KINETICS AND MECHANISM OF OXIDATION OF COBALT (II) BY IRON (III) IN THE PRESENCE OF 1,10 PHENANTHROLINE

Bassem F. Shraydeh[1]

ملخص

لقد تمت دراسة سرعة وميكانيكية تفاعل أكسدة عنصر الكوبالت في الحالة الثنائية بواسطة الحديد الثلاثي بوجود المتصلة (١ر١٠ فيناثرولين).

تبين الدراسة ان درجة التفاعل بالنسبة للحديد الثلاثي هي واحد أما بالنسبة لعنصر الكوبالت فان درجة التفاعل تساوي ٣ر٠ عندما يكون تركيز الكوبالت عاليا و ٧٩ر٠ عندما تكون تراكيز الكوبالت منخفضة . لقد وجد ان جزيئات الحامض تبطيء التفاعل وجزيئات المتصلة العضوية تزيد سرعة التفاعل لقد تم وضع ميكانيكية للتفاعل الذي تتفق مع هذه النتائج المخبرية.

ABSTRACT

The kinetics of oxidation of cobalt (II) by iron (III) in the presence of 1,10 phenanthroline has been investigated spectrophotometrically. Hydrogen ions exhibited an inhibitory effect on the rate of the reaction while 1,10 phenanthroline showed an accelarating effect. The order with respect to iron (III) was found to be unity. On the other hand, the order with respect to cobalt varies with its concentration being 0.3+ 0.004 at high concentration and 0.79±0.019 at low concentrations. A plausible mechanism was postulated and a rate law was derived that accounted for the various experimental results obtained.

INTRODUCTION

The presence of ligands as complexing agents would in general modify oxidation reduction potentials so as to stabilize certain

---

[1] Chemistry Department, An-Najah N. University , Nablus-West Bank

oxidation states whereby the oxidation of cobalt(II) by Fe^{3+} is quite decidedly unfavorable and does not occur if the species are simple aquated ions, However on complexation with 1,10 phenanthroline, the formal reduction potential of the cobalt species in greatly diminished while that of the iron species is appreciably increased; consequently the oxidation of cobalt(II) by iron(III) becomes highly favorable. Really the enhanced oxidation strength of iron(III) salts in the presence of 1,10 phenanthroline was utilized for the determination of cobalt [1-2]. Although the analytical application of this important reaction has been studied[1], there exists no reports concerning its kinetics and mechanism. Hence a detailed kinetic study was made and the results are hereby discussed.

EXPERIMENTAL

All solutions were prepared from deionized waterand analytical reagent grade chemicals. The source of hydrogen ions was nitric acid. Potassium nitrate was used for the preparation of the solution and standardized compleximetrically.

To offset possible hydrolysis, dilute solutions of ferric nitrate were prepared daily and standardized as required. A O.IM stock solution of 1,10 phenanthroline was prepared by dissolving the appropriate amount in absolute ethanol. In all the kinetic runs, ortho-phenanthroline was taken in large excess in comparison to iron(III) and cobalt(II) so that the decrease in the concentration of the ligand through complex formation with iron(II) and cobalt(II) was negligible. The kinetic study was conducted with a Pye-Unicam Sp8-100 spectro-photometer equipped with kinetic facilities and fitted with a thermostated cell holder (± 0.1°c) and using 10 mm silica and quartz cells.

RESULTS

Products and Stoichiometry:

The product of the oxidation was confirmed to be ferroin. This was verified from the superimposable absorption spectra obtained with the product of the reaction and the complex prepared separately by mixing iron(II) and phenanthroline in stoichiometric ratio. Hence the course of the reaction was followed by measuring the optical density of the product ferroin at 510nm. Stoichiometry determination was achieved by mixing (5×10^{-5} M) of the iron(III) with (3×10^{-5} M) of cobalt(II) in the presence of phenanthroline (4×10^{-3}M) and H^+ (0.07M), thus reacting a known excess of iron(III) with cobalt(II). On completion of the reaction, the absorbance was found to be 0.33 which corresponds to 3×10^{-5}M of Fe^{+2}. This result indicated that one mole of Fe(III) reacted with one mole of cobalt(II).

KINETIC ORDERS

Kinetic runs were performed under the condition phen >> Co^{2+} > Fe^{3+} thus isolating the latter. To avoid any effect of light, the reactants were thermostated in dark 25 ml vessels. When thermal equilibrium has been achieved, the reaction was started by adding Fe^{3+} the last.

A plot of In (A_∞ - A_t) where A_∞ and A_t are the absorbances at infinity and at time t respectively, against time was linear suggesting a unity order with respect to Fe^{3+}. This result was further verified by the differential method where a plot of log rate against log concentration of Fe^{3+} gave a straight line of a slope of 0.97 ± 0.04.

The pseudo first order rate constant (k_1) referred to in this work was calculated from the slope of the straight line plot of (In A_∞ - A_t) against time under the conditions above. The order with respect to cobalt could be misleading if only integral method analysis was employed. The second order plot of $\frac{1}{a-x}$ vs. time (where a= [Fe(III)] = [Co (II)] = 5 x 10^{-5}M) was linear. Since the order with respect to Fe^{3+} was confirmed above to be unity, this suggests that the order with respect to cobalt was also unity. However the true picture was revealed from the differential method which showed that the order of cobalt changes with its concentration being 0.79 ± 0.019 at low concentrations and 0.30 ± 0.004 at higher concentrations. Figure (1). This change of order failed detection by the integral analysis where at low concentration of cobalt (5 x10^{-5}M) an overall order of nearly 1.8 fitted fairly well in a second order equation. This result is different from that used by using 2,2'-bipyridyl as the, ligand[3].

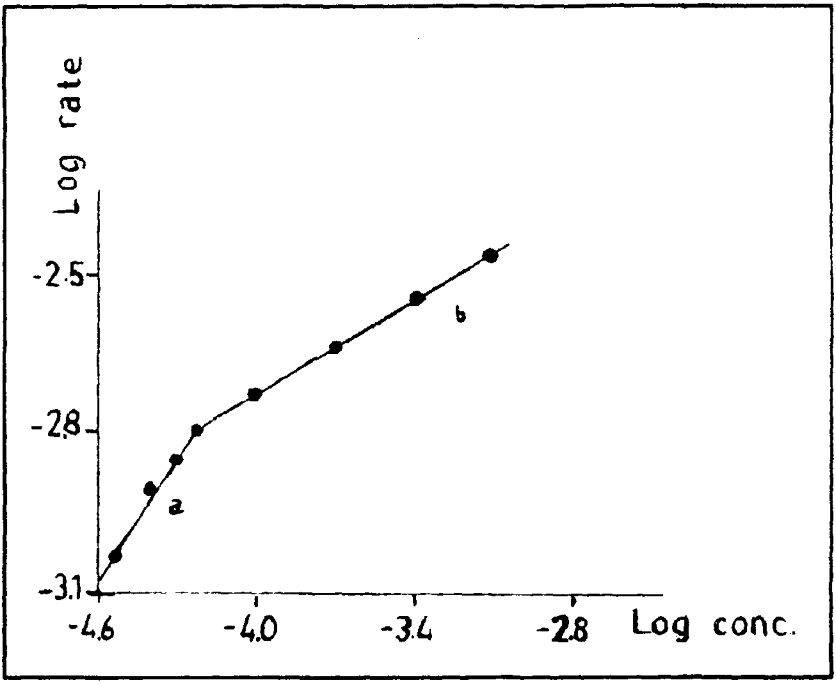

Figure 1 : A plot of log rate versus log concentration of $[Co^{2+}]$
$[Fe^{3+}] = 5 \times 10^{-5}M$, [phen] = 4 $10^{-3}M$.,
$[H^+] = 6.89 \times 10^{-2}M$, EtOH = 20% (V/V)
Temp. = 25°c.,
a. order = 0.79 ± 0.019
b. order = 0.30 ± 0.004

Effect of various reagents and parameters:

Inspection of Table (1) shows that phenanthroline accelarates the reaction while hydrogen ions have an inhibiting effect. All the work

Table (1): Effect of various reagents and parameters on reaction rate

<u>Second order conditions:</u>

Fe(III) = Co(II) = 5 x 10^{-5}M
EtOH = 20% (V/V) cell (glass)

<u>First order conditions :</u>

Fe(III) = 5 x 10^{-5}M
Co(II) = 5 x 10^{-4} M cell (glass)
EtOH = 20% (V/V) $\mu = 0.25$

Temp/°c	10^3 xk_1(S^{-1})	k ($M^{-1}S^{-1}$)	[phen x 10^3M]	[H^+ x 10^2M]
2.50		79	4.00	6.98
28.0		53	4.00	6.98
28.0		80**	4.00	6.98
34.0		28	4.00	6.98
34.0		40	8.00	6.98
34.0		65	12.00	6,98
34.0	4.1		4.00	6,98
34.0	5.0*		4.00	6,98
34.0	5.0**		4.00	6,98
34.0	1.6		4.00	19.00
34.0	0.5		4.00	25.06
34.0	0.6*		4.00	25.06

* Quartz cell
** (Adding Co^{2+} the last)

performed in this study applies when the reaction was started by adding Fe^{3+} the last. However when some runs are made by adding Co^{2+} the last different rates were obtained suggesting that the order of addition is crucial. Also the reaction seems to depend on the type of vessel for different rates are obtained by using glass and quartz cell. The effect of temperature showed that the second order rate constant decreases with increasing temperature.

DISCUSSION

It is believed that the active oxidising agent in this work is a 1:2 complex between Fe^{3+} and the ligand. This complex forms on direct mixing and has been reported in the literature[4]. This complex is different from ferriin where the latter cannot be obtained by direct reaction of Fe^{3+} and the ligand but only by the oxidation of ferroin.

Furthermore the use of the direct reaction complex in studying the kinetics of oxidation of organic compounds has been established in the literature[5-8] Milburn and Vosburgh[9] proved that Fe(III) does not dimerize if present at concentrations less than 1.0×10^{-3}M. Since the iron (III) concentration employed in the kinetic study is equal to 5×10^{-5} M then it is reasonable to assume that there is no appreciable dimerization occuring under the conditions of the investigation. Besides, the hydrolysis is suppressed since the ligand is present in large excess and the concentration of hydroxylated iron(III) could be neglected also in view of the low hydrolysis constant (3.1± 0.2). The greater oxidising ability of Fe(III) when mixed with 1,10 phenanthroline is presumable due to its stabilizing the lower valence state Fe(II) through back bonding with a consequent increase in the redox potential of Fe(III) / Fe(II) system. The catalysis by 1.10 phenanthroline may also be due to the possibility that electron transfer is facilitated by the π-electron system present in the ligand. In view of the above discussion and in the absence of dimerization and hydrolysis then the first s2tep in the mechanism should be the formation of the active oxidising agent complex which can be represented as thus.

$$Fe(aq)^{3+} + 2phenH^{+} \xrightleftharpoons{K_1} \underset{X}{Fe(phen)_2^{3+}} + 2H^{+}$$

Where phenanthroline exists in singly protonated form at high acid concentration as reported[10]. In view of the high stability constant of $Co(phen)_3^{2+}$ (log β = 16.02) it is then postulated that cobalt (II) exists mainly in the form $Co(phen)_3^{2+}$ which participates in the reaction. The rate-determining step in this mechanism is thought to be the attack of the active oxidising agent $Fe(phen)_2^{3+}(X)$ on the cobalt (II) species above.

On The basis of the above discussion the following mechanism is postulated.

$$Fe^{3+}(aq) + 2phen\ H^{+} \xrightleftharpoons{K} \underset{X}{Fe(phen)_2^{3+}} + 2H^{+}$$

$$\underset{X}{Fe(phen)_2^{3+}} + Co(phen)_3^{2+} \xrightarrow{k} Co(phen)_3^{3+} + Fe(phen)_2^{2+}$$

$$Fe(phen)_2^{2+} + H\ phen^{+} \xrightarrow{fast} Fe\ (phen)_3^{2+} + H^{+}$$

On the application of the equilibrium treatment the mechanism leads to the rate law

$$\frac{-d}{dt}[Fe(III)] = \frac{kK\,[Fe(III)]\,[Co(II)]\,[phen]^2}{[H^+]^2 + K\,[phen]^2}$$

This rate law accounts for the orders of unity with respect to Fe(III) and Co(II) at low concentrations of cobalt. It also accounts for inhibition by H^+ and accelaration by phenanthroline. The accurence of the $[phen]^2$ term in the rate law suggests that the active oxidising agent is a 1:2 complex between Fe^{3+} and the ligand 1,10 phenanthroline as described. The decrease of rate constant with temperature may be due to the decomposition of the active oxidising agent described in the mechanism at high temperatures. The decrease of order of cobalt at high concentrations may be due to the involvement of a side reaction which decreases the concentration of cobalt (II) such as adsorption. The extant of adsorption may differ in silica and quartz cells which reflect the different rates in these vessels. However, more work need to be made on this point before making any conclusions.

REFERENCES

1. F. Vydra and R. Pribil, Talanta., 3, 103 (1959).
2. F. Vydra and R. Pribil, Talanta., 5, 44 (1960).
3. K.V. Subbaiah, K. Srinivas and P.V. Subba Rao, Indian J. Chem., Sect. A. 20, 4, 399 (1981).
4. Jr. Gains, L.P. Hammett and G.H Walden, J. Amer. che. Soc.,58, 1668 (1936).
5. P.V. Subba Rao, B.A.N. Murty, R.V.S Murty and K.S. Murty, J. Ind. Chem. Soc., LV, 207 (1978).
6. M.S. Frank, A. Kodanda Ramaiah and P.V. Krishna Rao, Ind. J. Chem., 18 (A), 369 (1979).
7. A.S.P. Vittal, P.V. Krishna Rao, and K. Jagen Mohano Rao, Rxn Kin and Cat. Letters 23(1-2) 175 (1983).
8. P.V. Subba Rao. G.V. Saradamba and K. Rama Krishna. J. Indian Chem. Soc. L14, 463, (1987).
9. R.M. Milburn and W.C. Vosburgh, J. Amer. chem. Soc., 77, 1352 (1955).
10. Analytical applications of 1,10 phenanthroline and related compounds by Alfred A. Schilt Pergamon (1969) Page 3.