

SOLVENT INFLUENCE ON THE OXIDATION OF IRON (II) CITRATE COMPLEX BY MOLECULAR OXYGEN

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The oxidation of iron (II) citrate complex by molecular oxygen was investigated in aqueous acidic solutions of alcohols, e.g. methanol, ethanol and isopropanol. The reaction was first order in iron (II). It was found that the rate constant increases with the addition of alcohols to the aqueous solutions in the order: isopropanol > ethanol > methanol. The rate constant also increases with the increase of the percentage of alcohol. These effects are probably as a result of structural changes in the inner sphere of Fe (II). Activation parameters for all systems are reported.

Key words: Iron (II), Oxidation, Solvent.

INTRODUCTION

The oxidation of iron (II) by molecular oxygen in aqueous acidic and alkaline media has been extensively studied by many workers [1-5]. However, the study of solvent effects on such a reaction has received very little attention. Many studies dealing with the influence of changes of organic solvents on electron transfer reactions involving ions such as iron (II) and cobalt (II) with oxidizing agents other than oxygen have recently appeared in the literature [6-9]. These studies demonstrated that the reactions were strongly affected by the addition of organic solvents to the aqueous solutions and this was interpreted in most cases as being due to changes in the solvation of the coordination spheres of the reactant metal ions as well as the activated complexes.

The aim of this paper is to elucidate the effects of alcohols such as methanol, ethanol and isopropanol on the oxidation of iron (II) citrate by molecular oxygen in water-alcohol mixtures. The study of this reaction is of interest because of its relation to the biologically occurring reactions of oxygen carriers containing iron (II) such as hemoglobin [10]. Moreover, the Fe-citrate complex is related to the aconitase (citrate (isocitrate) hydrolyase) which is the Krebs cycle enzyme which requires Fe (II) for the activation of its catalytic activity (11).

EXPERIMENTAL

Reagent grade chemicals and redistilled water were used throughout. All solutions were isothermal before they

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were mixed in each experiment. An air thermostat was used. The iron (II) citrate complex was prepared in solution by mixing ferrous ammonium sulphate with trisodium citrate in the ratio of 1:5. Precalculated amounts of redistilled water and alcohol was added to bring the concentration of the complex to 0.001 M. The pH of the reaction mixtures was maintained at 5.0 by a citric acid-sodium citrate buffer which was essential in studying the solvent effects on the reaction rate by preventing the change of $[H^+]$ during the oxidation process, because the oxidation of iron (II) is quite sensitive to $[H^+]$. The present work as well as the previous work showed that oxygen concentration affects the rate of oxidation of iron (II) complexes. For this reason all experiments were carried out in an open bottle with constant stirring in order to replace the consumed oxygen during the reaction. The oxidation of iron(II) complex was followed by determining the amount of iron (III) produced after different intervals as follows. Aliquots of the reaction mixture at certain calculated times were transferred into a brown bottle containing 5 ml of 6N H_2SO_4 to lower the pH in order to stop the oxidation process of iron (II). Then, an excess amount of 0.1 M NH_4SCN was added. The concentration of the red $Fe^{III}(SCN)_6^{3-}$ ion complex was determined spectrophotometrically.

RESULTS AND DISCUSSION

The rate of the oxidation of iron(II) citrate by molecular oxygen at constant pH of 5.0 were measured in various alcohol water mixtures. The reaction was first order in iron (II). The concentration of oxygen was kept fixed during the course of reaction as described previously in the

experimental section. The second-order rate constant, K_2 , values for each system were calculated, $K_2 = K_1/[O_2]$, where K_1 is the pseudo-first order rate constant. However, the reaction in the different water-alcohol systems has three main features. Firstly, the value of the rate constant, K_2 , increases with the addition of alcohols as given in Table 1 and represented in Fig. 1 for reactions at 30° .

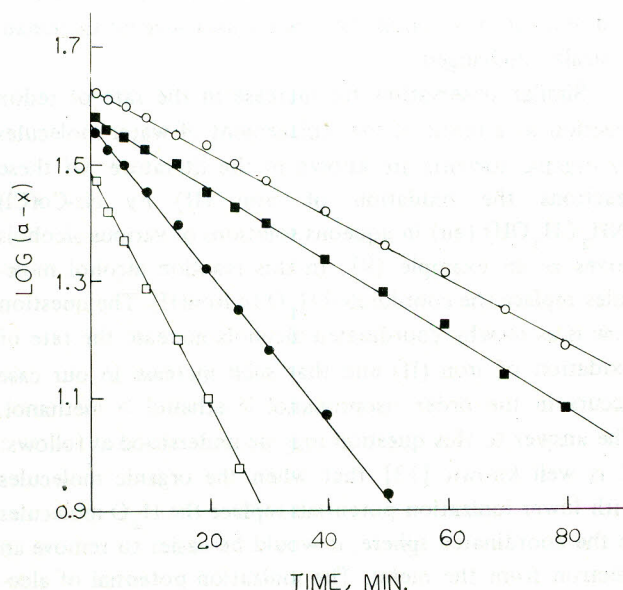


Fig. 1. Pseudo-first-order plots of the oxidation of iron(II) citrate in water-alcohol mixtures (4.29M alcohol) at $30^\circ \pm 0.1$. \circ : no alcohol, \blacksquare : methanol, \bullet : ethanol, \square : isopropanol.

Table 1. Rate constant and activation parameters for the oxidation of iron (II) citrate with O_2 in water-alcohol mixtures at $30^\circ \pm 0.1$

Alcohol	Rate constant, $K_2, M^{-1} \text{Min}^{-1}$	ΔE^* Kj mol^{-1}	ΔH^* Kj mol^{-1}	ΔS^* $\text{J k}^{-1} \text{mol}^{-1}$
25% (v/v)				
No alcohol	12.86	53.6	51.1	-80.9
Methanol	25.89	59.3	56.8	-56.3
Ethanol	28.09	63.0	60.6	-42.9
Isopropanol	31.14	82.3	79.7	+21.1
4.29 M				
No alcohol	12.86	53.6	51.1	-80.9
Methanol	14.60	62.3	59.9	-41.6
Ethanol	28.09	63.0	60.6	-42.9
Isopropanol	34.60	65.06	62.55	+33.1

Such an increase in the K_2 values goes parallel with the increase of the number of carbon atoms of the alcohols: isopropanol > ethanol > methanol > H_2O .

Secondly, the values of the rate constant, K_2 , increase with increase in the mole fraction of the added alcohol of the same type as given for methanol in Table 2 and represented in Fig. 2. The rate of reaction increases with rise in temperature.

Any comment on the data in Tables 1 and 2 must take into account the complexity of such a system and the difficulties involved in interpreting the data. The rate constant, K_2 , has a minimum value in the absence of any alcohol and a maximum value in presence of isopropanol. Addition of alcohol to water increases the rate constant between 15 and 100%. The presence of alcohol in the system appear to favour the rate determining step and makes it relatively quicker. A definite mechanism does not seem to be at present clear. However, the effects of alcohol on the rate of oxidation of iron (II) citrate complex by molecular oxygen could be treated in the light of the following factors:

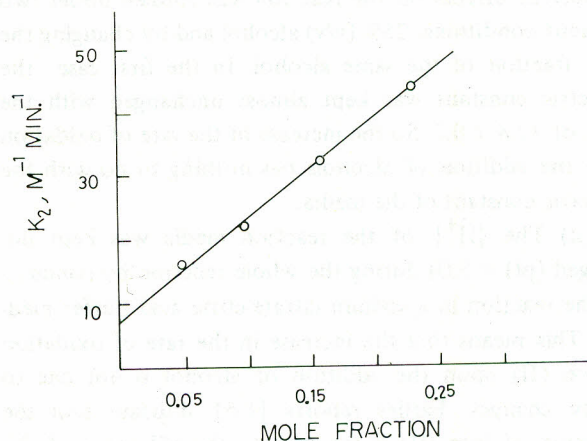


Fig. 2. Plots of the second-order rate constant of the oxidation of iron(II) citrate in aqueous solutions of methanol vs. mole fraction of methanol at $30^\circ \pm 0.1$.

Table 2. Rate constants for the oxidation of iron (II) citrate in water-methanol mixture at different fractions of methanol at $30^\circ \pm 0.1$

Mole fraction of methanol	Rate constant, $K_2, M^{-1} \text{Min}^{-1}$
0.047	16.45
0.100	21.93
0.160	32.16
0.228	43.87

Table 3. Rate constants for the oxidation of iron(II) citrate in aqueous solution of alcohols and alcohol basicity at 30°.

Alcohol	Rate constant, K_2 , $M^{-1} \text{ Min.}^{-1}$		
	25% (v/v) alcohol	Alcohol = 4.29 M	Basicity [@]
Methanol	25.89	14.60	0.60
Ethanol	28.09	28.09	0.77
Isopropanol	31.14	34.60	0.92

@: refs. 15 - 16.

(i) The macroscopic dielectric constant of the medium. It is well known [12] that the macroscopic dielectric constant of the reaction medium decreases with increase in the alcohol's content and the free energy due to coulombic repulsion for the electron transfer reaction would increase with decrease in the macroscopic dielectric constant. This will ease the oxidation process. In our case the solvent effects on the reaction was studied under two different conditions: 25% (v/v) alcohol and by changing the mole fraction of the same alcohol. In the first case the dielectric constant was kept almost unchanged with the value of 72.8 ± 0.7 . So the increase of the rate of oxidation upon the addition of alcohols has nothing to do with the dielectric constant of the media.

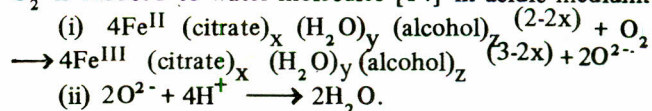
(ii) The $[H^+]$ of the reaction media was kept unchanged (pH = 5.0) during the whole reaction by conducting the reaction in a sodium citrate-citric acid buffer medium. This means that the increase in the rate of oxidation of iron (II) upon the addition of alcohol is not due to acidity changes. Earlier reports [1-5] indicate that the oxidation of iron (II) is sensitive to the pH value of the medium.

(iii) The change in the first coordination sphere of iron (II) would probably be the main reason for the increase in the rate of oxidation of iron (II). This would occur by replacing H_2O molecules by alcohols. This conclusion seems to agree with the thermodynamic parameters of the reaction given in Table 1. The values of ΔS^* with the exception of isopropanol solutions bear a -ve sign. A maximum entropy decrease is noted for purely aqueous media. A possible suggestion would be to assume partial solvation of the iron(II) species. Addition of alcohols affects the solvated species by releasing some of the bound water molecules to the iron(II) species. Such tendency reaches maximum in presence of isopropanol. Entropy changes for methanol and ethanol solvent mixtures are of

the same order of magnitude suggesting a similar behaviour for the system. Addition of isopropanol introduces a structural change which affects the solvation by water molecules and changes the ΔS^* sign. The energy of activation has a positive sign. This suggests that the process is indeed endothermic. Their order of magnitude is merely the same (Table 1), particularly for the reactions of the same concentration of alcohol (4.29 M). This suggests that in presence and absence of alcohols, the mechanism seemed to remain basically unchanged.

Similar observation for increase in the rate of redox reaction as a result of the replacement of water molecules by organic solvents are known in the literature. Of these reactions the oxidation of iron (II) by *cis*-Co(Cl)(NH_2CH_2OH) (en) in aqueous solutions of various alcohols serves as an example [9]. In this reaction alcohol molecules replace the coordinated H_2O to iron(II). The question now is as to why coordinated alcohols increase the rate of oxidation of iron (II) and that such increase in our case occurs in the order: isopropanol > ethanol > methanol. The answer to this question may be understood as follows: It is well known [13] that when the organic molecules with lower ionization potentials replace the H_2O molecules in the coordinated sphere, it would be easier to remove an electron from the metal. The ionization potential of alcohols decreases with increase in the number of carbon atoms and this goes quite well with the fact that the basicity of alcohols increases with an increase in the number of carbon atoms (i.e. in our case in the direction from methanol to isopropanol) in the same order as that of the rate constant as given in Table 3. Since the basicity of the ligand is a measure of its δ -donor properties to the metal ion, the increase of such δ -donation power from the alcohol would increase the electron density on the iron (II) and hence facilitate electron transfer from the metal ion to molecular oxygen.

From the foregoing discussion, in the acidified water-alcohol mixture, the main species of iron(II) may be present as $Fe^{II}(\text{citrate})_x(H_2O)_y(\text{alcohol})_z(2-2x)$. The overall reaction mechanism may be given on the basis that O_2 is reduced to water molecules [14] in acidic medium:



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spontaneous... the 10th week after flowering for... weight and then the 15th the 16th week after flowering for... for C. citrifolia... The amount and composition of... were prepared by the procedure used by M. E. Fisher [5]. The... and oils were extracted separately from... seeds of given maturity stage of the fruit species by... in a two volume of methanol for 2 min using a... The fruit was dried and the litter was saved. The litter... was separated in two volumes of acetone/benzene... and filtered. The residue was washed with two... volumes of acetone/benzene (1:1) mixture and discarded. The... were then washed... to another separator funnel and dried with... volume of ethyl ether and two volumes of water. The... after the formation of a clear phase. The... was withdrawn and discarded. The ether phase was... with an equal volume of water. The... phase was washed by pouring several... times with one volume portion of water. The ether and... were contained, dried with... and distilled under pressure to leave the oil... The residue was weighed and... in which... was added to remove any traces of water... and the... were... in 100-200 ml of... and...

INTRODUCTION

In earlier studies the seed oil of Citrus sp. have been... to elucidate their structure [1]. The... of Citrus... and... have been studied for determining the... and... in their... and... are among the... and... are frequently determined in... In general they are significant because of their... and the... in the... and... [2]. The... of the... are used as... it was necessary not only to know their... but also the amount of... and... Therefore, there is a... and... relationship... The... of seeds. The... from the... to the... while... the... of... However, the... of... increased with the maturity of... seeds at the... stage.

MATERIALS AND METHODS

Four... (Green... and... also seed samples were... from the... of... Laboratory, Faculty... and...