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Novel Mechanistic Aspects of the Reduction of Iron(III) Phenanthroline Complexes by Aquo Iron(II). Temperature Dependence of the Substituent Effect

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There is strong evidence that the reduction of $Fe(phen)_3^{3+}$ *by* Fe_{aq}^{2+} *occurs via an inner-sphere path mediated by water molecules coordinated at the carbon atom adjacent to the ring nitrogen of the phenanthroline ligands. Water thus acts as a catalyst. The rate constant measured is related to the product* Kk_2 *of the equilibrium constant of the covalent hydration of* $Fe(phen)_3^{3+}$ *and the rate constant of subsequent bridge formation to give* $(Fe(phen)_3{\cdot}H_2O{\cdot}Fe_{aq})^{5+}$. *The two reaction steps are inversely influenced by the electronic effect of substituents at the phenanthroline (*K *and* k_2 *increase and decrease, respectively, with acceptor substituents). These opposing effects involved can readily be invoked to account for the non-linear Hammett plot and further for the occurrence of anti-compensation of the experimental activation parameters. There is a dominant influence of the substituents on the pre-equilibrium since the net rates are enhanced with acceptor substituents.*

The reaction mechanism proposed brings the following features under one roof: dependence of rate on acid and ionic strength and substituents, the non-linear Hammett plot, the pattern in activation parameters, and the anti-compensation effect.

Introduction

In dealing with mechanisms of redox reactions between metal complexes, we recently pointed to the opposite substituent effects on the iron(II) reduction of tris(phenanthrolino)iron(III) and tris(oxinato)-manganese(III), both substituted in the 5-position [1]: electron-withdrawing substituents enhance the former, but slow down the latter. This would mean that the former reaction site acts as an acceptor, and the latter as a donor.

It transpires however that a conclusive interpretation of substituent and other effects cannot be made unless their temperature-dependence is known. The reason is that opposing effects may alternatively occur, if the experimental temperature for one series lies above and for the other below the respective isokinetic temperature (if such exists, of course, for the reaction series under consideration. Otherwise the underlying effects cannot be interpreted physically and unambiguously).

As for the second-order precursor formation involved in the iron(II) reduction of 5-substituted manganese(III) oxinates in propylene carbonate, we have shown that the isokinetic relationship (IKR) holds [1]. Since the isokinetic temperature (T_{iso}) is essentially higher than the experimental range, indicating an almost isoentropic reaction series, the substituent effect observed is electronic in nature. The rate enhancement on the introduction of donor substituents is then interpretable via an increased basicity of the oxygen of the oxinates which promotes the attack of iron(II). Thereby the precursor formation is accelerated.

We now turn over to the interpretation of the rate decrease by donor substituents of the iron(II) reduction of substituted iron(III) phenanthroline complexes in water [2]. For this purpose we report on the temperature-dependence of the substituent effect in question. Though there is an extensive body of publications on redox kinetics involving metal polypyridine complexes, it must be admitted that the mechanistic details of that type of reactions remain rather obscure.

Experimental

Basically, the procedures employed were the same as those of Sutin and Gordon [3] and Ford-Smith and Sutin [2].

Chemicals

Oxidizing agents

The ligands 1,10-phenanthroline and the methyl, chloro and nitro derivatives substituted in 5-position were used as received. The methoxy compound was obtained from the chloro derivative by a literature method [4]. Finally, 5,6-dimethyl-1,10-phenanthroline was prepared by a double Skraup reaction on 4,5-dimethylorthophenylenediamine.

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The iron(II) complexes were prepared by adding an equivalent amount of the appropriate ligand to a slightly HCl-acidic solution of iron(II) sulfate. To obtain the iron(III) complex, the resulting solution was acidified with dilute sulfuric acid and oxidized with excess lead(IV) oxide. The latter and the lead sulfate produced were removed by filtration and the perchlorate of the iron(III) complex was precipitated from the filtrate by adding dilute perchloric acid or sodium perchlorate, filtered and dried *in vacuo* at room temperature. A second method which employs more acidic solutions was preferred for preparing the less stable chloro and nitro compounds: from the solution of the iron(II) complex, obtained as above, the latter was precipitated with sodium perchlorate, redissolved in 75 vol% sulfuric acid and oxidized with cer(IV) sulfate. After cooling in an ice bath the solution was slowly diluted with cold water until the sulfuric acid was about 30 vol%, then dilute perchloric acid was added and the mixture filtered. The perchlorate of the iron(III) complex was now precipitated on adding sodium perchlorate and dried *in vacuo* as above.

Reducing agent

Iron(II) sulfate ($FeSO_4 \cdot 7H_2O$ *p.a.*, Merck) was used without further purification. The compound was practically 100% pure (checked spectrophotometrically, based on the extinction coefficient for Fe-(phen)$_3^{2+}$ formed on adding the ligand in slight stoichiometric excess).

Preparation of the Solutions

To begin with, iron(III) phenanthroline complexes are not stable in aqueous media unless the solutions are kept acidic. Ford-Smith and Sutin [2], who made the kinetic measurements in both 0.5 *M* perchloric acid and 0.5 *M* sulfuric acid, reported that with some of the compounds extensive decomposition took place during the time required to perform a series of runs. For this reason we chose higher concentrations in acid, taking the iron(III) complexes in 4.5 *M* perchloric acid. In return, the solutions of the reducing agent, $FeSO_4$, were used practically acid-free (some drops of dilute perchloric acid were added in order to prevent eventual clouding). Hence the kinetic measurements were done in 2.25 *M* perchloric acid (we ascertained in some runs that there is no observable difference between the values of the rate constants thus obtained and those when using oxidant and reductant each in 2.25 *M* perchloric acid).

A further reason for employing perchloric acidic solutions was the desire to comprise substituents of a large variety of Hammett constants. As the redox reactions under investigation are about one order of magnitude larger in sulfuric acid of similar strength, reactions involving strong acceptor substituents such as the nitro group are too fast to be measured in sulfuric acid by means of the stopped-flow method. Of the other hand it is noted that the perchlorates of the iron(III) complexes are poorly soluble in perchloric acid: saturated solutions are about 10^{-5} *M* (except in the case of the unsubstituted compound which is better soluble). These were used for the kinetic measurements and were prepared immediately before by dissolving the complexes and filtration. Triply-distilled water was used for diluting the perchloric acid and in preparing the reductant solutions.

Kinetic Procedure

The kinetic measurements on the DURRUM D-110 stopped-flow spectrophotometer were carried out as before [1], excepting a new thermostatting equipment, LAUDA thermostat TUK 30D by which the temperature could be maintained to ±0.1 °C. Measurement of temperature was in the bath fluid (Ultra-Therm SK super frigor) of the valve block by means of a LAUDA Pt 80 resistance thermometer, displayed by a LAUDA digital thermometer R 42/2. The course of the reaction was followed at 510 to 516 nm corresponding to the maxima for ferroin formation. The reactions are first-order each in reductant and oxidant. In all runs iron(II) was in excess. In most cases pseudo-first-order conditions were applied with the iron(II) in an eight- to tenfold excess. For the faster reactions, involving acceptor substituents, second-order conditions were chosen with Fe(II) employed in about twofold excess. In the latter case, the concentration of deficient oxidant was estimated from the deflection obtained on the oscilloscope. Corrections were made for the change in the total absorbance due to the disappearance of iron(III) phenanthroline during the reaction. (At 510 nm, the absorbance of the latter is about 2.6% of that of the corresponding iron(II) compound). The reactions were measured between 0 °C and 30 °C. For each pair of reactants and temperatures at least seven series of runs were carried out and the mean of the rate constants was calculated. Individual determinations differed from the mean by less than 10%.

Results

The second-order rate constants for the reactions investigated at various temperatures, and the activation parameters are listed in Table I. For testing whether the isokinetic relationship is valid and for evaluating the isokinetic temperature, we used the statistical method developed by Exner [5, 6]. The way of proceeding was as previously reported [1, 7]. Figure 1 displays the Arrhenius plot in Exner's terms. Since the isokinetic standard deviations from the regression lines are smaller than the unconstrained ones ($s_o < s_{oo}$), the isokinetic hypothesis is to be accepted unconditionally. The isokinetic temperature is clearly in the negative range, $T_{iso} \sim -470$ K.

TABLE I. Rate Constants and Activation Parameters for the Oxidation of Fe^{2+}_{aq} by 5-substituted $Fe(phen)_3^{3+}$ in 2.25 *M* Perchloric Acid.

Subst.	σ_m	$k\,M^{-1}\,s^{-1}$				$\Delta H^{\ddagger\,a}$ kJ mol^{-1}	$\Delta S^{\ddagger\,a}$ J K^{-1} mol^{-1}
		0 °C	10 °C	20 °C	30 °C		
$(CH_3)_2$	−0.14	1.6×10^3	1.9×10^3	2.1×10^3	2.7×10^3	10.3 (10.9)	−146 (−143)
CH_3	−0.07	5.0×10^3	5.9×10^3	7.0×10^3	8.5×10^3	9.6 (9.2)	−138 (−140)
H	0	1.3×10^4	1.4×10^4	1.7×10^4	2.0×10^4	8.2 (7.9)	−136 (−136)
CH_3O	0.12	1.3×10^4	1.4×10^4	1.9×10^4	2.0×10^4	7.9 (7.9)	−136 (−136)
Cl	0.37	6.9×10^4	8.2×10^4	8.4×10^4	1.0×10^5	5.4 (5.3)	−132 (−132)
NO_2	0.71	3.9×10^5	4.6×10^5	4.6×10^5	5.0×10^5	2.6 (2.7)	−127 (−127)

[a] Isokinetic (*i.e.* with the constraint of a common point of intersection) values in parentheses.

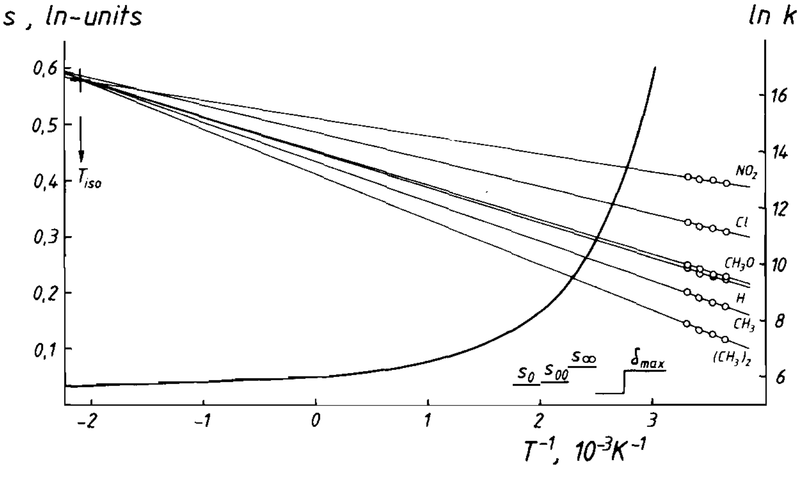


Fig. 1. Graphical representation of the Exner analysis of the Arrhenius plot. The full line is the function s_x (constrained standard deviation from the regression lines) of x ($x = T^{-1}$). Further, δ_{max} denotes the maximum experimental error.

Discussion

It is seen that the IKR holds for the reaction series under consideration and that T_{iso} is far above the experimental temperature range. These findings allow a physical interpretation of the increase in rate with acceptor substituents in that the reaction site of the iron(III) phenanthroline complexes acts as an acceptor in the rate-determining step of reduction. This result fits in with the current models of outer-sphere redox reactions according to which the electron-transfer is thought to occur within a collision complex which is so built up that appropriate donor and acceptor orbitals overlap thereby providing the electron-transfer pathway. Thus the iron(III) phenanthroline reaction with Fe^{2+}_{aq} may be envisaged as proceeding in either of two ways [8]. i) The octahedral face of the aquo ion may sit above the channel between the phenanthrolines enabling direct, though poor, t_{2g}–t_{2g} overlap. ii) The octahedral face of the aquo ion may sit above the plane of a phenanthroline ring so that there is Fe^{2+}_{aq} t_{2g}–phen π^* interaction.

Acceptor substituents, then, would facilitate the taking over of electrons by reducing the electron density in the d-orbitals of iron(III) or the π^*-orbitals of the ligand. However, while speculating which of the two possibilities might be more probable, *viz.* whether there is ligand mediation or not, we dismissed either and adopted quite another view on the mechanistic details. In actuality, the mechanism to be favored should allow also for all the peculiar features in the chemistry of polypyridine complexes as summarized by Gillard [9] who called them classical anomalies. Above all, as far as our work is concerned, the strong pH-dependence of the reaction rate, although acid is not contained in the redox equation, must be rationalized. Gillard has shown that the idea of the accessibility to nucleophilic attack by Lewis bases (in our case, water) at the carbon atom adjacent to the ring nitrogen can indeed

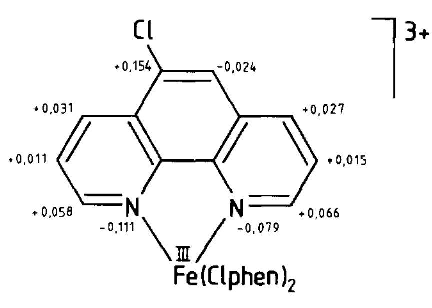
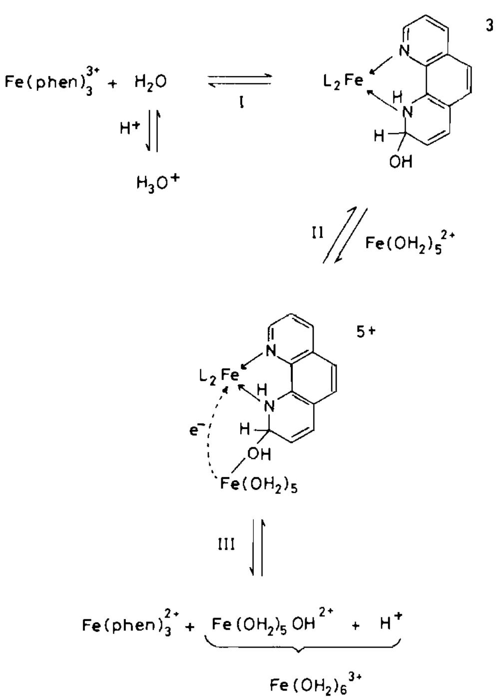


Fig. 2. Charge-distribution in 5-chloro-substituted iron(III) phenanthroline calculated by a population analysis (CNDO/2) based on known geometry [11] of $Fe(phen)_3^{2+}$ [12].

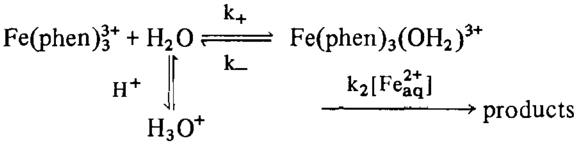
cope with many long-standing unexplained properties [10]. Incidentally, highly positive charges at the 9 and 2 position are also suggested from CNDO calculations (Fig. 2). Further, there is also experimental evidence for the coordination of water to metal polypyridine complexes, *e.g.* via infrared studies of water bound to such complexes when extracted from water in nitromethane [13].

In the light of these arguments the mechanism of the redox process under consideration may be proposed as follows (cf. [39]).



The necessity of the OH-group for mediating in Fe_{aq}^{2+} attack can be understood in terms of making the hydrophobic phenanthroline bound hydrophilic. This provides orbital coupling through a bond system rather than through space (as implied from outer-sphere models). The attacking Fe_{aq}^{2+} can be either a hexa- or a penta-coordinated species. Though there is a recent MO approach [14] suggesting that water itself may be an excellent mediator for electron-transfer, the common feeling would be that the latter (*i.e.*, the penta-coordinate) is more reasonable. Then, of course, the title redox process is purely inner-sphere.

If step III in the above mechanism, involving electron-transfer, is fast, the reaction scheme applies,



$$\begin{tikzcd} Fe(phen)_3^{3+} + H_2O \arrow[r, shift left, "k_+"] \arrow[d, shift left, "H^+"'] & Fe(phen)_3(OH_2)^{3+} \arrow[l, shift left, "k_-"] \arrow[r, "k_2[Fe_{aq}^{2+}]"] & \text{products} \\ H_3O^+ \arrow[u, shift left] & & \end{tikzcd}$$

(A subsequent equilibrium involving deprotonation of $Fe(phen)_3(OH_2)^{3+}$ [10, 11] must not be considered in the highly acidic solutions employed). In the case that $k_- \gg k_2$, and denoting $k_+/k_- = K$, the rate equation can be written as

$$d[P]/dt = \frac{Kk_2[Fe(phen)_3^{3+}][Fe_{aq}^{2+}][H_2O]}{1 + K[H_2O]} \tag{1}$$

If further $K[H_2O]$ were negligible compared to unity and if Fe_{aq}^{2+} is added in large excess, the effective rate constant is pseudo-first-order,

$$k_{eff} = Kk_2[Fe_{aq}^{2+}]_0[H_2O] \tag{2}$$

It is interesting to note that a rate equation similar to (1) has been proposed for the racemization of $Ni(phen)_3^{2+}$ [15].

The inclusion of a preceding covalent hydrate equilibrium brings the following features under one umbrella.

Effect of Substituents

That the rate constants dealt with are composites is strongly supported by the non-linearity of the Hammett plot in Fig. 3. A concave-down plot is what would be expected if the substituents have opposite

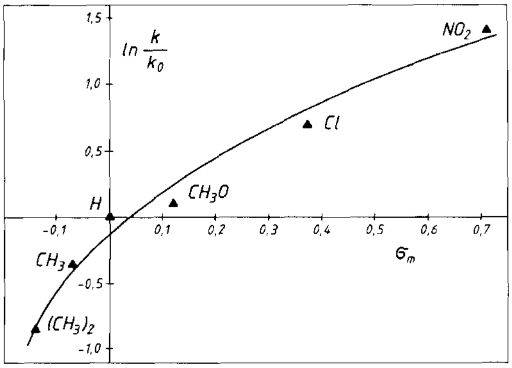


Fig. 3. Hammett plot for the iron(II) reduction of 5-substituted and 5,6-dimethylsubstituted $Fe(phen)_3^{3+}$ with the points representing the data at 30 °C.

effects on K and k_2, and the reaction constant ρ_2 is negative [16]. Acceptor substituents will increase the equilibrium constant by draining away electron density from the ring and thus facilitate the nucleophilic water attack. On the other hand, the Fe^{2+}_{aq} attack on the OH-group will be favored the more basic the oxygen is (*cf.* the decrease in rate of the reduction of $Mn(oxinate)_3$ by acceptor substituents [1], quoted in the introduction).

For a rate constant of the form, $k = (k_2K)/(1 + K)$, there are two limiting cases.

(a) $K = K_o \cdot 10^{\rho_1 \sigma} \ll 1$. Then

$$k = k_2K = \text{const}_1 \cdot 10^{(\rho_1 + \rho_2)\sigma} \quad (3)$$

(b) The opposite extreme is when $K \gg 1$, in which case,

$$k = k_2 = \text{const}_2 \cdot 10^{\rho_2 \sigma} \quad (4)$$

Since K depends on σ, case (a) will shift to case (b) within a certain σ range. In other words, the rate-determining step will shift on substituent variation. The form of the Hammett plot in Fig. 3 then means that we are essentially in the range of case (a) and that $|\rho_1| > |\rho_2|$, *i.e.*, that there is a dominant influence of the substituent on the position of the pre-equilibrium. For the substituents $(CH_3)_2$, CH_3, H, and CH_3O, the simplification of eqn. (2) might suffice, but for the electron acceptor substituents Cl and NO_2, the condition $K[H_2O] \ll 1$ will no longer be valid. If the σ values could be further increased, lg k should pass through a maximum and then approach a straight line with the negative slope of ρ_2.

In the light of these remarks we should expect non-linear Arrhenius plots particularly for the reactions involving Cl and NO_2. The linear behavior in Fig. 1 then may simply be due to the narrow temperature range available. This means further that the numerical value of the negative isokinetic temperature depends on the experimental temperature and thus is of no immediate physical relevance.

Effect of Acid

Increase in acid decelerates the redox process owing to a decrement in free water: equilibrium I in the above reaction mechanism is shifted to the left. Let us, in more detail, analyse the effect of acid on the reaction of parent $Fe(phen)_3^{3+}$ for which the simplification of eqn. (2) might hold as we said before. Inserting the material balance, $[H_2O]_o = [H_2O] + n[HClO_4(H_2O)_n]$, into the latter allows for the acid-dependence of the rate,

$$k_{eff} = Kk_2[Fe^{2+}_{aq}]_o([H_2O]_o - n[HClO_4(H_2O)_n]) \quad (5)$$

where $[H_2O]_o$ is the free water concentration in a neutral solution and n denotes the hydration number of perchloric acid. This equation suggests a linear decrease in k_{eff} with acid as is in fact found (Fig. 4).

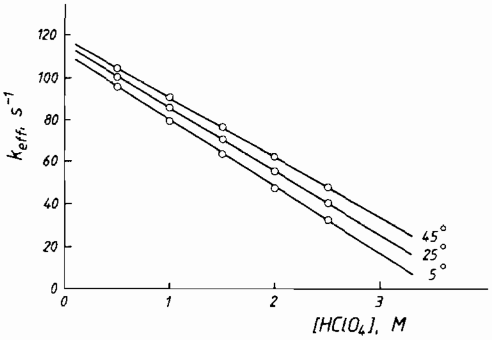


Fig. 4. Effect of perchloric acid on the pseudo-first-order rate constants for the reduction of the unsubstituted phenanthroline complex. $[Fe(phen)_3^{3+}] \sim 3.5 \times 10^{-5}$ *M*, $[Fe^{2+}_{aq}] = 2.7 \times 10^{-3}$ *M*.

The straight-line plot is at the same time the proof of the validity of the condition, $K[H_2O] \ll 1$. Slope and intercept allow us to calculate the products nKk_2 and $Kk_2[H_2O]_o$, respectively. Equating $[H_2O]_o$ with the analytical water concentration and having consideration for the density changes with temperature enable estimates to be made of the hydration number of perchloric acid. Values of about 14 for n seem quite reasonable, implying two hydration spheres. Further, the decrease with temperature is surely what would be expected.

Both Kk_2 and nKk_2 are linear in Arrhenius coordinates giving net activation energies of $\Delta H^{\ddagger} = -1.2$ kJ mol^{-1} and -4.5 kJ mol^{-1}, respectively. The very small temperature-variation of Kk_2 is proof that the equilibrium involved is exothermic.

Indeed, some may argue that the experiments for Fig. 4 have not been performed at constant ionic strength and thus do not preclude salt effects. This remark brings us to the third point.

Effect of Ionic Strength

Principally, for an outer-sphere reaction between two cations, one would expect an increase in rate

Temperature	$[H_2O]_o$, *M*	Kk_2, M^{-2} s^{-1}	nKk_2, M^{-2} s^{-1}	n
5 °C	55.50	7.4×10^2	1.2×10^4	16
25 °C	55.34	7.7×10^2	1.1×10^4	14
45 °C	54.96	7.9×10^2	1.0×10^4	13

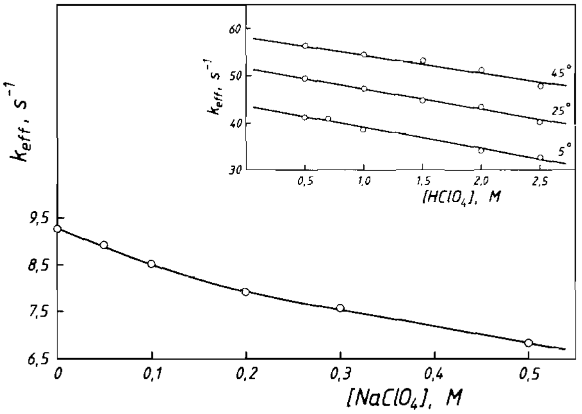


Fig. 5. Salt-effect on the pseudo-first-order rate constant for the reduction of the unsubstituted phenanthroline complex. $[Fe(phen)_3^{3+}] \sim 3.5 \times 10^{-5}$ *M*, $[Fe_{aq}^{2+}] = 5 \times 10^{-4}$ *M*, t = 25 °C, $[HClO_4] = 2.25$ *M*. Subfigure: Effect of perchloric acid on the same reaction with $[Fe(phen)_3^{3+}] \sim 3.5 \times 10^{-5}$ *M*, $[Fe_{aq}^{2+}] = 2.7 \times 10^{-3}$ *M*, at constant ionic strength: $[HClO_4] + [NaClO_4] = 2.5$ *M*.

upon adding salts [14, 17]. Contrary to prediction there is a decrease, as shown in Fig. 5 where various amounts of sodium perchlorate have been added to a reaction mixture specified in the legend. It should be noted that about linear plots of k *versus* the ionic strength have been reported to be indicative of reactions between an ion and a neutral molecule [18], and this is the reaction type being involved in our mechanism. The suggestion that the effects of acid and salt are similar in nature for the case in question is borne out in that there is nearly no acid-dependence left when compensating a variation in perchloric acid by sodium perchlorate (Subfigure to Fig. 5, note the different abscissa scales). The slight decrease in rate remaining is surely due to the higher water affinity of the proton compared to that of the sodium ion.

Thus it is safe to assume that the observed decreases in rate on adding acid or salt reflect the decreased availability of water in concentrated solutions: either H^+ and Na^+ are more strongly hydrated than the phenanthroline complex and thereby remove water molecules from the latter. The reactivity pattern is more common in organic chemistry, as for instance discussed along with the solvolysis of acetylimidazole in concentrated acid and salt solutions [19]. Also worthwhile mentioning is the decrease in the water activity with salt [20].

Hence eqn. (5) may describe the salt effect when substituting $NaClO_4$ for $HClO_4$. The slight curvature in Fig. 5 appears to be due to activity changes of the sodium ion, *viz.* variation in the coordination number.

Anti-compensation

Anti-compensation in the case of the system under consideration is established by the negative sign of the isokinetic temperature in Fig. 1, from where $T_{iso} \sim -470$ K, and likewise by Table I showing that, as $\Delta H^{\ddagger}$ increases, $\Delta S^{\ddagger}$ becomes more negative. The dealing with composite rate constants involving two reaction steps oppositely affected by substituent (or other parameter) variation offers a simple explanation for the hitherto highly obscure anti-compensation effect. The point is that one reaction step more strongly affects the overall energy and the other the overall entropy of activation.

Since in our case the observed rate constant is related to the product Kk_2,

$$\begin{aligned} \Delta H^{\ddagger}_{obs} &= \Delta H^{\circ} + \Delta H^{\ddagger}_2 \\ \Delta S^{\ddagger}_{obs} &= \Delta S^{\circ} + \Delta S^{\ddagger}_2 \end{aligned} \qquad (6)$$

As concerns energy it is obvious from the above considerations that ΔH° largely contributes to $\Delta H^{\ddagger}_{obs}$. In contrast, as for entropy, it is safe to assume that $\Delta S^{\ddagger}_2$ dominates $\Delta S^{\ddagger}_{obs}$ because of the seizing of large Fe^{2+}_{aq} which gives rise to a large loss in entropy. The result then is that, *e.g.* in passing from the H-substituted to the NO_2-substituted complex, $\Delta H^{\ddagger}_{obs}$ decreases owing to the enthalpic favor of nucleophilic water attack, and $\Delta S^{\ddagger}_{obs}$ becomes less negative due to a less molecular strain within the precursor as the oxygen of mediating OH is less basic. In fact, this is the experimental pattern in the activation parameters (Table I).

It should be noted in passing that, in more detail, ΔH° and ΔS° in eqn. (6) can be further resolved into the contribution of water activation (which is kept constant in considering the substituent effect, since the measurements were made at constant $[H^+]$) and that of water coordination. That the former plays a vital role for the magnitude of the overall activation energy, making it essentially positive, may be seen when recasting the experimental data from Fig. 4 in Arrhenius coordinates: there is a large variation in $\Delta H^{\ddagger}_{obs}$ (between 0 and +10 kJ) over the series of acid variation from 0.5 to 2.5 *M*. In contrast, the variation in $\Delta S^{\ddagger}_{obs}$ is very small (between −140 and −150 J). Noteworthy, the effect is compensatory in nature (*i.e.*, an increase in acid causes an increase in $\Delta H^{\ddagger}_{obs}$ and a shift in $\Delta S^{\ddagger}_{obs}$ to less negative values). This observation is in favor of the above interpretation of anti-compensation involved in the substituent effect (which, as we said, occurs due to $\Delta S^{\ddagger}_2$ of eq. (6)).

This is what we believe to be the first time of rationalizing the anti-compensation effect which would not be admitted, from a theoretical point of view [21], for an elementary reaction. Incidentally it was the very occurrence of negative isokinetic temperatures which has originated the view that the isokinetic temperature itself lacks any immediate physical meaning [22]. It is thus tempting to adopt the attitude that all negative isokinetic temperatures are simply the result of dealing with effective rate constants like the above. This view is strengthened if one notes that all examples of anti-compensation (to our knowledge) from the literature fit in this frame. *E.g.*, anti-compensation involved in the substituent effect on the thermodynamic functions of the ionization of meta-substituted phenols [23] is readily explained if the reaction energy is mainly due to the intrinsic ionization, whereas the reaction entropy is controlled by the solvation of the phenoxide anion. It is then predicted that electron-withdrawal from the reaction site would bring about a decrease in ΔH_{obs} and less negative ΔS_{obs}. This is just what is found experimentally.

It is interesting to note that also other reaction types of metal phenanthroline complexes involve anti-compensation, for instance the substituent effects on the acid fission of ferroins [24] and on the dissociation rates of nickel(II)–phenanthroline and –bipyridine complexes [25]. For the former we calculated, according to the method of the present paper, a value for $T_{iso} \sim -500$ K and for the latter, $T_{iso} \sim -250$ K. Further, the Hammett plot of either reaction series is non-linear and shows the same pattern as that in Fig. 2. These common features would suggest a unique reaction mechanism involving nucleophilic water attack as the initiating step of each dissociation, ligand exchange and Fe(II) reduction.*

The Absolute Values of the Activation Parameters

A mechanism involving a ligand bridge between the reactants is strongly supported by the values of the activation parameters (Table I): small $\Delta H^{\ddagger}$ values (or even negative values for the analogous $Ru(bipy)_3^{3+}$ reaction [26, 27]) and large negative $\Delta S^{\ddagger}$ values. By contrast, the intramolecular electron transfer mediated by 4,4-bipyridine and related bridging groups is characterized by activation entropies close to zero and activation enthalpies of about 80 kJ mol^{-1} [28].

There are many examples of the classical view [29] that electron transfer through bridges to be formed have low energies of activation and negative entropies [30]. The reason why this possibility was ruled out for the title redox process was that inorganic chemists really could not imagine in which way polypyridine complexes might be involved in such a pathway. This gave rise to sophistications of the general Marcus–Hush treatment so as to accommodate the 'unusual' activation parameters in the framework of outersphere electron transfer [31].

It is worthwhile to reiterate that the experimental rate constants of the reaction type in question are largely smaller than anticipated from the Marcus treatment such that this case is considered to be a special one. In a recent analysis it was shown that large disagreements seen between experiment and outer-sphere electron-transfer theory are compatible with the presence of large unfavorable work terms required to form the binuclear collision complex prior to electron transfer [32]. In this respect it is interesting to contrast briefly the self-exchange and the cross reactions for the iron phenanthroline (and similar) complexes. Concerning the former, there are reasons to believe that stacked overlap of the ligands provides a π^*–π^* electron transfer [8]. *E.g.*, the exchange rate is considerably faster than the cross reaction, but nevertheless two orders of magnitude smaller than predicted for a simple outer-sphere process [33]. Noteworthy, the exchange is enhanced by donor substituents (note the reactivity order inverse to that of the cross reaction) explainable in terms of increased ligand–metal bond strengths which could increase the delocalization of the t_{2g} electron and thus increase the rate of transfer of one of them [34]. A second point is the appearance of steric effects. For instance the electron-exchange rate is 15 times smaller when cyclohexyl is substituted for hydrogen in the 4, 7 positions, rationalizable via the hindrance to stacked overlap.

In contrast, the cross-reaction of substituted $Fe(phen)_3^{3+}$ complexes with Fe_{aq}^{2+} sees no specific steric effects suggesting that the ferrous ion penetrates the space between the phen groups [2]. This is indeed in line with the attack at the 2- or 9-position.

In passing we wish to point to the difference found between the activation enthalpy of −1.2 kJ mol^{-1} estimated from the temperature-dependence of the product Kk_2 (see under point 2), and the value of 8.2 kJ mol^{-1} for the reaction of parent $Fe(phen)_3^{3+}$ from Table I. This difference of about 10 kJ obviously displays the activation enthalpy necessary to elicit H_2O molecules from 2.25 *M* perchloric acid to be coordinated at $Fe(phen)_3^{3+}$. On these bases, it is suggested that water activation largely contributes to the gross activation energies for the oxidation of Fe_{aq}^{2+} by metal polypyridine complexes.

Thiocyanate Catalysis

Substituting HSCN for H_2O in our reaction scheme may readily account for the mode of thiocyanate catalysis in the iron(II) reduction of $Fe(phen)_3^{3+}$ [10]. Already 10 years ago Sutin and Forman [35] suggested that this reaction proceeds via a bridged intermediate involving nucleophilic attack of the sulfur atom of SCN^- on a carbon of the ligand ring system bearing a partial positive charge. There are however problems in the interpretation of the pertinent data owing to unknown effects of

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*Recently, the observation of identical positive pressure-independent values of the activation volume for OH^- and CN^- substitution reactions of $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ has been rationalized in terms of a dissociative interchange mechanism [40]. Alternatively, however, this activation volume pattern is consistent with a rapid unfavorable pre-equilibrium of nucleophilic attack. See also [41].

coordination of NCS$^-$ by Fe^{2+}. Further, Fe(phen)$_3^{3+}$ appears to be reduced by thiocyanate ions themselves. Thus we shall analyse these interesting reactions in more detail in a forthcoming paper.

Conclusion

Recalling the introductory remarks it is worthwhile to pinpoint the opposite substituent effects on the iron(II) reduction of Mn(oxinate)$_3$ and Fe(phen)$_3^{3+}$. In either case the electron-transfer takes place through bridges whose formation is rate-determining. For a bridge to be formed, in the former the *Lewis-basicity* of the ring oxygen is of primary importance. In the latter, a direct bridge cannot occur unless water does intervene which event is favored by increasing *Lewis-acidity* of a ring carbon atom.

Caution is thus advisable in classing a redox process with outer-sphere reactions. It would seem, in our opinion, that electron-transfer through bond systems rather than through space are of more importance than might be expected from current models of electron-transfer. This view is supported by quantum mechanical calculations [36] and further from studies so far made on redox systems in non-aqueous solvents [37]. To quote an example, cobalt-(III) acetylacetonate in acetonitrile, though being inert, does not take up an electron from iron(II) unless a chelate ring is opened and a direct bridge is made [38].

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