a favorable electron transfer pathway. There are other observations suggesting particular interactions between phen and An. For instance, phen does not fit the isokinetic relationship found in substitution kinetics of nickel(II) with pyridine ligands in An (in which solvent complex formation is much faster with phen than with the other ligands used [17, 18]). These features, though being claimed not to be limited to acetonitrile [19], have been attributed to exceptional outer-sphere stabilization caused by electrostatic or π-orbital interaction of phenanthroline present in the outer-sphere with the polarized acetonitrile molecules of the inner-sphere. As another example, the LFER for the solvent effect on the racemization of $Ni(phen)_3^{2+}$ is not obeyed by acetonitrile and pyridine, hinting at a change of mechanism in these solvents [20].

The form of the precursor resembles the thiocyanate catalysis of the Fe^{2+}–$Fe(L–L)_3^{3+}$ reaction in water, as studied by Sutin and Forman [21]. In fact, the close analogy is obvious between a possible attack of HSCN (or SCN^-) and CH_3CN on phenanthroline. Complexing by metal ions would make the phen ligand essentially electron-deficient and thus electrophilic towards the outer-sphere environment, giving rise to the following modes of interaction: either carbon atoms of the ligand ring system [22–26] or hydrogens [27] act as σ acceptors, or the ligand π system [21] acts as a π acceptor.

The idea of the accessibility to nucleophilic attack by Lewis bases at the carbon atom adjacent to the ring nitrogen has been put forward by Gillard [23]. On adopting this view, hitherto unexplained features of the Fe^{2+}–$Fe(L–L)_3^{3+}$ reaction in water could be brought under the umbrella of one treatment. Acetonitrile, however, is too poor a (σ) donor to make this mechanism attractive. On the other hand, the π orbitals of the C–N triple bond (which are directed at right angles to the C–N axis) are reported to be good π donor centers [28] which can interact with the π orbitals on the peripheries of $Fe(tmphen)_3^{2+}$ (and likewise to any $Fe(phen)_3^{n+}$). The lone pair orbital on the N atom of CH_3CN is then free for complexing pentacoordinate Fe_a^{3+} and thus mediating between the latter and $Fe(tmphen)_3^{2+}$. In this connection it is worthwhile noting that there are complexes containing benzonitrile which simultaneously bind two metal atoms side-on and end-on [29].

In the light of these considerations we envisage the intermediate in question as follows:



(II)

The visible spectra during the progress of the reaction only showed the characteristic bands of reactants and products. Impurities of acetonitrile, *viz.* traces of water or acrylonitrile, do not play a mediating role because addition of catalytic quantities of these compounds slowed down the reaction drastically.

Reaction Step Pertinent to k_a (eqn. 3)

The underlying aim of studying redox reactions under intramolecular electron transfer conditions is to shed light on the electron-transfer act itself. However, redox intermediate decomposition rates are not necessarily interpretable in such terms. Though there are no longer complications by the need of assembling the reactants, at least two problems must be taken into consideration. The first concerns the measured rate constant itself, and the second the activation parameters calculated from the temperature dependence.

Regarding the first, precursor decomposition is to be considered as a sequence of at least two elementary steps,

$$\text{precursor} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \text{successor} \xrightarrow{k_2} \text{products} \qquad (6)$$

each of which can be rate determining [30, 31]. If the dissociation into the final products controls the rate, then the measured rate constant is equal to $k_2K/(1 + K)$ where $K = k_+/k_-$. If in the opposite extreme, electron transfer is rate determining, k_+ is the value being measured. A means of diagnosing which case might apply (or whether both steps are of equal probability) is to determine the temperature dependence of the rate constant. A linear Arrhenius plot over a wider temperature range would be supportive of electron transfer being measured. This would seem to be realized in the present case, where the temperature has been varied over a range of up to 50 °C. The conclusion that the final dissociation does not occur in the rate determining step is further strengthened by the considerably negative activation entropies encountered throughout the reaction series.

The activation parameters are not easily interpretable as they suffer on the whole from the problem of reflecting not only the intrinsic electron transfer but also the differences in the solvation of precursor and successor complexes. This is in actuality the second complication mentioned above. As expected, intramolecular electron transfer steps conform to the common rule that in solution, where charged particles are involved, solvation effects often dominate the entropy of activation. This gives rise to the charge-redistribution concept [32, 33]. For the present case however the intrinsic contributions must be assumed to be of even greater importance. In discussing the dramatically large variations in the activation parameters from Table IV it is essential to bear in mind the features of our reaction series being (i) the rate decreases as the Lewis base strength of the ligands at the solvate moiety is increased, (ii) there is a linear relationship between the enthalpy and entropy of activation, and (iii) the isokinetic temperature is below the experimental temperature range.

Recently the mechanistic value inherent in studying substituent and ligand effects has been summarized by the guiding principle [10, 15] that rate acceleration by acceptor (donor) substituents is indicative of the reaction site being an acceptor (donor), providing the experimental temperature is below the isokinetic temperature. The opposite would be true if $T_{exp} > T_{iso}$ because of the reversal of the reactivity sequence within a reaction series as the temperature passes through T_{iso}. The above features would mean that the L_5Fe^{3+} moiety acts as a *donor* in the precursor. The necessity remains of assuming the π basicity of L_5Fe^{3+} to determine the activation energy, to be understood in the light of the low affinity of nitrile N for Fe(III) [9], such that even small π interactions have a stabilizing effect. Thus the interpretation of the variation in $\Delta H^{\ddagger}$ is straightforward in that an increase in the donor strength of L leads to an increase in π basicity of L_5Fe^{3+}, which in turn gives rise to an increased electronic coupling. Beyond that, solvation effects do not appear to affect appreciably the activation energy as may be implied from the small solvent effect on the temperature variation of the self-exchange rates of $Fe(phen)_3^{2+/3+}$ couples [34, 35].

We turn now to a consideration of the activation entropies. Part of the considerably negative values is undoubtedly due to the stronger solvation of the ferrin moiety compared to ferroin: about 100 J K^{-1} mol^{-1} represents the loss in reaction entropy on going from the divalent to the trivalent complex in the solvent acetonitrile [36]. It is, however, not known what part of that is involved in the activation process. Anyway, the overall solvation term of the activation entropy must be further decreased by the entropy gain due to solvent release around the FeL_5^{2+} moiety. Substitution of An for L in the latter is also to be taken into consideration. In fact, $Fe(TMP)_6^{2+}$ in acetonitrile is transformed into the An-solvate within some minutes, in contrast to $Fe(DMF)_6^{2+}$ which is sufficiently stable for kinetic measurements [5]. This conforms to the rule that in a given solvent a metal ion complex is more stable the higher the donor strength of its ligands. Considering now the fact that the IKR holds for the reaction series under discussion, meaning that there is one interaction mechanism operative, substitution processes at the iron(II) solvate occurring within the life-time of the precursor can be ruled out. It is safe to assume that solvation effects alone cannot account for the large variation in $\Delta S^{\ddagger}$ in question. Rather, there is an intrinsic effect arising from steric crowding in the successor. The reason is bond-shortening, in that the bridging acetonitrile molecule becomes more strongly bound to the $Fe(phen)_3^{3+}$, whose phenanthroline ligands are more π deficient than in the reduced state as well as to FeL_5^{2+} whose iron center is essentially more π basic than the trivalent state [37, 38]. Thus the experimental activation parameters, and particularly the direction of their variations along the series of ligands, are corroborative evidence of the proposed intermediate structure (II).

In sum, the large decrease in activation entropy (due to steric crowding and additional changes in solvation) strongly overcompensates the favorable activation enthalpy change (due to electronic coupling). The reaction series is entropy-controlled, as is recognized by an isokinetic temperature below the experimental temperature range. This study appears to provide an excellent example of revealing the importance of analysing the temperature variation of any effects in order to arrive at a meaningful interpretation of the correlations. Without the knowledge of the present work one of us [39] interpreted the decrease in rate with increasing donor number of L in FeL_5^{3+} on the basis of a naive donor-acceptor concept saying that "decreasing positive fractional charge at the coordination center by coordination means an increase in electron density of the orbital which accepts the electron from the reducing agent." Caution is thus urged in the premature interpretation of relative reactivities without having details on the enthalpic and entropic contributions to the activation barrier.

Reaction Step Pertinent to k_i (eqn. 2)

For the rate constant k_i of the outer-sphere path there is a behavior similar to k_a: decrease in rate as the donor number of L in FeL_6^{3+} is increased [4], holding of the isokinetic relationship and an isokinetic temperature below the experimental temperature. Therefore the outer-sphere path can be considered as occurring by the same 'intimate mechanism' as the inner-sphere route. In Fig. 5 we have drawn the isokinetic plot for both series treated in a fashion which regards each T_{iso} as −70 °C (so as to obtain parallel lines). It is noteworthy that the line pertinent to (second-order) k_i is shifted by about 45 J in the direction of more positive entropy compared to the line for (first-order) k_a. This is interesting with respect to

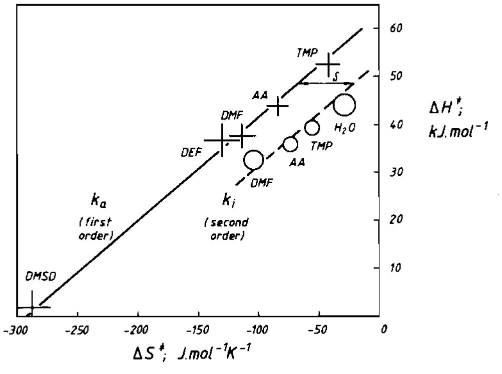
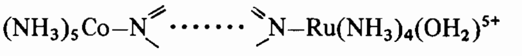


Fig. 5. Isokinetic plot pertinent to the rate constants k_a and k_i, letting T_{iso} = −70 °C for both.

a calculation of Moelwyn-Hughes [40] suggesting that the activation entropy of a bimolecular reaction according to collision theory is at 25 °C more positive by 47.2 J K^{-1} mol^{-1} than the activation entropy calculated for a first-order process using Eyring's formula.

The large variation in the activation energy in our reaction series of changing the non-bridging ligands* contrasts with those of changing the structure (but not the donor atoms) of the bridging ligands. Remember the constant $\Delta H^{\ddagger}$ of about 83 kJ for intramolecular electron transfer in complexes of the type [41]

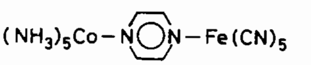


$(NH_3)_5Co{-}N\cdots\cdots N{-}Ru(NH_3)_4(OH_2)^{5+}$ (III)

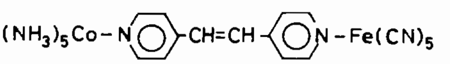
or the value of about 100 kJ [33, 42] in

$(NH_3)_5Co{-}N\cdots\cdots N{-}Fe(CN)_5$ (IV)

where the bridging groups are pz (pyrazine), bpy (4,4′-bipyridine) *etc.*, where in the latter the pyridine rings are connected either directly or *via* groups such as $-CH_2-$, -S-, -CH=CH-, -C≡C-. These observations highlight the great importance of π interactions between the metal center and the bridge in determining the energy needed for electron transfer: the more the π electron density is delocalized from the metal center to the bridge, the lower the energy [31, 42]. The issue is of course obscured in the above series (III) and (IV) as these involve one sort of donor atoms only (and essentially conjugated bridges). Rate differences, in this case by structural changes of the bridge, are reflected mainly in $\Delta S^{\ddagger}$, explained in terms of *e.g.* varying solvation barrier to electron transfer. This is in accordance with calculations made recently [43] suggesting that even long conjugated bridges are completely conducting. As an example note the difference in activation parameters for electron transfer [33, 42, 44] in



(V)



(VI)

	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/K mol
(V)	103	+77
(VI)	102	+44

In contrast, the variation in the bridging atom as in

$(NH_3)_5Co{-}X{-}Fe(DMSO)_5^{4+}$ (VII)

where X is a halide, causes the overall activation enthalpy in DMSO as solvent [45] to increase in the series F ≪ Cl < Br, which is the order of Van der Waals radii. Part of this effect can be interpreted as being due to the variation in the Fe(II)–X bond length resulting in a changing efficiency of electronic coupling [46].

Thus the suggestion quoted in the introduction, namely that the smaller rate of electron transfer in $(SO_3)(NH_3)_4Ru(bpy)Co(NH_3)_5^{3+}$ compared to $(H_2O)(NH_3)_4Ru(bpy)Co(NH_3)_5^{5+}$ is due to the π acidity of sulfite, is reinforced.* A point of concern is that in this case the ligand variation is in the reductant while in the present work it is in the oxidant, nevertheless causing the energy to change in the same direction. On this, the concept of π basicity of metal centers (which is similar to Gaswick and Haim's 'symmetry factor' [47]) offers the possibility of a qualitative ordering of activation energies of electron transfer *e.g.*, the higher energies for both the Co(III)–Fe(II) and Co(III)–Ru(II) complexes compared to present Fe(III)–Fe(II) is due to the lower π basicity of Co(III) compared to Fe(III). The lower $\Delta H^{\ddagger}$ of series (III) than that of (IV) can be understood in terms of the higher π basicity of Ru(II) compared to Fe(II), that difference being further increased as the ammonia ligands increase the former, but the cyano ligands decrease the latter [48].

It is interesting to contrast the title reaction and the $Fe(phen)_3^{3+}/Fe_{aq}^{2+}$ reaction in water. The latter has been considered for a long time as 'necessarily outer-sphere' [49], biased however more by the circumstance that other possibilities were not obvious. The chief evidence was thought to be the variation in rate with phen substituents conforming to the change in E^0 for the various $Fe(phen)_3^{3+/2+}$ couples [7]. However, linear free-energy relationships are also found for inner sphere reactions [50]. This is not strange since the LFER simply testifies to a continuity of mechanism in the reaction series.

Quite recently the suggestion has been put forward [10] that the $Fe(phen)_3^{3+}/Fe^{2+}$ reaction in water proceeds via an inner-sphere path mediated by water molecules coordinating, in a rapid unfavorable pre-equilibrium, at a ligand ring carbon. The experimental rate constant has then the significance of the product of the equilibrium constant of covalent hydration of ferrin and the rate constant of subsequent bridge formation to give $(Fe(phen)_3{\cdot}H_2O{\cdot}Fe(OH_2)_5)^{5+}$. Only these lines were shown to cope with all the peculiar features of the system being the decrease in rate with increasing acid and salt concentration, the non-linear Hammett plot (indicating a composite rate constant), and the pattern in activation parameters involving the phenomenon of anti-compensation. A simple outersphere activated complex model on the other hand would not seem able to accommodate these observations. The catalytic role of water is now

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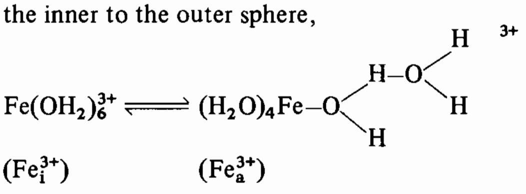
*Note however that five ligands are varied at the same time.

*The activation enthalpy for the hydrato-complex is 84 kJ mol^{-1} [41]. For the sulfito-complex no value is available but for comparative purposes that for the pyrazine bridged analogue [2] (91 kJ mol^{-1}) may be relevant.

further advocated in the light of the present study, for the following reasons:

(i) The $\mathrm{Fe(phen)_3^{3+}/Fe(DMF)_6^{2+}}$ reaction in acetonitrile, occurring by the same mechanism as the title process [5], proceeds at a rate commensurable with the $\mathrm{Fe(phen)_3^{3+}/Fe^{2+}}$ reaction in water [7] in spite of the high acidities employed. In a neutral solution the rate would be orders of magnitude larger. This observation hints at water playing a particular role, such as that in the pseudo-first-order rate constants of the oxidation of $\mathrm{Fe(tmphen)_3^{2+}}$ ($5 \times 10^{-4}\ M$) by $\mathrm{Fe(TMP)_6^{3+}}$ ($1 \times 10^{-4}\ M$), which is increasing in the order of solvents nitromethane (NM) < propylenecarbonate (PC) ≪ An [8]. The observed values are 0.10, 0.24 and 13 $\mathrm{s^{-1}}$, respectively. Certainly, the about one hundredfold higher rate in An reflects the catalytic role of that solvent.

(ii) A very important piece of information comes from the kinetics of $\mathrm{Fe(tmphen)_3^{2+}}$ oxidation by the iron(III) hydrate, $\mathrm{Fe(OH_2)_6^{3+}}$, measured in the same three solvents, as this system features the connecting link between the $\mathrm{Fe(phen)_3^{3+}/Fe^{2+}}$ reaction in water and the $\mathrm{Fe(tmphen)_3^{2+}/FeL_6^{3+}}$ reaction in acetonitrile (the $\mathrm{Fe(phen)_3^{3+}/Fe(OH_2)_6^{2+}}$ reaction cannot be analyzed in An, because $\mathrm{H_2O}$ is readily replaced by solvent molecules [5], in contrast to $\mathrm{Fe(OH_2)_6^{3+}}$.) The equilibrium between hexa- and penta-coordinated species in the hydrate case differs from that of the organic ligands in so far as the sixth ligand, instead of leaving completely (eqn. 1), changes merely from the inner to the outer sphere,



$$\underset{(\mathrm{Fe_i^{3+}})}{\mathrm{Fe(OH_2)_6^{3+}}} \rightleftharpoons \underset{(\mathrm{Fe_a^{3+}})}{\mathrm{\left[(H_2O)_4Fe{-}O(H){-}H{-}O(H)H\right]^{3+}}}$$

This is concluded from the finding that the relative amount of $\mathrm{Fe_a^{3+}}$ in this case does not change with the total hydrate concentration [9]).

The vital point now is that the reaction of hydrate $\mathrm{Fe_a^{3+}}$ with $\mathrm{Fe(tmphen)_3^{2+}}$ does not utilize the acetonitrile-catalyzed pathway. This is implied from the kinetic results showing that no intermediate could be detected, and that acetonitrile no longer plays an outstanding role. The reactivity order is NM > An > PC, with k_a values of 4×10^6, 1×10^6, and $8 \times 10^4\ M^{-1}\ \mathrm{s^{-1}}$, respectively.* These observations can be interpreted to mean that there must be another even more favorable pathway and hence testify to the mediating role of water. Then, the $\mathrm{Fe_a^{3+}/Fe(tmphen)_3^{2+}}$ reaction can easily be reviewed in that outer-sphere coordinated water is already put in order so as to pass over to the phenanthroline complex and establish the bridge.

There appears to be a well-defined reaction series with an isokinetic temperature below the experimental range: the variation in $\Delta H^{\ddagger}$ is more than offset by an even greater variation in $T\ \Delta S^{\ddagger}$, so that a change in sign of the variation in $\Delta G^{\ddagger}$ occurs. The lower T_{iso}, the larger is the range of the variation in the activation entropy. In our case $\Delta S^{\ddagger}$ moves to negative values which might be incompatible with a first order process.

Another point of interest is the fact that the concept of the isokinetic ligand (substituent, solvent) [13] is no longer hypothetical, as in this series that particular ligand is available experimentally: for DMSO, practically no temperature dependence of the rate remains.

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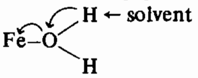
*This order was suggested to parallel the different outer-sphere effects of the solvents [9] leading to a change in charge distribution,



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