Kinetics and Mechanism of Autocatalytic Oxidation of $Fe(phen)_{3}^{2+}$ and $Fe(bpy)_{3}^{2+}$ by Nitric Acid

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The kinetics of the title reactions has been studied and the investigation of the oxidation of the iron(II) agua ion by nitric acid has been extended. All three reactions are autocatalytic in nature. Oxidation of $Fe(aq)^{2+}$ is practically complete at $[HNO_3] > 0.5$ mol dm⁻³. In the case of the two other complexes the process is reversible; the conversion in the equilibrium state depends on the initial concentrations of reactants. Values of the equilibrium constants have been determined from experimental data and compared to those calculated from standard electrochemical potentials. The autocatalytic S-shaped kinetic curves have been measured by means of spectrophotometry and potentiometry and are characterised using the time coordinate (t_i) and the slope (r_{max}) of the concentration vs. time curves at the inflection point. The general mechanism of autocatalytic nitric acid oxidations has been applied in order to fit single experimental curves and all concentration dependences. The validity of the proposed mechanism is supported by the agreement between experiments and the results of the numerical integration of differential rate equations derived from the mechanism. An interesting local maximum and minimum are found in the t_i vs. $[Fe^{2+}]_0$ curves both experimentally and numerically.

In the course of a systematic study of autocatalytic oxidations by nitric acid¹ we observed that ferroin, $Fe(phen)_{3}^{2+}$, is oxidized by moderately concentrated nitric acid in an autocatalytic reaction. Similar behaviour was found in the case of the complex $Fe(bpy)_{3}^{2+}$. The oxidation of the iron(II) aqua ion $Fe(aq)^{2+}$ was studied recently^{2,3} and proved to be autocatalytic. The oxidation of ferroin by bromate⁴ is similarly autocatalytic, but that of $Fe(aq)^{2+}$ was found to be first-order for both of the two reactants.⁵ We were unable to find any study of the title reactions in the literature. [In the following Fe^{2+} and Fe^{3+} or Fe^{II} and Fe^{III} indicate the oxidation states of any of the aqua, phenanthroline (= phen) and bipyridyl (= bpy) iron complexes.]

Experimental

Reagents

Highest-grade commercially available HNO₃ (65%), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, o-phenanthroline ($C_{12}H_6N_2 \cdot H_2O$), 2,2'-dipyridyl (C_5H_4N), NaNO₂, $K_4Fe(CN)_6$, ferrocene and dimethylformamide (DMF) were used without further purification. Nitric acid solutions were prepared by dilution and purged for 1 h with N₂ to remove gaseous nitrogen oxides. The Griess–Ilosvay reagent for nitrite determination was prepared as described in ref. (6). Solutions of the complexes were made by dissolving weighed amounts of the ligand in an ammonium iron(II) sulphate solution.

Instruments

A Hitachi model 100–60 spectrophotometer with a home-made rapid-mixing device (dead time *ca.* 1 s, thermostatted at 25 °C), together with a Radiometer pHm-25 pH-mV



Fig. 1. Dependence of t_1 on initial concentration of nitric acid (×), ferroin (+) and nitrite (\bigcirc). ×, $[Fe(bpy)_3^{2^+}]_0 = 1.8 \times 10^{-4}$, $[HNO_2]_0 = 1 \times 10^{-6}$; +, $[HNO_3]_0 = 2.5$, $[HNO_2]_0 = 1 \times 10^{-6}$; \bigcirc , $[Fe(phen)_3^{2^+}]_0 = 1.4 \times 10^{-3}$, $[HNO_2]_0 = 1 \times 10^{-6}$ mol dm⁻³.

meter with a smooth Pt electrode and an Hg/Hg_2SO_4 reference electrode, was applied. The continuous stirred tank reactor (c.s.t.r.) used in this study has been described earlier.⁷

Kinetic runs were started by mixing two pre-thermostatted solutions in a spectrophotometer cell or in the rapid-mixing device. No separate measurements were made for equilibrium calculations: for these the final readings of the kinetic runs were used.

The stoichiometry of the reaction was checked by reading the absorbance of the final complex concentration on the spectrophotometer and by simultaneous determination of the nitrite concentration using the Griess–Ilosvay reagent. It was necessary to work rapidly with solutions that had reached equilibrium, owing to side reactions involving iron(III) complexes.

Results

The stoichiometry of the reactions is given by

$$2Fe^{2+} + NO_3^{-} + 3H^{+} = 2Fe^{3+} + HNO_9 + H_9O_1$$

The autocatalytic behaviour of the reactions is reflected in the S-shaped (or sigmoidaltype) kinetic curves. For the phen and bpy complexes the reductant vs. time and product vs. time traces are symmetric, which indicates the absence of any intermediate in measurable quantities, in contrast to the oxidation of $Fe(aq)^{2+}$, where an intensely coloured intermediate FeNO²⁺ appears. Both reactions are reversible. The final state is a true equilibrium state. It can be shifted in either direction by adding further amounts of the reactants or products or by dilution. Further, it was possible to calculate equilibrium constants from these final concentrations and to compare the values to those derived from standard redox potentials.

In order to characterise the kinetic curves quantitatively we use three parameters:¹ (i) the length of the induction period (t_i) , which is at the inflection point of the curve, (ii)



Fig. 2. Dependence of r_{max} on initial concentration of nitric acid (×), ferroin (+) and nitrite (\bigcirc). Initial concentrations are as in fig. 1.



Fig. 3. Dependence of X% on initial concentration of nitric acid (×), ferroin (+) and nitrite (\bigcirc). Initial concentrations are as in fig. 1.

the maximum rate of the reaction (r_{max}) and (iii) the extent of the reaction at the final state (expressed in conversion, x, or percentage conversion, X%).

It is obviously necessary to study the effect of the initial concentrations of the reactants, nitric acid and the iron(II) complex. However, the product HNO_2 has a marked effect on the kinetics of the reactions. Therefore it was necessary both to control the initial HNO_2 content of the reaction mixture and to study the effect of initial HNO_2 concentration.



Fig. 4. Dependence of t_i values on $[Fe^{2+}(aq)]_0$ values at $[HNO_3]_0 = 2.5$ and $[HNO_2]_0 = 1 \times 10^{-7} \text{ mol dm}^{-3}$.

The concentration ranges used were determined by practical reasons. In the case of nitric acid, at initial concentrations above ca. 5 mol dm⁻³ the rate became too high, and the induction period disappeared. Below 1.5–2 mol dm⁻³ the rate was quite low, and hydrolysis of the iron(II) complexes became significant. The initial complex concentration was bounded from below by the measurability of its absorbance (10⁻⁶ mol dm⁻³) and from above by its solubility (10⁻¹ mol dm⁻³). The original HNO₂ content of the nitric acid was ca. 10⁻⁷ mol dm⁻³, and was increased to ca. 10⁻³ mol dm⁻³, where the induction period disappeared. The [HNO₂] value at which this occurred also depended on the concentration of the reactants.

In order to reduce the number of figures we present only part of our experimental results. These show the influence of the three reactants (iron complex, nitric acid and nitrous acid) on the kinetic parameters t_i (fig. 1), r_{max} (fig. 2) and X% (fig. 3). In all cases the points are measured values and the lines are the results of calculations (*cf.* Discussion section).

As we shall explain in the Discussion section, it was necessary to extend the earlier study³ of the $Fe(aq)^{2+}$ -nitric acid system to lower iron(II) initial concentrations. Owing to the very low concentration of the brown intermediate $FeNO^{2+}$ under these conditions we followed the reaction by a potentiometric technique. These results are presented in fig. 4. The reaction was also followed potentiometrically at high initial ferroin concentrations.

Discussion

First we evaluate the experimental data from an equilibrium point of view. According to the stoichiometric equation we can write

$$K = \frac{[\mathrm{Fe}^{3+}]_{\mathrm{e}}^{2}[\mathrm{HNO}_{2}]_{\mathrm{e}}}{[\mathrm{NO}_{3}^{-}][\mathrm{Fe}^{2+}]_{\mathrm{e}}^{2}[\mathrm{H}^{+}]^{3}}.$$

Taking into account the degree of conversion x, the mass balances $[Fe^{2+}]_e = [Fe^{2+}]_0$ (1-x), $[Fe^{3+}]_e = [Fe^{2+}]_0 x$, $[HNO_2]_e = 0.5([Fe^{2+}]_0 x + [HNO_2]_0)$ and neglecting changes in $[H^+]$ and $[NO_3^-]$, we have

$$K = \frac{[\mathrm{Fe}^{2+}]_0^2 x^2 \times 0.5[\mathrm{Fe}^{2+}]_0 x}{[\mathrm{NO}_3^-][\mathrm{Fe}^{2+}]_0^2 (1-x)^2[\mathrm{H}^+]^3}.$$

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Because $[HNO_2]_0$ is much smaller than $[Fe^{2+}]_0 x$ and $[HNO_2]_e = 0.5([Fe^{2+}]_0 - [Fe^{2+}]_e)$

$$K = \frac{[\mathrm{Fe}^{2+}]_0 x^3}{2[\mathrm{NO}_3^-][\mathrm{H}^+]^3 (1-x)^2}.$$

A plot of the experimental concentration data of the equilibrium states is shown in fig. 5. Fitting these points by a least-squares method we find

$$K = (5 \pm 1.5) \times 10^{-4} \text{ mol}^{-3} \text{ dm}^9 \text{ for Fe(phen)}_3^{2+}$$
$$K = (9 \pm 2.5) \times 10^{-4} \text{ mol}^{-3} \text{ dm}^9 \text{ for Fe(bpy)}_3^{2+}.$$

The standard redox potentials of the redox couples involved in these systems are as follows:⁸ $\varepsilon_0(aq) = 0.771 \text{ V}$, $\varepsilon_0(phen) = 1.03 \text{ V}$, $\varepsilon_0(bpy) = 1.025 \text{ V}$, $\varepsilon_0(NO_3^-/HNO_2) = 0.94 \text{ V}$, $\varepsilon_0(2NO_3^-/N_2O_4) = 0.80 \text{ V}$ and $\varepsilon_0(HNO_2/NO) = 1.00 \text{ V}$. Using these values one obtains $K = 8.8 \times 10^{-4} \text{ mol}^{-3} \text{ dm}^9$ for Fe(phen)²⁺₃ and $K = 1.3 \times 10^{-3} \text{ mol}^{-3} \text{ dm}^9$ for Fe(bpy)²⁺₃. The agreement can be characterized as fairly good, taking into consideration the differences between electrochemical and kinetic measurements and the difficulties in defining the values of a_{H^+} .

It is thus evident why $Fe(phen)_3^{2+}$ and $Fe(pby)_3^{2+}$ complexes reduce nitric acid in a reversible way, and why oxidation of $Fe(aq)^{2+}$ by nitric acid is practically complete. In this last case the value $K = 5.2 \times 10^5$ mol⁻³ dm⁹ follows from the redox potentials, which leads to an equilibrium shifted far to the right under the concentration ranges investigated here and earlier.³ It also explains why HNO₂ is reduced to NO by $Fe(aq)^{2+}$ but not by the other two complexes.

To interpret the kinetic results we started from the general picture of autocatalytic nitric acid oxidations and postulated a simple two-step mechanism:

$$NO_{3}^{-} + HNO_{9} + H^{+} = 2NO_{9} + H_{9}O$$
 (1)

$$NO_2 + Fe^{2+} + H^+ = HNO_2 + Fe^{3+}.$$
 (2)

The first step is common in all autocatalytic nitric acid oxidations. The form of the rate equations and the values of the rate constants are known. These proved to be suitable for describing similar oxidations of nitrogen monoxide,⁹ the $Fe(aq)^{2+}$ ion,³ thiocyanate¹⁰ and bromide.¹¹

The second step is obvious, because the iron complexes are one-electron reductants, and the ligands are not oxidized under these circumstances. It must evidently be a reversible step, and owing to its simplicity it is probably an elementary one. Thus its rate equation follows from the mass-action law. In order to estimate the rate constants we relied on data for similar processes.^{2,9,10} According to these, k_2 should lie in the range 10^4-10^5 mol⁻¹ dm³ s⁻¹. The value of k_{-2} is determined by the equilibrium constants of the overall process. The rate equations are as follows:

$$r_1 = k_1[H^+][NO_3^-][HNO_2] - k_{-1}[NO_2]^2$$

$$r_2 = k_2[NO_2][Fe^{2+}][H^+] - k_{-2}[HNO_2][Fe^{3+}].$$

For numerical integration we used a program based on the Gear method¹² and applied it using VAX 780 and Sinclair QL computers. In the course of the calculations we varied k_2 values systematically (k_{-2} was changed automatically according to the relation $k_{-2} = k_2/K_2$) and finally choose the value which gave the best agreement between experiment and calculation. The calculated values of the three characteristic parameters are plotted together with experimental values. The data presented were obtained using rate constants obtained from the best fit. A similar degree of agreement was reached over a narrow range of rate-constant values for both complexes. Taking this into consideration we can give best values and uncertainty ranges for the rate constants (table 1).

We made an attempt to study reaction (2) directly. NO₂ gas was injected into an acidic

and

complex	<i>K</i> (pot) ^{<i>a</i>} /mol ⁻³ dm ⁹	<i>K</i> (kin) ^b /mol ^{−3} dm ⁹	$k_2 \over /{ m mol}^{-2} { m dm}^6 { m s}^{-1}$	$k_{-2} / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
Fe(aq) ²⁺	5.2 × 10 ⁵		3 × 10 ⁴	6×10^{-4c}
Fe(phen) ₃ ²⁺	8.8×10^{-4}	5×10^{-4}	$(4\pm0.4)\times10^{4}$	20 + 2
$Fe(bpy)_{3}^{2+}$	1.3×10^{-3}	9×10^{-4}	$(3\pm0.3) \times 10^4$	13 ± 2

 Table 1. Equilibrium and rate constants

^a Calculated from potentiometric data. ^b Calculated from the equilibrium values of the present kinetic experiments. ^c Data from ref. (3).



Fig. 5. Plot of equilibrium concentration values for calculation of equilibrium constant in the case of $Fe(phen)_{3}^{3+}(\bigcirc)$ and $Fe(bpy)_{3}^{3+}(+)$ complexes. (For details see text.)

solution of ferroin from a syringe. The red colour turned to blue immediately, indicating a rapid reaction. A quantitative study was not performed because disproportionation of NO₂ [reaction (-1)] is similarly rapid, and this and the kinetics of NO₂ dissolution leads to complications and difficulties. Our value for k_2 qualitatively supports this observation.

It is unusual to present results historically; however, in performing calculations we found, in agreement with experiment, that on increasing the initial ferroin concentration (from ca. 10^{-5} to ca. 5×10^{-3} mol dm⁻³), t_i values decreased, as expected from chemical intuition. However, at higher [ferroin]₀ values the calculated induction period began to increase after reaching a minimum value. This behaviour seemed strange to us; we checked it experimentally and found the same trend. Extending the calculations to lower initial ferroin concentrations, another change in the trend of inflexion times occurred. This unusual result was also observed experimentally. The results are presented in fig. 1. The prediction of this behaviour of the system by the above mechanism is an indication of its validity.

As a further step we considered the results of Epstein *et al.*^{2,3} on the $Fe(aq)^{2+}$ -nitric acid reaction. Studying the kinetics of this reaction they found a -0.6 order in describing the effect of initial iron(II) concentration on the t_{max} values. t_{max} is the time at which the brown intermediate $FeNO^{2+}$ reaches its maximum concentration, and is nearly the same as t_i . In the mechanism which they used successfully in describing the

kinetics of the reaction, $Fe(aq)^{2+}$ appears in three steps where it has only positive order. The intermediate $FeNO^{2+}$ is assumed to be a non-reactive species, but this would not explain the inhibitory effect of iron(II), because $FeNO^{2+}$ captures only a few percent of the total $Fe(aq)^{2+}$ present. So the apparent contradiction may not be explained this way. To see what is the situation in other concentration ranges we extended the investigations toward lower initial $Fe(aq)^{2+}$ concentration ranges both experimentally and numerically. This time we followed the reaction by means of potentiometry. The results (fig. 5) were successful and convincing: on decreasing the initial $Fe(aq)^{2+}$ concentration the t_i values begin to increase.

Having found the same unusual behaviour of the t_i vs. [reactant] curves in two different systems we became interested as to how far this behaviour is general in autocatalytic systems. The aforementioned results are confirmed: they are inherent properties of such mechanistic models and are not peculiarities of nitric acid or iron chemistry. The results of such analytical and numerical investigations of generalized model systems will be published in a separate paper.¹³

A large number of iron(II) complexes are known, offering the possibility of studying a broad variety of similar reactions: this is not our aim. We are looking rather for bistability in autocatalytic reactions in a c.s.t.r. in order eventually to produce oscillations.¹⁴ We did carry out a few preliminary experiments with $Fe(CN)_6^{3-}$ and with ferrocene. The first complex is not oxidized in an autocatalytic way, but in a complex manner where a deep brown colour is found and precipitation occurs. In the mixed solvent DMF-H₂O ferrocene is oxidized autocatalytically. Further experiments are in progress in our laboratory.

We put the system $Fe(phen)_3^{2+}$ -nitric acid into a c.s.t.r. in order to check whether or not it shows bistability. In the concentration ranges $[HNO_3]_0 = 1.2-3$ and $[Fe(phen)_3^{2+}]_0 = 5 \times 10^{-4}-5 \times 10^{-3}$ mol dm⁻³ with flow rates $k_0 = (1-17) \times 10^{-3}$ s⁻¹ no bistability was found. The calculations gave the same result, so it may be stated with confidence. Bistability was found in the nitric acid oxidations of $Fe(aq)^{2+}$,³ thiocyanate¹⁰ and bromide.¹¹ We are working on the explanation for its absence in this system.

Travelling waves and the effect of gravity on their velocity¹⁵ were observed in the ferroin-nitric acid system, as in the $Fe(aq)^{2+}$ -nitric acid reaction.¹⁶ The results of these and other wave experiments will be presented elsewhere.¹⁷

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