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Central Role of Phenanthroline Mono-*N*-oxide in the Decomposition Reactions of Tris(1,10-phenanthroline)iron(II) and -iron(III) Complexes

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1,10-Phenanthroline mono-*N*-oxide (phenO) is a product of the decomposition of tris(1,10-phenanthroline)iron(III), Fe(phen)$_3^{3+}$, and has a slight autocatalytic effect on the overall reaction. The mechanism is proposed to involve Fe(phen)$_3^{4+}$ as a minor intermediate. The addition of phenO significantly influences the kinetic features of the decomposition of Fe(phen)$_3^{3+}$ and the oxidation of Fe(phen)$_3^{2+}$ by HSO_5^-. The autocatalytic decomposition explains the difficulties in the preparation of Fe(phen)$_3^{3+}$ and may contribute to exotic kinetic phenomena studied using Fe(phen)$_3^{3+}$/Fe(phen)$_3^{3+}$ as a supposedly innocent indicator.

The iron complexes of 1,10-phenanthroline (phen) are widely used as redox indicators and model compounds of biologically active substances.[1−5] The interconversion between the intensely red ferrous complex, Fe(phen)$_3^{2+}$, and the deep blue ferric complex, Fe(phen)$_3^{3+}$, is thought to be rapid and reversible in most cases and is often used to visualize otherwise less obvious changes in reactions showing exotic kinetic phenomena.[6−9] Fe(phen)$_3^{3+}$ is often used as a coordinatively saturated, strong, one-electron oxidant.[10−15] Irreversible decomposition reactions of these complexes may be a major source of unwanted interference and are of primary importance in all of the systems where Fe(phen)$_3^{3+}$/Fe(phen)$_3^{2+}$ is used as an indicator. These processes also offer some fundamental insight into the redox chemistry of metal complexes.

Fe(phen)$_3^{2+}$ is easily prepared by mixing Fe^{II} and the ligand in water at a suitable pH. Fe(phen)$_3^{3+}$, on the other hand, can only be synthesized by oxidizing Fe(phen)$_3^{2+}$.[1,11,12] The typical chemical oxidants used for this purpose are lead(IV) oxide and chlorine. The latter method necessarily introduces chloride ion as a byproduct into the solutions of Fe(phen)$_3^{3+}$, which is unfortunate for many applications. The use of lead(IV) oxide, however, has distinct advantages: the oxidant is solid, and the oxidation byproduct lead(II) sulfate is also insoluble in the sulfuric acid medium used for the reaction. Therefore, a reasonably pure solution of Fe(phen)$_3^{3+}$ can be obtained in this way. Our synthetic efforts showed that three aspects, not usually emphasized in the relevant literature, are crucial. First, the synthesis reaction needs to be carefully timed. The optimal reaction time depends on the initial concentration of Fe(phen)$_3^{2+}$, acidity, overall volume, and stirring speed. Even a 30% deviation from the optimal reaction time could result in a significant difference in the Fe(phen)$_3^{3+}$ concentration and seriously decrease the reproducibility of later experiments. The second important factor is the method of filtration. Filter paper must be avoided; only glass filters should be used, which is understandable because Fe(phen)$_3^{3+}$ is a strong oxidant and filter paper is an oxidizable material. The filter material influences not only the yield of Fe(phen)$_3^{3+}$ but also the reproducibility of later experiments. The third important factor is the amount of lead(IV) oxide used in the heterogeneous reaction, which must also be optimized. The need for careful reaction timing is most probably due to the further oxidation of Fe(phen)$_3^{3+}$ by excess lead(IV) oxide. This leads to the formation of 1,10-phenanthroline mono-*N*-oxide (phenO), which will be shown to be a major source of kinetic complexity in the decomposition reaction of Fe(phen)$_3^{3+}$.

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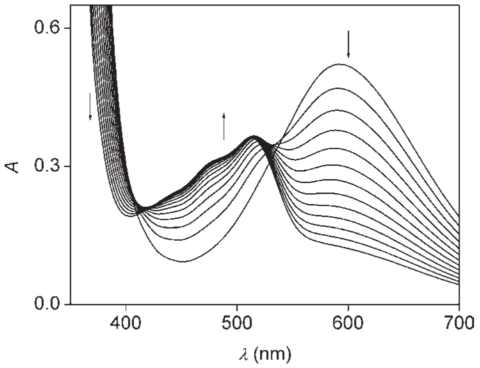


Figure 1. Spectral changes in $Fe(phen)_3^{3+}$ decomposition. $[Fe(phen)_3^{3+}] = 0.62$ mM, $[H_2SO_4] = 1.0$ M, $T = 25.0$ °C, path length = 1.000 cm, and time interval = 60 min.

The preparation of $Fe(phen)_3^{3+}$ must be done in a highly acidic medium (usually 1 M or more concentrated H_2SO_4). $Fe(phen)_3^{3+}$, similar to the analogous Ru^{III} and Os^{III} complexes, is also able to oxidize hydroxide ion with a simple outer-sphere electron-transfer mechanism;[5,11,12] therefore, meaningful experiments are usually limited to the acidic region. $Fe(phen)_3^{3+}$ is also known to undergo acid dissociation to aqueous ferric ion and the protonated ligand ($phenH^+$).[2,5] Our spectrophotometric studies revealed that some $Fe(phen)_3^{2+}$ is produced as a product of $Fe(phen)_3^{3+}$ decomposition. Figure 1 shows that the decrease in absorbance around 591 nm [peak of $Fe(phen)_3^{3+}$, $\varepsilon = 8.43 \times 10^2\ M^{-1}\ cm^{-1}$] is accompanied by a simultaneous increase of absorbance around 510 nm [peak of $Fe(phen)_3^{2+}$, $\varepsilon = 1.095 \times 10^4\ M^{-1}\ cm^{-1}$]. Taking into account the significant difference in the molar absorption coefficients, Figure 1 confirms that only a fraction of $Fe(phen)_3^{3+}$ produces $Fe(phen)_3^{2+}$, and most $Fe(phen)_3^{3+}$ dissociates without redox decomposition. $Fe(phen)_3^{2+}$ can only be produced in a disproportionation of $Fe(phen)_3^{3+}$. Oxidizable impurities remaining at low concentrations in the solution cannot be significant in this case for two reasons. First, our efforts to further purify the water used in the studies by distillation did not lead to any change in the spectral observations. Second, the oxidation product of the disproportionation was identified beyond any doubt and a stoichiometric analysis did not require further reagents. Linear algebraic decomposition of the UV−vis spectra[16] (Figures S1−S3 in the Supporting Information) showed that phenO was formed, and the presence of this compound was also detected by electrospray ionization mass spectrometry (ESI-MS; Figure S4 in the Supporting Information).

The initial rate of the overall reaction was studied by variation of the concentrations of the reactants and products. The product phenO has an accelerating effect (Figure 2); therefore, the process is slightly autocatalytic with the following experimental rate equation (see also Figure S5 in the Supporting Information):

$$\frac{d[Fe(phen)_3^{3+}]}{dt} = (k_1 + k_2[phenO])[Fe(phen)_3^{3+}] \qquad (1)$$

The values $k_1 = (2.90 \pm 0.06) \times 10^{-5}\ s^{-1}$ and $k_2 = (1.47 \pm 0.07) \times 10^{-2}\ M^{-1}\ s^{-1}$ were determined. The k_1 term corresponds to the known acid dissociation of $Fe(phen)_3^{3+}$, which is a straightforward first-order process but is subject to large medium effects previously interpreted by ion-pair formation.[2] The concentrations of $Fe(phen)_3^{2+}$, $Fe(phen)_3^{3+}$, phenO, and, in certain cases, free phen could also be calculated individually based on the spectral decomposition method mentioned earlier without making any mass balance assumptions (Figure S3 in the Supporting Information). These results confirmed that $Fe(phen)_3^{2+}$ and phenO are produced in a 1:1 ratio, in agreement with the sequence of reactions shown in Scheme 1 for interpretation. The acid dissociation of $Fe(phen)_3^{2+}$ is relatively slow[2,3] ($k = 5.8 \times 10^{-5}\ s^{-1}$ at our conditions) and does not influence the observations for the first 2 h. Actually, disproportionation of $Fe(phen)_3^{3+}$ and formation of $Fe(phen)_3^{4+}$ were postulated earlier to interpret kinetic observations in the cerium(IV)−$Fe(phen)_3^{2+}$ system.[17,18] However, the confirming experiment to test the decomposition of $Fe(phen)_3^{3+}$ was not carried out in those works. We found that disproportionation of $Fe(phen)_3^{3+}$ and its autocatalytic nature may significantly influence the reactions where $Fe(phen)_3^{2+}$ is a reductant. An example of this phenomenon is shown in Figure 3, where kinetic traces recorded during the reaction between $Fe(phen)_3^{2+}$ and a peroxomonosulfate ion (HSO_5^-) are depicted. It should be noted that the study of the reaction

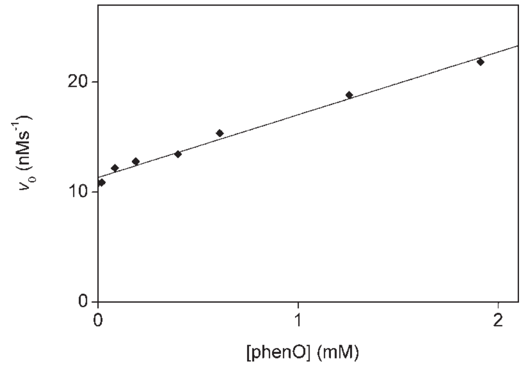
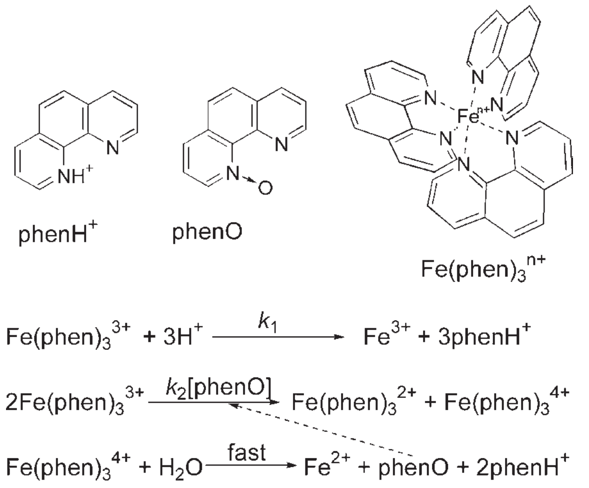


Figure 2. Initial rate of $Fe(phen)_3^{3+}$ decomposition as a function of the phenO concentration. $[Fe(phen)_3^{3+}] = 0.390$ mM, $[H_2SO_4] = 0.987$ M, and $T = 25.0$ °C.

Scheme 1



$$Fe(phen)_3^{3+} + 3H^+ \xrightarrow{k_1} Fe^{3+} + 3phenH^+$$

$$2Fe(phen)_3^{3+} \xrightarrow{k_2[phenO]} Fe(phen)_3^{2+} + Fe(phen)_3^{4+}$$

$$Fe(phen)_3^{4+} + H_2O \xrightarrow{fast} Fe^{2+} + phenO + 2phenH^+$$

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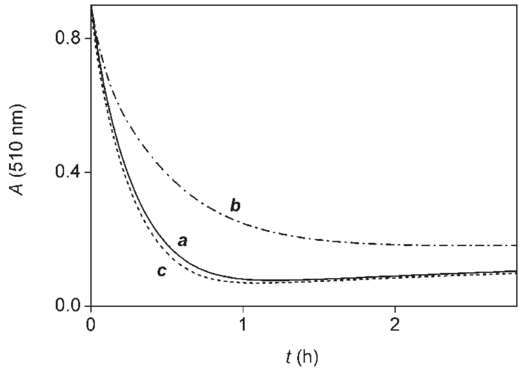

Figure 3. Kinetic traces detected in the reaction between $Fe(phen)_3^{2+}$ and HSO_5^-. $[Fe(phen)_3^{2+}]$ = 81 μM, $[HSO_5^-]$ = 30 mM, T = 25.0 °C, and path length = 1.000 cm: (a) without additional reactants; (b) 80 μM phenO added before the reaction; (c) 80 μM Fe^{3+} added before the reaction.

between this oxidant and aqueous Fe^{II} gave somewhat unexpected results because clear multistep kinetics was observed but no intermediate could be detected.[19] A striking feature of the $Fe(phen)_3^{2+}-HSO_5^-$ reaction is the absorbance minimum at about 1 h (curve a). This minimum disappeared when phenO was added before initiation of the reaction (curve b) but was not influenced by the previous addition of ferric ion (curve c). $Fe(phen)_3^{2+}$ and HSO_5^- do not react with phenO under these conditions. The simplest explanation for the exotic nature of the displayed kinetic curve is the autocatalytic reaction between $Fe(phen)_3^{3+}$ and phenO, which was again detected as a product by both ESI mass spectrometry and spectral decomposition (Figures S4 and S6 in the Supporting Information).

The addition of phen did not influence any kinetic observations; therefore, a fully dissociative explanation is out of the question. The catalytic role of phenO is interpreted with the assumption that it can be oxidized to a radical by $Fe(phen)_3^{3+}$, which can, in turn, oxidize another $Fe(phen)_3^{3+}$ to $Fe(phen)_3^{4+}$, completing a catalytic cycle for the *N*-oxide. Some experimental support for the involvement of a $Fe(phen)_3^{4+}$ species was provided by ESI-MS in the $Fe(phen)_3^{2+}-HSO_5^-$ reaction. As shown in Figure 4, a low-intensity, but clearly identifiable set of peaks was found that corresponded to the formula $FeC_{36}H_{24}N_6O_4S^{2+}$. This can be interpreted as an ion pair formed by $Fe(phen)_3^{4+}$ and SO_4^{2-}, the highest positively and negatively charged ions in the solution. The ion pair could be formed in the mass spectrometer only, but it may be present in solution as well, similar to ion pairs proposed for $Fe(phen)_3^{3+}$.[2] In collisionally induced dissociation experiments, a loss of SO_3 was detected from this ion (Figure S7 in the Supporting Information), which shows that the sulfate moiety is intact in

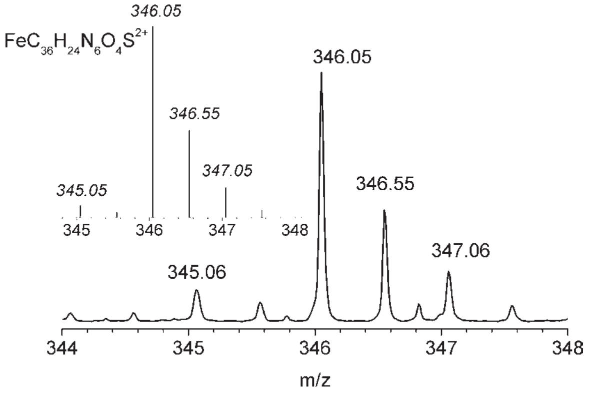

Figure 4. ESI-MS identification of $Fe(phen)_3(SO_4)^{2+}$ in the reaction between $Fe(phen)_3^{2+}$ and HSO_5^-. Inset: theoretically calculated mass spectrum for $FeC_{36}H_{24}N_6O_4S^{2+}$.

$FeC_{36}H_{24}N_6O_4S^{2+}$. Adventitious oxidation during ionization is very unlikely because the ESI-MS conditions used were reductive: $Fe(phen)_3^{2+}$ was the dominant signal even in spectra that were taken of $Fe(phen)_3^{3+}$ solutions containing less than 1% $Fe(phen)_3^{2+}$.

Possible complexation between free aqueous Fe^{II} and Fe^{III} and phenO was also experimentally tested. No spectral changes could be observed upon mixing of the metal and suspected ligand in an acidic medium of the studies; therefore, any interference from *N*-oxide complexation can be ruled out (Figure S7 in the Supporting Information).

In summary, we have shown that phenO is a product and a catalyst of the decomposition of $Fe(phen)_3^{3+}$. The autocatalytic effect can be the primary reason for the reproducibility problems with $Fe(phen)_3^{3+}$ and the unusual kinetic curves observed in the reaction between $Fe(phen)_3^{2+}$ and HSO_5^-. Further studies are needed to explore whether this process contributes to the triggering of the exotic phenomena[7-9] studied using $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ as a supposedly innocent indicator. We have seen no similar effects when the ligand phen was replaced by 2,2-bipyridyl. To our knowledge, analogous reactions have not been observed for $Ru(phen)_3^{3+}$ and $Os(phen)_3^{3+}$.[12,20,21]

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Supporting Information Available: Experimental section, spectral decomposition of UV−vis spectra, and additional graphs referred to in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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