Decomposition of Hydrogen Peroxyde by Ferric Ions-The Equilibrium Concentration of Ferrous Ions in this System

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Özet: Hidrojen peroksidin demir (II) ve demir (III) iyonları ile katalitik parçalanması, bilhassa son on yıl içinde bir çok araştırma merkezlerinde incelenmiştir. Haber ve arkadaşlarının teklif ettiği reaksiyon mekanizmaları değişiklere uğramış, fakat bütün denel gerçekleri açıklıyabilen mekanizmalar verilememiştir.

Baxendale ve arkadaşları, hidrojen peroksidin demir (III) iyonları ile parçalanmasında, demir (II) iyonlarının zincir reaksiyonunu taşıdığını, demir (II) ve demir (III) iyonları ile cereyan eden katalitik reaksiyonlar arasında temel bir fark olmayıp, bunların yalnız başlama kademelerinde birbirlerinden ayrıldığını ileri sürmüşlerdir.

Bir başka araştırma merkezinde, Christiansen ve arkadaşları, demir (III) iyonları ile parçalanmada zincir reaasiyonlarının rol oynamadığınını bildirmişlerdir.

Parts ve arkadaşlarının Enstitümüzde yaptıkları çalışmalar, Christiansen - Andersen mekanizmasının bütün pH bölgesinde doğru olamıyacağını göstermiştir. Ayrıca, serbest radikallere karşı hassas olan akrilonitril gibi bir monomer reaksiyon ortamında bulunursa, hidrojen peroksidin parçalanması 56 kere yavaşlamaktadır.

Bu çalışmada, önce, demir (III) - hidrojen peroksit sisteminde teşekkül eden demir (II) iyonlarının α,α'-dipiridil ile verdiği sağlam kompleksten faydalanarak bu iyonların kararlı hal konsentrasyonu hesaplanmıştır. Bundan başka zincir reaksiyonlarının yalnız demir (II) iyonları ile taşınmadığı HO_2 OH radikallerinin taşıdıkları bir zincir reaksiyonunun da bulunabileceği ileri sürülmüştür.

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INTRODUCTION

Decomposition of hydrogen peroxide by ferric ions has been the subject of many papers especially over the last decades. The free radical mechanism proposed by Haber and his co-workers [1] was altered, but a reaction mechanism which explain all kinetic evidence was not established. Due to the very important features and various applications as indicated by Medalia and Kolthoff [2] the reaction was taken into consideration by different research centers.

The following reaction mechanism of Haber and Weiss:

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$
$$Fe^{+++} + HO_2^- \longrightarrow Fe^{++} + HO_2$$
$$H_2O_2 + HO_2 \longrightarrow O_2 + H_2O + OH$$
$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^-$$
$$OH^- + H^+ \longrightarrow H_2O$$

which does not include a chain reaction was found to be inconsistent. [2,3]

Barb, Baxendale, George and Hargrave [4] proposed the following mechanism:

$$Fe^{+++} + H_2O_2 \longrightarrow HO_2 + Fe^{++} + H^+ \qquad (i)$$
$$Fe^{++} + H_2O_2 \longrightarrow OH + OH^- + Fe^{+++} \qquad (o)$$
$$OH + H_2O_2 \longrightarrow HO_2 + H_2O$$
$$Fe^{+++} + HO_2 \longrightarrow O_2 + H^+ + Fe^{++}$$
$$OH + Fe^{++} \longrightarrow OH^- + Fe^{+++}$$
$$HO_2 + Fe^{++} \longrightarrow HO_2^- + Fe^{+++}$$

In this reaction scheme the authors accepted, by analogy with cobaltic ion reaction that initation reaction is the reaction between ferric and HO_2^- ions. Furthermore, excluding the probable chain reaction of

$$HO_2 + H_2O_2 \longrightarrow OH + O_2 + H_2O$$
$$OH + H_2O_2 \longrightarrow HO_2 + H_2O$$

they indicated that there is no essential difference between ferric and ferrous ion catalysis of hydrogen peroxide. The only difference between the ferrous and ferric systems as they have shown in the first part of their work [5], is that reaction (i) is not important relative to (o) in the ferrous ion hydrogen peroxide reaction. In the case of high peroxide to ferric ion concentration ratio the overall decomposition rate which was given by

$$-\frac{d(H_2O_2)}{dt}=\frac{k_{d'}}{[(H^+)+K_F]}(Fe^{+++})(H_2O_2)$$

is verified by kinetic results. In two other cases, namely, in the case of low peroxide to ferric ion concentration ratio and in the case of very high ferric ion to peroxide concentration ratio kinetic experiments did not verify the results given in these cases by the above reaction mechanism.

The other group which was working on the kinetics of ferric ion catalysed decomposition of hydrogen peroxide includes Christiansen and his co-workers.

To explain his experimental results Andersen proposed the following reaction mechanism [6,7]

$$Fe^{+++} + HO_2^- \rightleftharpoons FeOOH^{++}$$
$$FeOOH^{++} \rightleftharpoons FeOH^{++} + O$$
$$O + HO_2^- \longrightarrow O_2 + OH^-$$

Later, however, Christiansen and Andersen revised the above mechanism [8]. They proposed that an active form of H_2O_2 anions (HO_2^{-*}) must be assumed in ferric salt catalyzed hydrogen peroxide decomposition to be in equilibrium with $FeOOH^{++}$ instead of O atoms. The reaction sequence now is:

$$Fe^{+++} + HO_2^- \rightleftharpoons FeOOH^{++}$$
$$FeOOH^{++} \rightleftharpoons Fe^{+++} + HO_2^{-*}$$
$$HO_2^{-*} + H_2O_2 \longrightarrow O_2 + H_2O + OH^-$$

In an other paper [9] Christiansen insisted on the above mechanism and declared that "any objections can only be seriously discussed on the basis of new experimental evidence„ .

Onat and Parts [10,11] investigating the reaction between ferric ions and hydrogen peroxide, changing the pH range of the solution from 2.48 to 0.96 (the pH range in Andersen's experiments was from 1.9 to 1.4 in nitrate solutions [8]) and using solutions containing either chloride or perchlorate found out that the kinetic expression of Andersen, i.e.

$$-\frac{d(H_2O_2)}{dt}=\frac{B(H_2O_2)^2}{(H_2O_2+A)}, \quad \text{where} \quad A=k\frac{(H^+)}{K_F+(H^+)}(Fe^{+++})$$

was in agreement wih experimental data up to 97 per cent of the original hydrogen peroxide concentration. They showed, however, that the value of the constant A falls off as the pH of the solution decreases and this is not in agreement with Andersen's results derived from the proposed reaction mechanism. The inconsistency of the Christiansen-Andersen reaction mechanism can be shown by polymerization experiments in which a monomer such as acrylonitrile is used in the reaction system. In another publication Parts [12] showed that, the velocity of decomposition of hydrogen peroxide by ferric ions in the presence of acrylonitrile is much slower than without it. In a special experiment given in that paper the decomposition of hydrogen peroxide was slowed down 56-fold, but in the above scheme of Andersen decomposition of hydrogen peroxide shoul have slowed down only 2-fold in case that all O atoms or actived HO_2^{-*} radicals are attacked by monomer molecules. This makes necessary a chain reaction in the system.

In his latest paper, [13] however, Christiansen agreed that a reaction pattern proposed by Koefoed [14] is in better agreement with general experimental evidence. Koefoed's so-called closed sequence is the following:

$$Fe^{++} + FeO_2H^{+2} \rightleftharpoons Fe_2O_2H^{+4}$$

$$Fe_2O_2H^{+4} \rightleftharpoons Fe^{+3} + FeO_2H^{+}$$

$$FeO_2H^{+} + H_2O_2 \longrightarrow O_2 + H_2O + HO^{-} + Fe^{+2}$$

It appears from the above reaction that Fe^{++} is a chain carrier and free radicals are bounded to ferric and ferrous ions.

In this paper we calculated the equilibrium concentration of ferrous ions in the reaction system of ferric ion and hydrogen peroxide. Holding α,α'-dipyridyl concentrations in excess we were able to calculate the rates of initiation in three different pH's. Our results indicate that besides the chain carrying effect of ferrous ions there should be another chain carrying mechanism.

EXPERIMENTAL

Materials.— The following materials were used throughout this work. Ferric ammonium sulphate was a Schering-Kahlbaum A.G. product. Hydrogen peroxide was destilled under reduced pressure. The complexing agent α,α'-dipyridyl was a Hopkins

& Williams Ltd. material. Sulphuric acid was always used to acidify the solutions. A triply distilled water was used throughout the experiments.

Procedure.— The concentration of ferrous ions which has been formed during the reaction of ferric ions and hydrogen peroxids was determined with the so-called "quenching" technique using α,α′-dipyridyl. The intensity of the red colour which has been formed during the course of the reaction was measured using a photo electric colorimeter which was described earlier [15]. The reactants i.e. solutions of ferric salts, hydrogen peroxide and α,α′-dipyridyl were mixed together in a reaction wessel. This wessel was fixed in a thermostat at 25.00 ∓ 0.02°C. In experiments indicated in Fig. 1, however, the addition of α,α′-dipyridyl to the mixture of ferric ion and hydrogen peroxide was made fifteen, thirty and sixty minutes after the mixing of the latters. The purpose of this was to furnish the necessary time for establishing the steady-state concentration of ferrous ions.

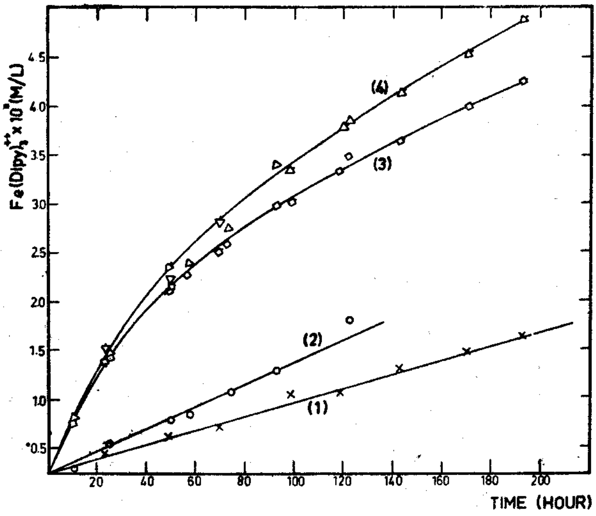

Fig. 1 — Formation of Fe $(Dipy)_3^{++}$ from ferric ion, dipyridyl and hydrogen peroxide, pH 3.0, at 25°C. Initial concentrations : 0.10 × 10^{-3}M H_2O_2 0.10 × 10^{-3}M Fe^{+++}, 1.07 × 10^{-3}M Dipy. Addition of Dipy to reactants: (1) immediately, (2) after 15 mins., (3) after 30 mins., (4) after 60 mins.

Brown comlex which is formed with the mixing of ferric ion solution with α,α'-dipyridyl has a yellow colour in our concentrations. This colour can be observed only the solutions of pH 2.5, and necessary correction in the red complex formation is being made in this pH. Solutions with higher pH values were clear and coluorless.

EXPERIMENTAL RESULTS AND DISCUSSION

To calculate the equilibrium concentration of ferrous ions in the system of ferric ion and hydrogen peroxide we mixed together 1.00×10^{-4}M Fe^{+++}, 1.00×10^{-4}M H_2O_2 and 1.065×10^{-3} M α,α'-dipyridyl solutions. The acidity of ferric solution was such that the final pH of the mixture was 3.05. It can be seen from Fig. 1 that the stationary state concentration of ferrous ions is not established if all reactants are mixed together at the beginning of the reaction. We may conclude, however, that the stationary state concentration of ferrous ion is reached if the addition of α,α'-dipyridyl reagent would be delayed for one hour.

Table I

Expt. No.	Fig No.	$(H_2O_2) \times 10^3$ (mole/l,)	$(Fe^{+++}) \times 10^3$ (mole/l.)	pH (final)	$(Dipy) \times 10^3$
1	1. curve (1)	0.100	0.100	3.05	1.065
2	2 » (1)	0.558	0.836	3.01	»
3	2 » (2)	0.279	0.836	3.01	»
4	2 » (3)	0.553	0.418	3.50	»
5	2 » (4)	0.279	0.418	3.50	»
6	3 » (2)	0.500	0.416	3.45	»
7	3 » (1)	0.250	0.416	3.45	»
8	3 » (3)	0.125	0.416	3.45	»
9	4 » (1)	0.250	0.416	3.45	»
10	4 » (2)	0.250	0.208	3.40	»
11	4 » (3)	0.250	0.126	3.50	»
12	4 » (4)	0.250	0.042	3.60	»
13	5 » (1)	1.150	0.615	2.45	»
14	5 » (2)	2.300	0.615	2.46	»
15	5,6 » (3)	0.570	0.615	2.45	»
16	6 » (4)	0.570	0.416	2.50	»
17	6 » (5)	0.570	0.208	2.54	»
18	6 » (6)	0.570	0.042	2.48	»

Using the initial part of curve (4) in Fig. 1 and the following equation for the formation of Fe (Dipy)$_3^{++}$ complex which was given by Krumholz [16]:

$$\frac{\Delta}{\Delta t_0}[\mathrm{Fe(Dipy)_3^{++}}] = \left[k_{f_0} + \frac{k_{f_1}}{K_\alpha}(H^+)\right](Fe^{++})(H\,Dipy^+)^3\left(\frac{K_\alpha}{K_\alpha + H^+}\right)$$

we were able to calculate the ferrous ion concentration in the system. In this equation k_{f_0} and k_{f_1} are the rate constants of the following reactions respectively:

$$Fe^{++} + Dipy \longrightarrow Fe(Dipy)^{++}$$

$$Fe(Dipy)^{++} + Dipy \longrightarrow Fe(Dipy)_2^{++}$$

and K_α is the equilibrium constant of the following dissociation:

$$(Dipy\,H)^+ \longrightarrow Dipy + H^+$$

The numerical values of k_{f_0}, k_{f_1} and K_α are 2.7×10^{15} min^{-1}, 1.75×10^{12} min^{-1} and 3.70×10^{-5} respectively. The calculated value of $(Fe^{++})_s$, therefore, is 1.6×10^{-11} mol/lit. at 25°C. This value is very low compared with the value 2.4×10^{-6} mol/lit. obtained by Baxendale and co workes. [4] Looking at the curves (3) and (4) in Fig. 1 which start nearly form the origin

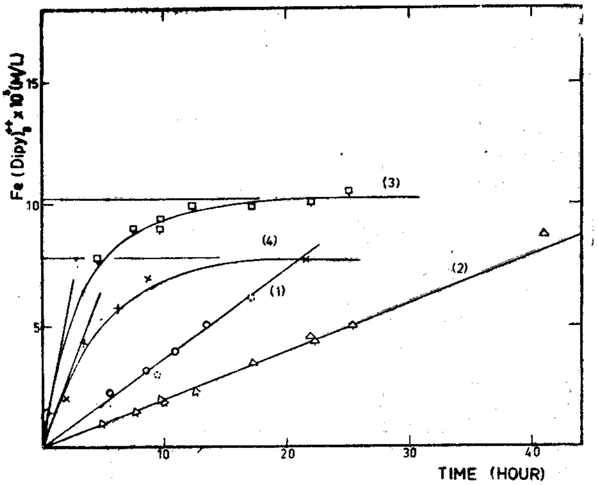

Fig. 2— Initial Concentrations: (1) 0.56×10^{-3}M H_2O_2, 0.84×10^{-3}M Fe^{+++}, pH 3.0; (2) 0.28×10^{-3}M H_2O_2, 0.84×10^{-3}M F^{+++}, pH 3.0; (3) 0.56×10^{-3}M H_2O_2, 0.42×10^{-3}M Fe^{+++}, pH 3.5; (4) 0.28×10^{-3}M H_2O_2, 0.42×10^{-3}M Fe^{+++}, pH 3.5. Dipy 1.065×10^{-3}M, 25°C.

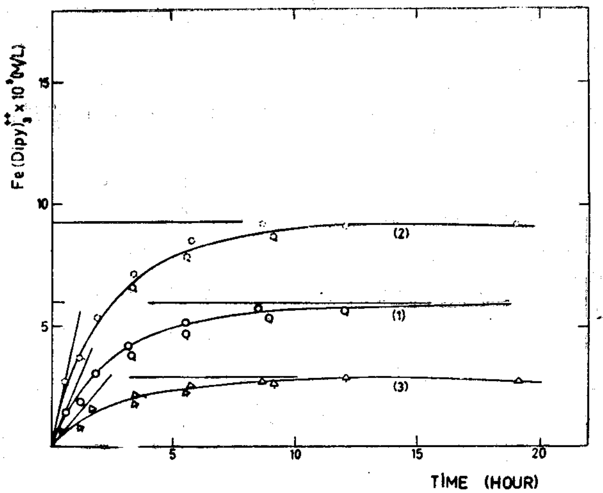

Fig. 3 — Initial Concentrations: (1) 0.25×10^{-3}M H_2O_2, 0.42×10^{-3}M Fe^{+++}, pH 3.45; (2) 0.50×10^{-3}M H_2O_2, 0.42×10^{-3}M Fe^{+++}, pH 3.45; (3) 0.125×10^{-3}M H_2O_2, 0.42×10^{-3}M Fe^{+++}, pH 3.45. Dipy 1.065×10^{-3}M, 25°C.

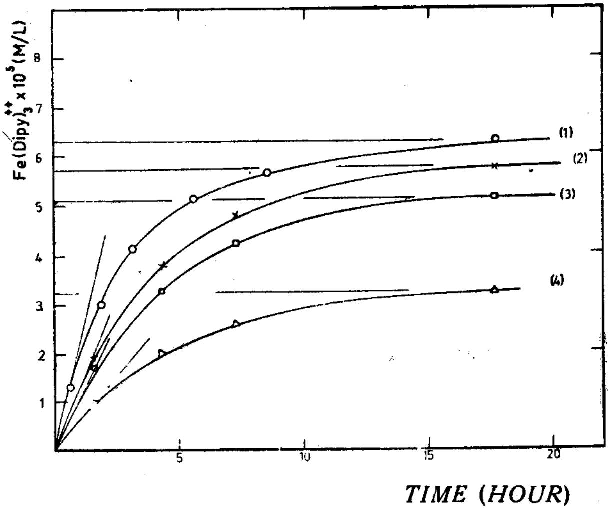

Fig. 4 — Initial Concentrations: (1) 0.42×10^{-3}M Fe^{+++}, pH 3.45; (2) 0.21×10^{-3}M Fe^{+++}, pH 3.40; (3) 0.13×10^{-3}M Fe^{+++}, pH 3.50; (4) 0.042×10^{-3}M Fe^{+++}, pH 3.60. H_2O_2 0.25×10^{-3}M, Dipy 1.065×10^{-3}M, 25°C.

it is possible to say that their large ext opolation to the time of mixing can bring some error which was indicated already by the authors.

Experimental data are tabulated in Table I, and the plots of ferrous complex concentrations which were formed during the reactions *versus* time are drawn in Figures 1 to 6. Experiments have been carried out in three different pH's: 2.5,3.0,3.5. It is shown from the graphs that for pH = 3.0 the three series of determinations are on straight lines. For pH = 3.5 the curves are concave against the time axis and seem to approaach asymptotically a maximum. For the remaining case of pH = 2.5 the curves are convex against the time axis and cut this axis asymptotically at about one hour time.

In the cases of pH 3.0 and 3.5 we were able to calculate the initial slopes of the curves. Supposing that the initiation reaction of hydrogen peroxide decomposition is

$$Fe^{+++} + HO_2^{-} \longrightarrow Fe^{++} + HO_2$$

it is possible to determine k_i, the initiation rate constant of decomposition which is defined by the following equation:

$$-\frac{d(H_2O_2)_r}{dt} = \frac{k_i}{(H^+)}(H_2O_2)(Fe^{+++})$$

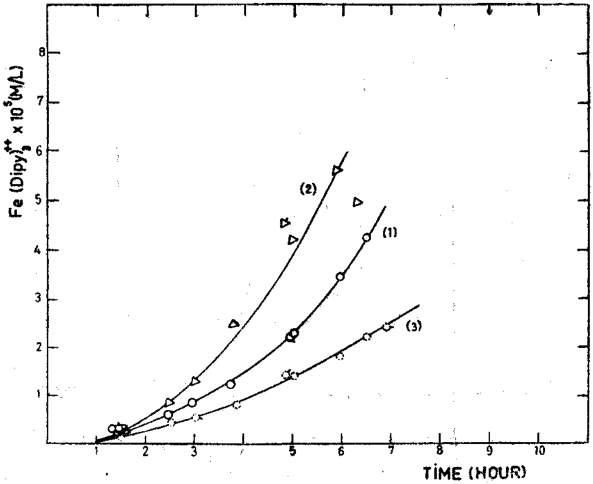

Fig. 5 — Initial Concentrations: (1) 1.15×10^{-3}M H_2O_2; (2) 2.30×10^{-3}M H_2O_2; (3) 0,57×10^{-3} H_2O_2, Fe^{+++} 0,615×10^{-3}M, Dipy 1.065×10^{-3}M, pH 2.45, 25°C.

Table II

Expt. No.	Initial Slope $\times 10^9$ (mole/*l*.sec)	$k_i \times 10^6$ (sec^{-1})	Fe (Dipy)$_3^{++} \times 10^5$ Maximum (mole/*l*.)	$\frac{\Delta(H_2O_2)}{\Delta(Fe^{+++})}$
1	0.028	3.9		
2	1.00	3.3		
3	0.54	3.4		
		3.5 (average)		
4	3.6	15.2	7.8	3.6
5	7.1	14.9	10.2	5.5
6	13.3	35.0	9.3	5.4
7	6.9	36.7	6.0	4.2
8	3.3	35.3	2.9	4.3
9	5.8	30.7	6.2	4.0
10	3.5	41.5	5.7	4.4
11	3.0	46.7	5.1	4.9
12	1.7	63.2	3.2	7.8
		35.5 (average)		4.9 (average)

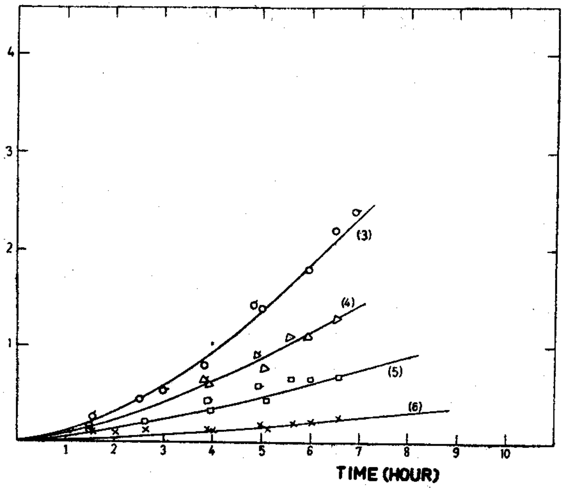

Fig. 6 — Initial Concentrations: (3) 0.615×10^{-3}M Fe+++, pH 2.45; (4) 0.42×10^{-3}M Fe+++, pH 2.50; (5) 0.21×10^{-3}M Fe+++, pH 2.54; (6) 0.042×10^{-3}M Fe+++, pH 2.48. H_2O_2 0.57×10^{-3}M, Dipy 1.065×10^{-3}M, 25°C.

We used the subscript r to indicate the reduced decomposition of hydrogen peroxide because of the presence of α,α'-dipyridyl with the reactants. The value of 2.40×10^{-12} is used for ionization constant of hydrogen peroxide. [17]

In Table II, besides the calculated k_i values we also gave the asympthotic maximum $Fe(Dipy)_3^{++}$ concentration values in the case of $pH = 3.5$. The asympthotic features of the curves indicate that in the case of $pH = 3.5$, the hydrogen peroxide which was originally put to the reaction mixture was used up. If we assume that complex formation of ferrous ions was stechiometric we can calculate the ratio of $\Delta(H_2O_2)/\Delta(Fe^{+++})$ which would be equal te the ratio of $\Delta(H_2O_2)/\Delta Fe(Dipy)_3^{++}$. The average value of chain length, $\Delta(H_2O_2)/\Delta(Fe^{+++})$ is 4. 9.

It is therefore necessary to accep the existance of chain reaction of the following type:

$$H_2O_2 + HO_2 \longrightarrow H_2O + OH + O_2$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$

Recently, Baxendale and his co-workers published a paper [18] on reactions with dipyridyl. Their calculation indicate that. in our experimental conditions, the competition between hydrogen peroxide and $\alpha_1\alpha'$-dipyridyl for ferrous ions is completely in favour of complex formation. In the same paper, the destruction of α,α'-dipyridyl during the reaction was attributed to the reaction of dipyridyl with free radicals which are present in the system. If this is true, than the above calculated value of chain length i.e. 4. 9 can be much higher in case that free radicals do not react with complexing agent.

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