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Kinetics of Reaction of $Fe(phen)_3^{2+}$ with Hydrogen Peroxide in Neutral Medium

MARIA CYFERT

Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

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Abstract

The kinetics of ferroin oxidation reaction with hydrogen peroxide in neutral aqueous solution at different H_2O_2 concentrations and temperatures were studied. The reaction orders, the reaction rate constants and the reaction rate law were determined. Taking into account the observed catalytic effect of the intermediate product a reaction mechanism was proposed.

Introduction

Oxidation of $Fe(phen)_3^{2+}$ depends upon the oxidant and on the reaction medium. Reactions with Ce(IV) [1, 2], Co(III) [3] and Mn(III) [3] in acid medium are fast. Reaction of ferroin with peroxodisulphate in aqueous medium is rather slow [4, 5] but can be accelerated by Ag^+ ions [6]. Shakhashiri and Gordon [7] have classified the reactions of $Fe(phen)_3^{2+}$ with different oxidants into two groups, depending on whether or not $Fe(phen)_3^{3+}$ was formed as a product. Reactions of the first group yielding the blue Fe(III) complex are of the first order in each reagent and usually take place in acidic solutions. These reactions proceed via an outer-sphere path since the electron transfer takes place rapidly and the first coordination sphere of the iron complex remains unchanged. The reactions of the second group take place in pH range 1–9 and their rates are controlled by the first dissociation step:

$$Fe(phen)_3^{2+} \rightleftharpoons Fe(phen)_2^{2+} + phen$$

They are usually independent of oxidant concentration. Reaction of $Fe(phen)_3^{2+}$ with chlorite [7] and peroxydiphosphate [8] belong to the second group since they are slow and do not yield $Fe(phen)_3^{3+}$ as a product. Their product is the iron(III)–phenanthroline dimer, $[(phen)_2Fe{-}O{-}Fe(phen)_2]^{4+}$ or $[(phen)_2Fe(OH)_2Fe(phen)_2]^{4+}$. Reaction of ferroin with hydrogen peroxide could also be classified in the second group since the oxidation product was not the blue Fe(III) complex. Examining this reaction at two excess H_2O_2 concentrations (0.45 and 0.9 M, at 25 °C), Burgess and Prince [9] found that the reaction is of the first order with respect to the complex and is nearly independent of hydrogen peroxide concentration. The loss of one ligand molecule from $Fe(phen)_3^{2+}$ seems to be the rate-determining step.

In the present paper the kinetics of ferroin oxidation reaction by hydrogen peroxide were studied at different temperatures and at H_2O_2 concentrations lower than those applied by Burgess and Prince [9].

Experimental

Reagents and Analysis

All reagents were of analytical purity grade and the water was triply distilled. The 0.01 M stock solution of ferroin was prepared by dissolving an appropriate amount of $FeSO_4 \cdot 7H_2O$ and 1,10-phenanthroline in water. The ferrous sulphate was crystallized from ethyl alcohol and the presence of ferric ions was examined by the rhodanate test. The stock ferroin solution was determined by titration of 0.01 M $Ce(SO_4)_2$ in acid medium.

The 0.05 and 0.5 M solutions of H_2O_2 were prepared from 30% hydrogen peroxide and were determined by tiration of the standard $KMnO_4$ solution in acid medium. Fresh solutions were prepared for each experiment.

Kinetic Measurements

Kinetic measurements were carried out at 298–318 K in a water thermostat equipped with a contact thermometer. The ferroin concentration was followed on a SPECOL spectrophotometer at 510 nm. In all cases the oxidized forms had a negligible absorption. Each reaction run was repeated 3 or more times and the difference never exceeded 10%. In some runs the H_2O_2 concentration was checked by taking a 10 cm^3 reaction sample and immediately titrating with $KMnO_4$ solution.

The reaction in the whole visible region was recorded on a SPECORD UV-VIS spectrophotometer at room temperature.

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TABLE I. Rate Constant Values, $[Fe(phen)_3^{2+}] = 5 \times 10^{-5}$ M.

Run	T	H_2O_2 (M)	$10^5 k_1$ (s^{-1})	$10^5 k_2$ (s^{-1})	$10^3 k_1/[H_2O_2]$	$10^2 k_2/[H_2O_2]$
1	298 K	0.475	7.2	3.2		
2	303 K	6.25×10^{-3}	2.0	8.7	3.2	1.39
3		1.25×10^{-2}	3.8	16.7	3.04	1.33
4	308 K	6.25×10^{-3}	3.0	12.3	4.8	1.97
5		1.25×10^{-2}	5.8	23.3	4.64	1.86
6	313 K	2.50×10^{-3}	1.8	7.2	7.2	2.88
7		6.25×10^{-3}	4.3	19.0	6.88	3.04
8		1.25×10^{-2}	8.8	37.0	7.04	2.96
9		4.50×10^{-2}	33.0	105.0	7.33	2.33
10		0.475	61.7	15.5		
11	318 K	6.25×10^{-3}	6.3	25.0	10.1	4.0
12		1.25×10^{-2}	13.0	50.0	10.4	4.0

Results and Discussion

Ferroin reacts with hydrogen peroxide in neutral aqueous solution, but with no detectable formation of the respective blue iron(III) complex. To find out whether in these conditions the oxidation of ferroin really occurred, the following experiments were made. To the post-reaction mixture, after having removed the peroxide by one drop of strong catalase, 1,10-phenanthroline was added. After a long period of time the solution turned slightly red. The same experiment, but with diluted sulphuric acid, gave the same effect. In the next experiment, potassium rhodanate was added to the post-reaction mixture. The solution did not change its colour, but addition of the diluted H_2SO_4 caused the immediate formation of the red Fe(III)–rhodanate complex. This indicates that in the neutral medium ferroin undergoes oxidation by hydrogen peroxide and a complexed form of Fe(III) is present in the reaction product.

The experimental data proved that the above reaction was of the first order in $Fe(phen)_3^{2+}$, in agreement with the literature data [8]. Attempts to determine directly the order with respect to hydrogen peroxide failed, because in the excess of ferroin it appeared impossible to determine currently the hydrogen peroxide concentration in the reaction mixture. This order was determined indirectly by carrying out the reaction at different initial H_2O_2 concentrations, but always with excess of peroxide in comparison with ferroin. The first order with respect to hydrogen peroxide was found in H_2O_2 concentration range: 2.5×10^{-3}–4.5×10^{-2} M. The obtained rate constant values divided by peroxide concentrations give the same value at a given temperature (Table I). This indicates the first-order dependence of the reaction in hydrogen peroxide. At peroxide concentrations higher than 4.5×10^{-2} M the order decreased, and it was near zero at 0.475 M H_2O_2 or higher.

Up to 80% of complete reaction, peroxide concentration changes only a little but consumption of H_2O_2 was higher than it could be expected from the simple stoichiometry of the reaction. At the end of the reaction enhanced decomposition of H_2O_2 and oxygen evolution were observed. The post-reaction mixture was light yellow, but the colour disappeared after some time.

In the visible region a decrease of the band intensity at 510 nm and an increase of the band intensity at 340–380 nm with a weak shoulder at about 355 nm were observed. After 80% reaction the band started to decrease and the shoulder began to disappear. No band at about 600 nm, corresponding to formation of $Fe(phen)_3^{3+}$, was observed. This is consistent with Shakhashiri and Gordon [7] and indicates that the reaction product was Fe(III)–phenanthroline dimer, which could next react with hydrogen peroxide and be transformed into other hydrolytic forms.

The studies carried out at the initial $Fe(phen)_3^{2+}$ concentration 5×10^{-5} M and various H_2O_2 concentrations (2.5×10^{-3}–4.5×10^{-2} M) revealed that the reaction rate depends upon hydrogen peroxide concentration. Experimental curves have the shape of autocatalytic curves (Fig. 1). Experimental data fulfilled the following equation:

$$\frac{dx}{dt} = k_1 \times (a_o - x) + k_2 \times x \qquad (1)$$

where: a_o = initial ferroin concentration, x = intermediate product concentration equal to the decrease of ferroin.

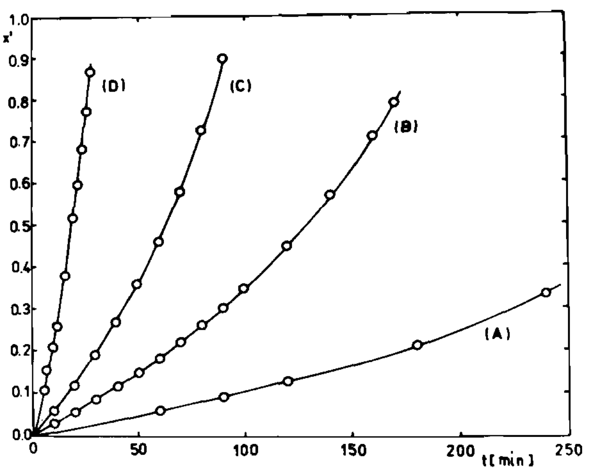

Fig. 1. Dependence of the degree of change (x') *vs.* time at 40 °C, at different initial hydrogen peroxide concentrations: (A): 2.5×10^{-3} M; (B): 6.25×10^{-3} M; (C): 1.25×10^{-2} M; (D) 4.5×10^{-2} M; $[Fe(phen)_3{}^{2+}] = 5 \times 10^{-5}$ M.

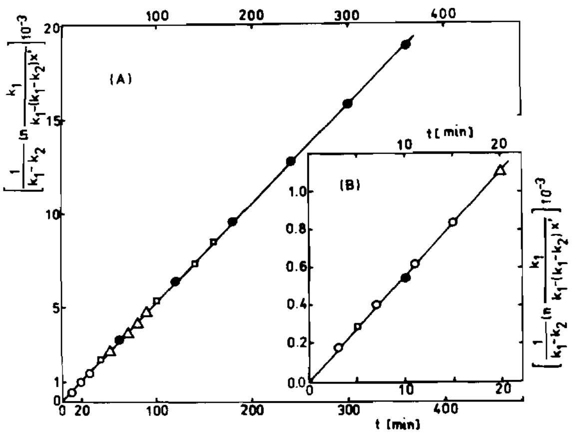

Fig. 2. Straight-linear dependence $[1/k_1 - k_2)]\ln\{k_1/[k_1 - (k_1 - k_2) \times x']\}$ *vs.* time at 40 °C: (○): 4.5×10^{-2} M H_2O_2; (△): 1.25×10^{-2} M H_2O_2; (□): 6.25×10^{-3} M H_2O_2; (●) 2.5×10^{-3} M H_2O_2.

Introducing the degree of change: $x' = x/a_o$, the eqn. (1) would be:

$$\frac{dx'}{dt} = k_1 \times (1 - x') + k_2 \times x' \qquad (2)$$

and after its solution:

$$\ln \frac{k_1}{k_1 - (k_1 - k_2) \times x'} = (k_1 - k_2) \times t \qquad (3)$$

Calculation of both rate constants (k_1, k_2) from eqn. (3) is impossible. Assuming that at the beginning of the reaction the first part of eqn. (2) is dominating and in the end of the reaction the second part plays the decisive role, k_1 and k_2 values were determined graphically. Rate constant values for different H_2O_2 concentrations at different temperatures are given in Table I. These constants (k_1, k_2) were introduced to eqn. (3) and $[1/(k_1 - k_2)] \times \ln\{k_1/[k_1 - (k_1 - k_2) \times x']\}$ *versus* time was plotted. The result was a straight line for different H_2O_2 concentrations at a given temperature (Fig. 2), which confirms the correctness of graphically determined rate constant values.

Reaction mechanisms could be proposed as follows:

$$Fe(phen)_3{}^{2+} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Fe(phen)_2{}^{2+} + phen \qquad (a)$$

$$Fe(phen)_2{}^{2+} + H_2O_2 \xrightarrow{k_b} Fe(phen)_2{}^{3+} + OH^- + \dot{O}H \qquad (b)$$

$$Fe(phen)_3{}^{2+} + \dot{O}H \xrightarrow{k_c} Fe(phen)_2{}^{3+} + OH^- + phen \qquad (c)$$

$$Fe(phen)_2{}^{3+} + H_2O_2 \xrightarrow{k_d} {}^*Fe(phen)_2{}^{3+} + 2\dot{O}H \qquad (d)$$

Considering $Fe(phen)_2{}^{2+}$ and $\dot{O}H$ as intermediates, the following rate law could be obtained on the basis of the steady-state approximation:

$$-\frac{d[Fe(phen)_3{}^{2+}]}{dt} = \frac{2k_a k_b [Fe(phen)_3{}^{2+}][H_2O_2]}{k_{-a}[phen] + k_b[H_2O_2]} + k_d[Fe(phen)_3{}^{3+}][H_2O_2] \qquad (4)$$

which at H_2O_2 excess could be written [7] as:

$$-\frac{d[Fe(phen)_3{}^{2+}]}{dt} = k_1 [Fe(phen)_3{}^{2+}] + k_2 [Fe(phen)_2{}^{3+}] \qquad (5)$$

Equation (5) is identical to eqn. (1).

Initiation of a process proceeds by the slow dissociation of $Fe(phen)_3{}^{2+}$ (reaction (a)). The formed $Fe(phen)_2{}^{2+}$ reacts with hydrogen peroxide to be oxidized to $Fe(phen)_2{}^{3+}$ and to produce $\dot{O}H$ radical. $Fe(phen)_2{}^{3+}$ formed in reactions (b) and (c) – as a result of collisions with H_2O_2 molecules (reaction (d)) – becomes a more active form – $^*Fe(phen)_2{}^{3+}$, which after rate-determining reactions is transformed into the dimer according to equation:

$$2{}^*Fe(phen)_2{}^{3+} + 2H_2O \rightleftharpoons [Fe(OH)(phen)_2]_2{}^{4+} + 2H^+ \qquad (f)$$

The $\dot{O}H$ radicals, additionally formed in reaction (d), can oxidize $Fe(phen)_3{}^{2+}$ and accelerate the reaction course. Reactions (c) and (d) may explain the autocatalytic character of the ferroin oxidation and the greater consumption of peroxide than would be expected from the simple stoichiometry. The shape of the reaction curves in Fig. 1 is additional evidence for this conclusion.

On the other hand, the reaction requires the dissociation of one 1,10-phenanthroline molecule, pointed out by the lack of $Fe(phen)_3^{3+}$ in reaction products.

In reactions of ferroin with chlorite [7] or peroxydiphosphate [8] the presence of the free phenanthroline slowed down considerably the reaction rate. In the present studies, at 40 ℃ and at $[Fe(phen)_3^{2+}] = 5 \times 10^{-5}$ M, $[H_2O_2] = 1.25 \times 10^{-2}$ M and of free phenanthroline concentration equal to 5×10^{-3} M, no changes in ferroin concentration were observed after two days, while in the absence of phenanthroline $Fe(phen)_3^{2+}$ disappeared in 90 minutes. Decomposition of hydrogen peroxide was very low (about 2%). Such behaviour of the reaction mixture confirmed the assumption that the reaction should be initiated by dissociation and that the reaction product, not substrate, is responsible for H_2O_2 decomposition.

In the H_2O_2 concentration range: 2.5×10^{-3}–4.5×10^{-2} M the k_1 value was about four times lower than k_2. At a H_2O_2 concentration equal to 0.475 M the k_1 exceeded k_2 twice at 25 ℃ and four times at 40 ℃. In these conditions k_1 is close to the ferroin dissociation rate constant (7.3×10^{-5} s^{-1} and 8.1×10^{-4} s^{-1} at 25 ℃ and 40 ℃ respectively, [10]) in acid solution. This is confirmation of Burgess and Prince's conclusion [9] that at high H_2O_2 excess the dissociation of $Fe(phen)_3^{2+}$ seems to be the rate-determining step.

The straight-linear temperature dependence of the k_1 and k_2 logarithms has been stated previously. The graphically determined activation energies are: $E_A^1 = 64$ kJ/mol and $E_A^2 = 57.7$ kJ/mol. The lower E_A^2 value points out that the second part in eqn. (1) is responsible for the autocatalytic process and for the peculiar shape of the ferroin oxidation curves in these conditions.

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