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Redox Kinetics of Metal Complexes in Non-aqueous Solutions. IV. Oxidation of Iron(II) Solvates by Iron(III) in Acetonitrile and Propanediol-1,2-carbonate

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The oxidation of iron(II) solvates by Fe(phen)$_3^{3+}$ in acetonitrile (An) and propanediolcarbonate (PDC) proceeds via the same reaction scheme as the reduction of iron(III) solvates by Fe(tetramethylphen)$_3^{2+}$. Solutions of iron(II) solvates in these solvents contain not only FeL$_6^{2+}$, but also complexes of lower coordination number. The lower the coordination number the faster the oxidation of the iron(II) species. In An an intermediate is formed between the pentacoordinated solvate and Fe(phen)$_3^{3+}$ which is obviously stabilized by the solvent.

Introduction

It has been pointed out recently that the rate constants of the reduction of various iron(III) complexes are tremendously sensitive to ligand donicity: the reduction rate decreases with increasing DN [1]. This can be interpreted in different terms, namely (a) decrease of the positive fractional charge at the coordination center equivalent to the enhancement of electron density of the orbital which accepts the electron from the reducing agent or (b) increase of the rearrangement energy.

For the oxidation process (a) should increase the rate with increasing DN, (b) should decrease the rate with increasing DN and (a) and (b) should cause little changes in rate with varying DN, provided that electron transfer and not coordination–chemical reactions are rate determining [2].

We wish to report on the study of the oxidation of iron(II) complexes with acetonitrile (An), trimethylphosphate (TMP), N,N-dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) by tris(1,10-phenanthroline)iron(III), Fe(phen)$_3^{3+}$. The solvents used were nitromethane (NM), acetonitrile (An) and propanediol-1,2-carbonate (PDC). Solvents of higher coordinating abilities cannot be used due to the instability of Fe(phen)$_3^{3+}$ in their solutions [3].

Experimental

Materials

Fe(phen)$_3$(ClO$_4$)$_3$ was prepared according to Sutin and Gordon [4], purified by recrystallisation from nitromethane–dichloromethane and dried by heating *in vacuo* at 50 °C. Literature methods were used to prepare the perchlorate salts of Fe(OH$_2$)$_6^{2+}$ [5] and Fe(An)$_6^{2+}$ [6]. Fe(DMF)$_6$(ClO$_4$)$_2$ was obtained by dissolving the hydrate in DMF and evaporating the solvent. This procedure was repeated twice. The residue was recrystallized from DMF, washed several times with absolute ether and dried *in vacuo* at 50 °C. Fe(TMP)$_6$(ClO$_4$)$_2$ and Fe(HMPA)$_4$(ClO$_4$)$_2$ were prepared in an analogous manner [7]. The purity of the solvates was checked by analysis of the iron(II) and iron(III) content. The products contained less than 0.5 percent of iron(III). The solvents were purified as described recently [3].

Kinetic Technique

Redox kinetics were followed at 25 °C using a Durrum D-110 stopped-flow spectrophotometer at wavelengths 510 nm and 600 nm, corresponding to maxima for ferroin formation and ferriin consumption, respectively. In the cases of too large absorbance changes at 510 nm the runs were followed at 550 nm. The preparation of the solutions and the procedure for analysing the kinetic curves are described in the preceding paper [3]. Depending on the half-lives of the reactions an oscilloscope or an X–Y recorder was used to trace the kinetic curves.

Results

The Oxidation of the Solvates in Acetonitrile

Fe(An)$_6^{2+}$ is not oxidized by Fe(phen)$_3^{3+}$. For Fe(TMP)$_6^{2+}$ the shape of the kinetic curves is dependent on the age of the solutions of the solvate. The older the solution the slower is the reaction and the smaller is the amount of Fe(phen)$_3^{2+}$ being formed. About twenty minutes' old solutions do not reduce ferriin furthermore. However, if some drops of TMP are added now, the solutions are again able to reduce

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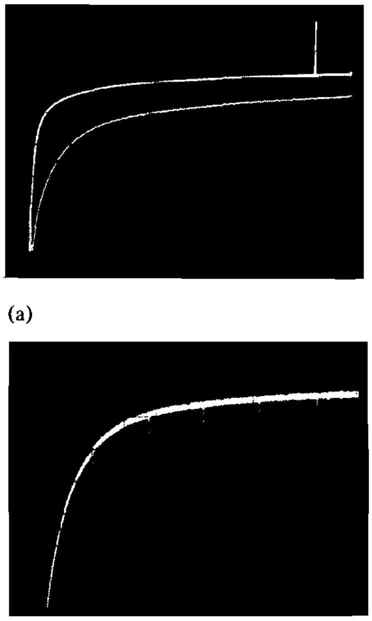
some Fe(phen)$_3^{3+}$, although the reducing power of a "fresh" solution is not reached.

Solutions of Fe(OH$_2$)$_6^{2+}$ in An are even less stable than those of the TMP solvate. A few minutes after preparation of the solution no reduction of ferriin was found to occur.

The complex Fe(DMF)$_6^{2+}$ is sufficiently stable in An. The kinetic data of runs with fresh solvate solutions were identical to those having stood for some hours. Oscilloscope traces for the oxidation by Fe(phen)$_3^{3+}$ indicate a complex reaction as shown in Figure 1. By suitable choice of reactant concentrations and oscilloscope adjustments various stages can be separated. With the solvate in more than threefold excess only the first stage is observed. The ratio of the absorbance changes due to the first and the second stage is independent of different excesses of Fe(phen)$_3^{3+}$. On the other hand, the relative absorbance changes due to the first stage are decreasing, if for a given excess of Fe(phen)$_3^{3+}$ the solvent concentration is increased (Table I). Runs with solvate solutions containing about equimolar amounts of DMF yielded smaller absorbance changes due to the first stage and slower reaction rates. With Fe(phen)$_3^{3+}$ in excess a third stage is noticeable (*cf.* Figure 1(b)).


(a)

(b)

Figure 1. Oscilloscope traces at 510 nm for the reaction of Fe(DMF)$_6^{2+}$ (2.5 × 10^{-4} *M*) with Fe(phen)$_3^{3+}$ (2.5 × 10^{-3} *M*) in An. The first and the second stage are illustrated in (a) with time bases 10 ms and 0.1 s/square respectively and sensitivity 1 V/square; (b) are traces of the second stage with time base 0.5 s/square and sensitivity 0.1 V/square. A following third stage as observed in (b) is due to the decay of residual Fe(phen)$_3^{3+}$.

TABLE I. Observed Rate Constants for the Reaction of Fe(phen)$_3^{3+}$ with Fe(DMF)$_6^{2+}$ in Acetonitrile.

Run	[Fe(phen)$_3^{3+}$] m*M*	[Fe(DMF)$_6^{2+}$] m*M*	$k_{exp(1)}$ s^{-1}	$k_{exp(2)}$ s^{-1}	%[a]
1	2.5	0.25	87	1.66	
2	2.5	0.5	90	2.0	70
3	2.5	1.0	80	1.8	65
4	2.5	1.5	85	0.42	60
5	2.5	2.0	80	0.10	50
6	5.0	2.0	95	2.6	
7	5.0	5.0	95	–	45
8	1.0	0.5	50	0.07	
9	1.75	0.5	70	1.3	
10	3.3	0.5	90	2.25	
11	5.0	0.5	100	3.7	
12	0.5	0.2	40	0.3	
13	1.5	0.5	70	1.20	
14	1.0	0.5	50	0.2	
15	1.0	0.25	50	0.9	
16	1.0	0.125	50	1.1	

[a] Estimated relative absorbance change due to the first stage based on quantitative reaction.

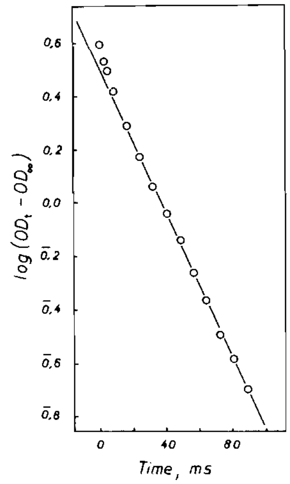


Figure 2. First-order plot for the first stage obtained from an equimolar mixture of 5 × 10^{-4} *M* Fe(DMF)$_6^{2+}$ and Fe(phen)$_3^{3+}$ in An.

First-order rate data ($k_{exp(1)}$) are obtained for the first stage even for equimolar mixtures of the reactants. A typical plot is shown in Figure 2, where the first stage is followed for four half-lives. The initial deviation from linearity is the greater the higher the solvate concentration. With increasing excesses of Fe(phen)$_3^{3+}$ the values of $k_{exp(1)}$ reach a maximum (Figure 3). Rate constants $k_{exp(2)}$ for the second stage were evaluated from plots of log ($OD_t - OD_\infty$) of the last five percent of the kinetic curves (Figure 1(b)) against time. Figure 4 shows the dependence of selected values of $k_{exp(2)}$ on the residual concentration of Fe(phen)$_3^{3+}$. Rate data are listed in Table I.

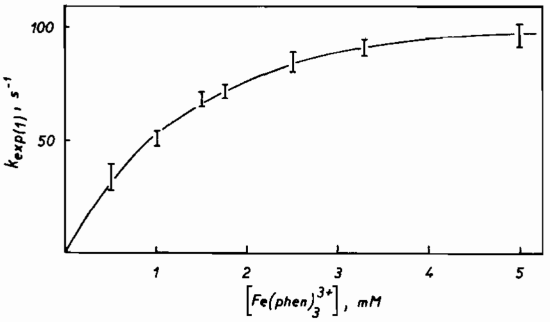


Figure 3. Plot of $k_{exp(1)}$ *vs.* $[Fe(phen)_3^{3+}]$ for the oxidation of $Fe(DMF)_6^{2+}$ in An.

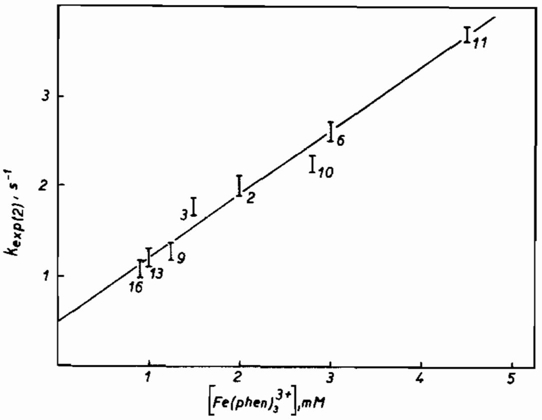


Figure 4. Pseudo-first-order rate constants $k_{exp(2)}$ for the second stage of the oxidation of $Fe(DMF)_6^{2+}$ as a function of the residual concentration of $Fe(phen)_3^{3+}$. The numbers refer to runs in Table I.

For $Fe(HMPA)_4^{2+}$ the shape of the absorbance–time curves is independent of the age of the solvate solutions. The oscilloscope traces indicate reactions with different half-lives. However, no pseudo-first-order conditions were found even with a tenfold excess of each of the reactants, respectively. Similar kinetic curves are monitored for the reaction of iron (III):

$Fe(phen)_3^{3+} + Fe(HMPA)_{4-6}^{3+}$*

where also $Fe(phen)_3^{2+}$ is one of the products. The half-lives of the above-mentioned reactions are of the same order of magnitude as those for the reduction of $Fe(phen)_3^{3+}$ by HMPA itself.

The Oxidation of the Solvates in Propanediol-1,2-carbonate

The Fe(II) solvates of H_2O, TMP and DMF are sufficiently stable in this solvent. The absorbance–time curves of "fresh" solutions and of those having stood for hours are nearly equal. Again various reaction stages are indicated (*cf.* Figure 1). Second-order kinetics are found for the first stage. Values of pseudo-first order rate constants $k_{exp(1)}$ are independent of the solvate concentration for a fixed excess of $Fe(phen)_3^{3+}$ and increase proportional to the excess of $Fe(phen)_3^{3+}$ (Table II). The relative absorbance changes due to the first stage based on quantitative reaction decrease with increasing solvate concentration.

TABLE II. Rate Data for the Reactions of FeL_6^{2+} with $Fe(phen)_3^{3+}$ in Propanediol-1,2-carbonate.

L	$[Fe(phen)_3^{3+}]$ m*M*	$[FeL_6^{2+}]$ m*M*	$k_{exp(1)}$ s^{-1}	$v_{0(2)}$ $M\,s^{-1}$	%[a]
H_2O	1	0.25	3.3	4×10^{-8}	70
	2	0.25	6.8		
	3.5	0.25	15		
	5	0.25	30		
	5	0.5	30		
	5	1	30		
TMP	0.8	0.25	2	4.5×10^{-8}	20
	2.3	0.25	6.1		
	3.8	0.25	10.5		
	3.8	0.75	10.0		
DMF	2	0.25	0.007	3.10^{-8}	10
	5	0.25	0.015		

[a] Relative absorbance change due to the first stage based on quantitative reaction.

For the second stage the initial rates $v_{0(2)}$ were determined from the slopes of the absorbance–time curves (Table II). However, these values of $v_{0(2)}$ are of the same order of magnitude as the rate of decay of pure solutions of $Fe(phen)_3^{3+}$ in PDC. For a 5×10^{-3} *M* solution a rate of decay $v = 2 \times 10^{-8}$ $M\,s^{-1}$ was found.

The Oxidation of the Solvates in Nitromethane

Solutions of the solvates are yellow indicating an oxidation of the iron(II) complexes by solvent molecules. A content of more than 10% iron(III) was found by complexometric titration. The rates of the reactions of these solutions with $Fe(phen)_3^{3+}$ were so fast that they could not be scanned by the stopped-flow equipment.

Discussion

Acetonitrile

As $Fe(An)_6^{2+}$ is not oxidized by $Fe(phen)_3^{3+}$ a stabilisation of the former in the lower oxidation state may be assumed as being due to back donation. While H_2O and TMP are substituted by An, the complexes of DMF and HMPA are inert. This is in agreement

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*The iron(III)–HMPA solvate used contained more than four and less than six HMPA molecules.

with the rule that in a given solvent a metal ion complex is the more stable the higher the donicity of its ligands [8]. As in the oxidized forms back donation can be excluded, the Fe(III) solvates of H_2O and TMP are found stable in An [1, 3].

The experimental results for the oxidation of $Fe(DMF)_6^{2+}$ by $Fe(phen)_3^{3+}$ are consistent with the redox reaction scheme discussed for the reduction of various iron(III) solvates in An [1]. It has been demonstrated that the complexity of the reaction is attributable to the existence of iron solvates with different coordination numbers, the first stage representing the reduction of a pentacoordinated iron solvate FeL_5^{3+}, the second stage consisting of the outer-sphere reduction of FeL_6^{3+} and the first-order formation of FeL_5^{3+} which is subsequently reduced [1]. Evidence for the existence of an equilibrium between complexes of different coordination numbers in the case of the divalent complex $Fe(DMF)_6^{2+}$ is furnished in the same manner. In the present paper Fe_a^{2+} stands for the penta-coordinated complex FeL_5^{2+} which is faster oxidized than the hexa-coordinated Fe_i^{2+}. The data of % in Table I refer to the percentage of Fe_a^{2+}. This value decreases with increasing solvate concentration as the equilibrium

$$Fe_i^{2+} \rightleftharpoons Fe_a^{2+} + L$$

is connected with an increase in the number of molecules.

With regard to the first stage the kinetics are first order even for equimolar mixtures of the reactants (Figure 2). This finding and the significant departure from linearity of $k_{exp(1)}$ with increasing excess of $Fe(phen)_3^{3+}$ require a fast equilibrium between the reactants followed by a second step which is rate determining:

$$Fe_a^{2+} + Fe(phen)_3^{3+} \overset{K}{\rightleftharpoons} [Fe_a\cdot Fe(phen)_3]^{5+} \xrightarrow{k_a} \text{Products}$$

In terms of this scheme $k_{exp(1)}$ is given by (for $Fe(phen)_3^{3+}$ in excess)

$$k_{exp(1)} = \frac{k_aK[Fe(phen)_3^{3+}]}{1 + K[Fe(phen)_3^{3+}]}$$

For high values of $[Fe(phen)_3^{3+}]$ $k_{exp(1)}$ becomes k_a, the rate constant of the electron transfer in the intermediate. The value for k_a of 130 s^{-1} is obtained as the intercept of the plot $1/k_{exp(1)}$ *vs.* $1/[Fe(phen)_3^{3+}]$. For low values of $[Fe(phen)_3^{3+}]$ the initial slope of the curve in Figure 3 is given by the product k_aK. The equilibrium constant K is then 513 M^{-1}. The initial curvature in Figure 2 implies the additional existence of complexes of even lower coordination number (obviously four) [3].

The linear plot with non-zero intercept in Figure 4 indicates that the observed rate constant of the second stage consists of two terms

$$k_{exp(2)} = k_{ia} + k_i[Fe(phen)_3^{3+}]$$

The rate constant k_i stands for the outer-sphere oxidation of Fe_i^{2+} and k_{ia} is the first-order rate constant of the formation of Fe_a^{2+} from Fe_i^{2+}. The respective values as calculated from the slope and the intercept are 700 M^{-1} s^{-1} and 0.5 s^{-1}. The 100-fold lower value of k_{ia} (0.006 s^{-1}) for the trivalent iron solvate $Fe(DMF)_6^{3+}$ is in agreement with the fact that Fe(II) is more labile than Fe(III) [1].

Values of $k_{exp(2)}$ were obtained in the presence of products from the first stage. Only those which have been calculated from runs where the concentration of free $Fe(phen)_3^{3+}$ is greater than that of the first-stage products fit in to the straight line in Figure 4. In the case of concentrations of the products much greater than of free $Fe(phen)_3^{3+}$ the values of $k_{exp(2)}$ are lower than expected (Table I). A retardation by products may be held responsible for this. In fact, $k_{exp(2)}$ increases for a fixed excess of $Fe(phen)_3^{3+}$ with decreasing solvent concentration (*cf.* Runs 14–16 in Table I). Thus the autoinhibition is demonstrated and easily understood in terms of the favouritism of $Fe(phen)_3^{2+}$, one of the products of the first stage, above the reactant $Fe(phen)_3^{3+}$ to form an intermediate with Fe_a^{2+} being produced during the second stage. The lower charge of $Fe(phen)_3^{2+}$ may be decisive, because no evidence for autoinhibition has been found in the case of the reduction of iron(III) solvates.

The kinetic behavior observed can be accommodated by the mechanism:

$$\begin{tikzcd}
Fe_a^{2+} + Fe(phen)_3^{3+} \arrow[r, shift left, "K"] \arrow[d, shift left, "k_{ia}"] & {[Fe_a\cdot Fe(phen)_3]^{5+}} \arrow[l, shift left] \arrow[d, "k_a"] \\
Fe_i^{2+} + Fe(phen)_3^{3+} \arrow[u, shift left] \arrow[r, "k_i"'] & \text{products}
\end{tikzcd}$$

The formation of the +5 charged intermediate – some π-complex of the phenanthroline group of $Fe(phen)_3^{3+}$ and the Fe(II) of a solvate with coordination number 5 – is obviously assisted by participation of acetonitrile. This can be said, because no evidence for an intermediate is found in the solvent PDC (*cf.* the following discussion).

The results from the oxidation of $Fe(HMPA)_4^{2+}$ indicate that $Fe(phen)_3^{3+}$ is partly reduced by free HMPA originating from the iron(II) solvate. This is further evidence for the existence of solvates with different coordination numbers in An. It will be shown in a forthcoming paper that the stability of $Fe(phen)_3^{3+}$ in solution depends on the donicity of the solvent or of dissolved donor molecules: the higher the DN the lower is the stability.

Propanediol-1,2-carbonate

Again, the kinetic results are consistent with those obtained for the reduction of iron(III) solvates [9]. The first stage can be interpreted in terms of the oxidation of a pentacoordinated iron solvate Fe_a^{2+}. Unlike to An this reaction is first order with respect to both the iron(II) solvate and $Fe(phen)_3^{3+}$. Either no intermediate is formed or it is very reactive and therefore only present at very small concentrations. The respective values of the rate constants of the reduction of $Fe(OH_2)_5^{2+}$, $Fe(TMP)_5^{2+}$ and $Fe(DMF)_5^{2+}$ are 6000, 2600 and 3 M^{-1} s^{-1}. Since these reactions are second-order, they are not electron-transfer controlled and thus it is not possible to get information from those data about the effect of ligands on the rate of electron loss.

Like for the reduction of iron(III) the second stage reactions consisting of the oxidation of Fe_i^{2+} and the formation of Fe_a^{2+} from Fe_i^{2+} are very slow. Since the rate of decay of $Fe(phen)_3^{3+}$ in pure PDC has the same order of magnitude as the above-mentioned reactions, an investigation in detail is not worthwhile. The data of % in Table II refer to the percentage of Fe_a^{2+}.

Nitromethane

Since iron(II) solvates are partly oxidized by NM, this solvent is not a suitable medium to search into redox reactions of that kind.

Conclusion

It is difficult to find a system which allows one to study the effect of ligands of a metal complex on the rate of electron loss. On the one hand $Fe(phen)_3^{3+}$ is a suitable oxidant and redox indicator in acetonitrile, because the oxidation of the pentacoordinated solvates is electron-transfer controlled. On the other hand it is not possible to investigate different ligands, because $Fe(phen)_3^{3+}$ is reduced by ligands of high donicity while ligands of low or medium DN are substituted by An, which appears as the only suitable medium possible. Nitromethane and nitrobenzene will oxidize Fe(II) solvates, while solvents of higher DN reduce $Fe(phen)_3^{3+}$. In other solvents of low DN the solubilities of the reactants are too low.

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References

1 R. Schmid, V. N. Sapunov and V. Gutmann, *Ber. Bunsenges. physik. Chem.*, in the press.
2 V. Gutmann and R. Schmid, *Coord. Chem. Revs.*, *12*, 263 (1974).
3 R. Schmid, V. N. Sapunov and V. Gutmann, *Ber. Bunsenges. physik. Chem.*, *80*, 456 (1976).
4 N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, *83*, 70 (1961).
5 G. Wada and W. Reynolds, *Inorg. Chem.*, *5*, 1354 (1966).
6 R. J. West and S. F. Lincoln, *Aust. J. Chem.*, *24*, 1169 (1971).
7 B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, *87*, 2372 (1965).
8 V. Gutmann, "Chemische Funktionslehre", Springer Verlag (1971).
9 R. Schmid, V. N. Sapunov and V. Gutmann, *Ber. Bunsenges. physik. Chem.*, *80*, 1307 (1976).