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SOLVENT EFFECTS OF THE OXIDATION OF IRON (II) - TARTRATE COMPLEX BY MOLECULAR OXYGEN IN AQUEOUS SOLUTIONS OF ALCOHOLS

By
E.M. NOUR,* H.M. KILLA**, M. ZAKY** and S.A. SADEEK**

**Department of Chemistry, Qatar University, Qatar.*

***Department of Chemistry, Faculty of Science,*
Zagazig University, Zagazig, Egypt.

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ABSTRACT

The solvent effects on the oxidation of Fe(II)-tartrate by molecular oxygen have been investigated in aqueous acidic solutions of alcohols such as methanol, ethanol, isopropanol and t-butanol. The second-order rate constant of the oxidation increases with the addition of alcohols to the aqueous solutions. The rate constant values at 27.5+ 0.1°C are 0.245 M^{-1} sec^{-1} in the absence of alcohols, 0.266, 0.280, 0.344 and 0.393 M^{-1} sec^{-1} in the presence of 10% (V/V) methanol, ethanol, isopropanol and t-butanol, respectively. The rate constant also increases with the increase of the percentage of alcohols. Activation parameters for all systems are evaluated. The effect of solvent on the oxidation of Fe(II) is understood on the basis of replacement of water molecules coordinated to Fe(II) by the alcohol molecules and that the increase of the basicity of the alcohol increases the rate of oxidation of Fe(II).

INTRODUCTION

The reactions between molecular oxygen and Fe(II)-complexes are of interest. This is because of their relation to the reaction of molecular oxygen with the transport proteins contain Fe(II), such as haemoglobin (Khan and Martell, 1974). Previous laboratory investigation on the oxidation of several Fe(II) compounds by molecular oxygen indicated that the rate of oxidation is increased by an increase of pH and by the presence of complexing agents (George, 1954; Cher and Davidson, 1955 and King and Davidson, 1958). Most of these reactions were carried out in aqueous acidic or alkaline solutions. Little attention was directed towards the effect of organic solvents on the rate of oxidation of Fe(II) complexes by molecular oxygen. However, solvent effects on the rate of oxidation of Fe(II) by other oxidizing agents are reported in the literature, for example, the oxidation of Fe(II) by $S_2O_8^{2-}$ in binary solvents (Blandamer et al 1980) and the oxidation of Fe(II) in Fe(II)-Fe(III) and in Fe(II)-Co(III) systems (Wada, 1971; Ohashi et al, 1971 and Ohashi et al, 1972). The rates of these reactions are strongly effected by the addition of organic solvents to the aqueous solutions.

Recently, (Hester and Nour, 1981), Raman spectroscopy has been used to study the effect of solvent on the oxidation of Co(III) complexes with O_2 the study indicated that both σ and π donor properties of the solvent play an important role in the oxygenation process. In this connection the present study is to examine the solvent effects on the rate of electron transfer in the oxidation of Fe(II) by molecular oxygen in the presence of tartrate ligand in water mixed with alcohols at constant value of pH.

EXPERIMENTAL

Reagent grade chemicals and redistilled water were used throughout. All solutions were used within a few days of preparation. The solutions of ammonium iron (II)-sulphate were standardised using $K_2Cr_2O_7$. Fe(II)-tartrate complex was prepared in solutions by mixing Analar ammonium iron (II)-sulphate with disodium tartrate in a ratio of 1:5. Precalculated amounts of redistilled water and alcohol were added. The pH of the reaction mixtures was maintained at a value of 5.10 using H_2S0_4 or NaOH. These conditions produce a buffer medium of sodium tartrate-tartaric acid. This buffer medium was very essential in studying the solvent effects on the reaction rate by preventing the change of $[H^+]$ during the oxidation process, since the oxidation of Fe(II) is very sensitive to $[H^+]$.

The temperatures of all solutions were brought to that of the experiment concerned before mixing. An air thermostat was used for this purpose. Aliquots of the reaction mixture were transferred after different time intervals, each into a flask containing 5 ml of 3M H_2SO_4 to lower the pH in order to completely stop the oxidation process at the desired time. Then the amounts of iron (III) produced from the oxidation were determined spectrophotometrically in the form of $[Fe(SCN)_6]^{3-}$ at 450 nm using a Beckman model 24-25 instrument. All experiments were carried out in amber glass bottles to eliminate the effect of light.

RESULTS AND DISCUSSION

The oxidation of Fe(II)-tartrate follows the pseudo-first order equation with respect to Fe(II) and it proceeds to completion. Early studies in aqueous solutions suggested the simple rate equation:

$$\frac{-d[Fe(II)]}{dt} = K_2\,[Fe(II)][O_2]$$

It was accepted that a similar rate equation is obeyed in water-alcohol mixtures. The second-order rate constant, K_2, was calculated according to the equation: $K_2 = K_1/[O_2]$, where K_1 is the pseudo-first order rate constant and $[O_2]$represents the concentration of oxygen. The pseudo-first order plots for the Fe(II)-tartrate oxidation by molecular oxygen in water and in water-alcohol mixture are shown in Figure 1. The values of the rate constants, K_2, of the oxidation of Fe(II)-tartrate increase with the addition of alcohols as shown in Table 1. Such increase in the rate constant values is parallel with the increase of carbon atoms of the alcohols; t-butanol > isopropanol > ethanol > methanol. Table 2, represents the temperature dependence of the oxidation of Fe(II). The values of the activation enthalpy, ΔH^*, for the oxidation in the different water-alcohol mixtures show strong dependence in the same directions of K_2 while the activation entropy, ΔS^*, does not show the same dependence as given in Table 1. Similar trends for the activation parameters were reported for other related redox systems (Mathews and Watts, 1976 and Ohashi et al 1972). The dependence of the second-order rate constant, K_2, for the oxidation of Fe(II) on the mole fraction of alcohol is given in Table 3, for the methanol as an example. This is represented in Figure 2. The data demonstrate that the rate constant increases with the increase of the mole fraction of methanol.

Table 1
The rate constants and activation Parameters for the oxidation of Fe(II)-tartrate with O_2 in water-alcohol mixtures at 27.5 + 0.1C.

10% (v/v) alcohol	**(a) Rate constant x10² M⁻¹Sec⁻¹**	**ΔE* K J mol⁻¹**	**ΔH* K J mol⁻¹**	**ΔS* J K⁻¹ mol⁻¹**
no alcohol	24.53	33.80	31.30	—110.11
methanol	26.64	35.95	33.45	—136.32
ethanol	28.02	47.64	45.14	—96.97
isopropanal	34.35	50.92	48.43	—256.60
t-butanol	39.31	58.42	55.92	—278.46

(a)$[Fe^{II}]$= $1x10^{-3}$M, μ = 0.04, pH = 5.10

Table 2
Temperature dependence of the rate constant of the oxidation of Iron (11)-tartrate in water-alcohol mixtures (10% (v/v) alcohol)

Temp.±0.1°C	**Rate Constant^a M⁻¹ Sec⁻¹ X10²**				
	no alcohol	**methanol**	**ethanol**	**Isopropanol**	**t-butanol**
20.0	15.77	16.43	17.10	20.37	21.50
27.5	24.53	26.64	28.02	34.35	39.31
35.0	32.25	34.80	43.48	59.10	66.33
42.5	43.73	49.47	66.49	87.30	113.66

(a) :$[Fe^{II}]$= $1X10^{-3}$ M, μ = 0.04, pH = 5.10

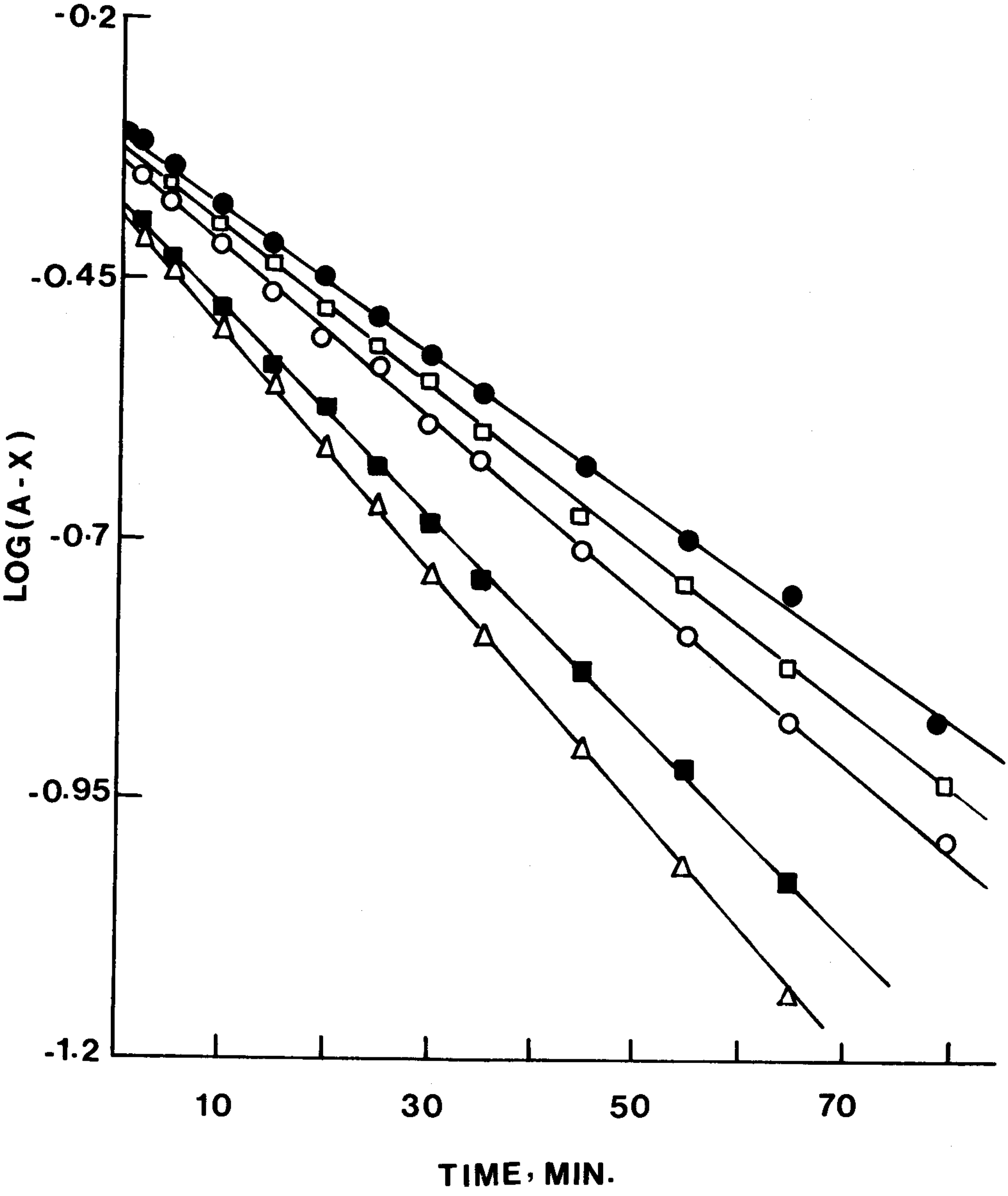

Figure 1. Pesudo - First-order Plots of the oxidation of Fe(II)-tartrate in water-alcohol mixtures 10% (v/v) at 27.5 ± 0.1°C.
● : no alcohol, □ : methanol, ○ - ethanol, ■ : isopropanol, △ : t-butanol.

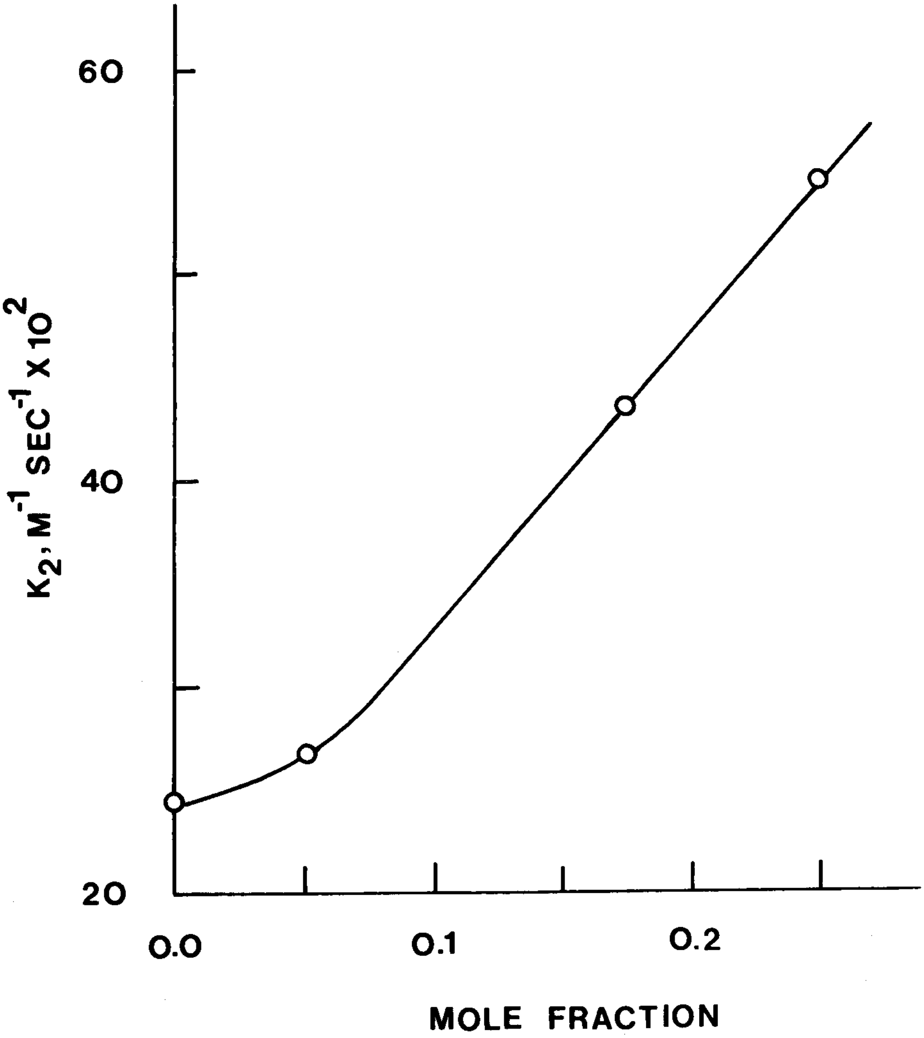

Figure 2. The Plots of the second - order rate constant of the oxidation of Fe (II)-tartrate in aqueous solution of methanol vs. mole fraction of methanol at 27.5 ± 0.1°C.

Table 3

The rate constants for the oxidation of Fe(II) -tartrate in water - methanol mixture at different mole fractions of methanol at 27.5 ± 0.1°C.

Mole fraction of methanol	**(a) Rate-constant $X10^2\ M^{-1}Sec^{-1}$**
0	24.53
0.053	26.64
0.177	43.48
0.250	54.35

(a) $[Fe^{II}] = 1X10^{-3}M$, $\mu = 0.04$, pH = 5.10.

The increase of the rate of oxidation of Fe(II) by O_2 upon the addition of alcohols to the aqueous solution may be understood by taking into consideration the following points. It is well established that the macroscopic dielectric costant of the reaction medium decrease with the increase of the content of alcohols and the free energy due to the coulombic repulsion for the electron transfer reaction would increase with the decrease in the macroscopic dielectric constant assuming that the same ionic species are present in the medium (Ohashi, 1971). In the case of our reaction the dielectric constant of the medium containing 10% (V/V) alcohol was kept almost unchanged with value 73.4 ± 0.5 so, the increase of the oxidation rate of Fe (II)-tartrate upon the addition of alcohols in the order : t-butanol > isopropanol > ehtanol > methanol is not dependent upon the value of the dielectric constant of the reaction medium. However, the fact that the rate of oxidation Fe(II) is essentially dependent of the $[H^+]$ seem to indicate that the marked increase in the rate with the addition of alcohol could be due mainly to an altration of the effective hydrogen ion concentration in the media because of the addition of alcohols to aqueous solutions. The possibility was also ruled out because all of the the reactions of Fe(II) were carried out in buffer medium of sodium tartrate-tartaric acid with constant pH of 5.10 during the course of the reation.

Now, we conclude that the increase of the rate of oxidation of Fe(II)-tartrate by molecular oxygen in water-alcohol mixtures can not be due to change in either the dielectric constant or the $[H^+]$ of the reaction medium. However, the increase of the rate of oxidation could be due to the change in the coordination sphere of Fe(II) by replacing the water molecules by the alcohols. This was concluded on the basis that the position of the absorption peaks of Fe(III)-tartrate undergo no significant changes upon the addition of alcohols to the aqueous media, and the fact that the molar extinction coefficient changes with the addition of alcohols. It increases with the increase of the molar ratio of alcohol as shown in Figure 3, in the case of methanol as an example. This suggests that some of the water molecules coordinated to Fe(II) may be replaced by the alcohol molecules. Similar observations were reported in the literature for other redox systems involve two metal ions. For example in the oxidation of Fe(II) by Fe(III) compounds the species $Fe(H_2O)_{6-n}(OS)_n^2$, where OS = solvent, was suggested to be formed (Wada et al, 1971 and Wadw et al). In the oxidation of Fe(II) by cis-Co(Cl)-($NH_2CH_2CH_2OH$)(en) species in aqueous solutions of various alcohols, the increase of the rate of oxidation upon the addition of alcohols was observed and it was concluded that the replacement of water molecules coordinated to Fe(II) by alcohols occured (Ohashi et al., 1971).

However, it was reported (Ohashi, 1971) that when organic molecules with lower ionization potentials replaced the H_2O molecules in the coordination sphere, it would be easier to remove an electron from the metal.

This agrees quite well with our observations, as we mentioned earlier in the text, that the rate of oxidation of Fe(II) in the presence of alcohols increases in the order: t-butanol > isopropanol > ethanol > methanol, and this accordingly is attributed to the fact that the ionization potential of the coordinated alcohol decrease with the increase of the number of carbon atoms. This also agrees with the fact that the basicity of the alcohol (Antonious, 1982) increases in the direction from methanol to t-butanol in the same order as that of the rate constant as shown in Figure 4. Since the basicity of the ligand is a measure of it's o - donor properties to the metal ion, the increase of such o-donation from the alcohol would increase the electron density on the Fe(II). This is expected to decrease the oxidation potential of the metal ion and so the electron transfer from Fe(II) to O_2. A similar conclusion was reported (Hester and Nour, 1981) for the oxidation of Co(II)-complexes by O_2 in different organic solvents.

Finally, we conclude that the change of the coordination sphere of Fe(II) upon the addition of alcohols and the higher basicities of alcohols compared with that of water are the main reason for the increase of the rate of oxidation of Fe(II) in water-alcohol mixtures. Accordingly, in the acidified Water-alcohol mixture, the main species of Fe(II) may be present as;

$Fe(tart.)_X(H_2O)_Y(alcoh)_Z^{(2-2x)}$

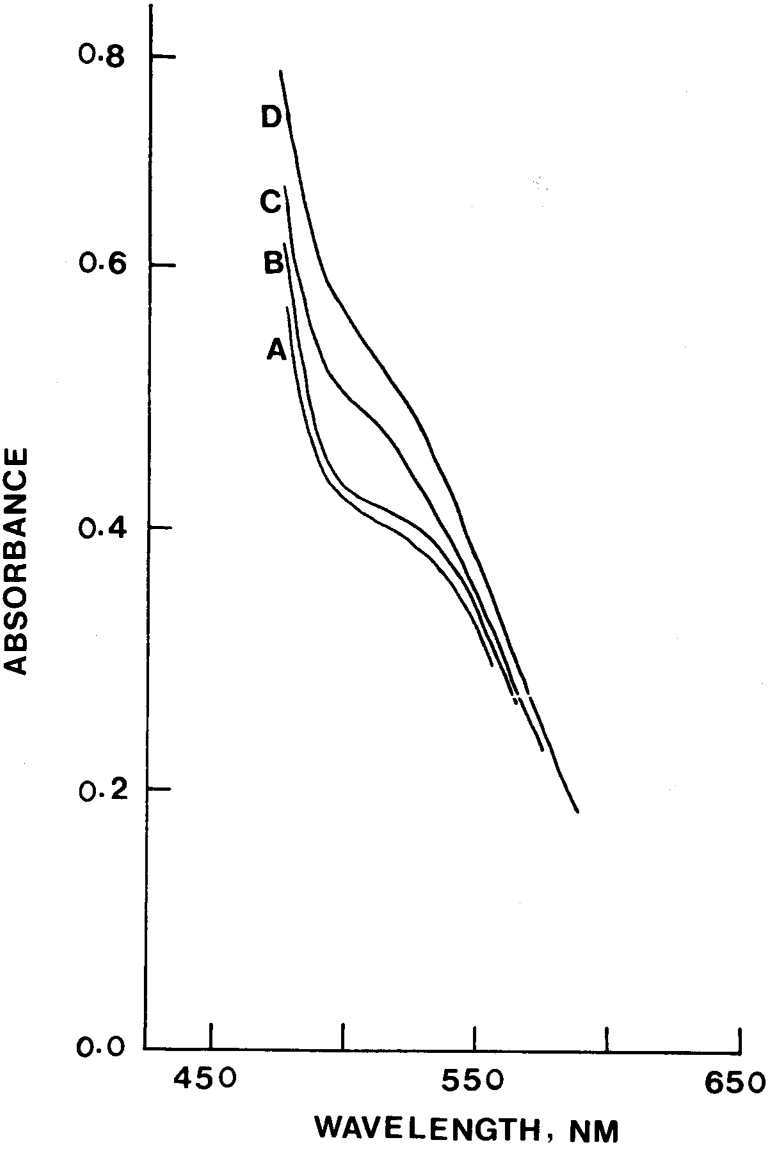

Figure 3. Absorption spectra of Fe (III) - tartrate in aqueous solution of methanol [Fe (III)]= 3 × 10^{-4}M.

a : aqueous solution
b : 0.053 mole fraction of methanol
c : 0.177 mole fraction of methanol
d : 0.250 mole fraction of methanol.

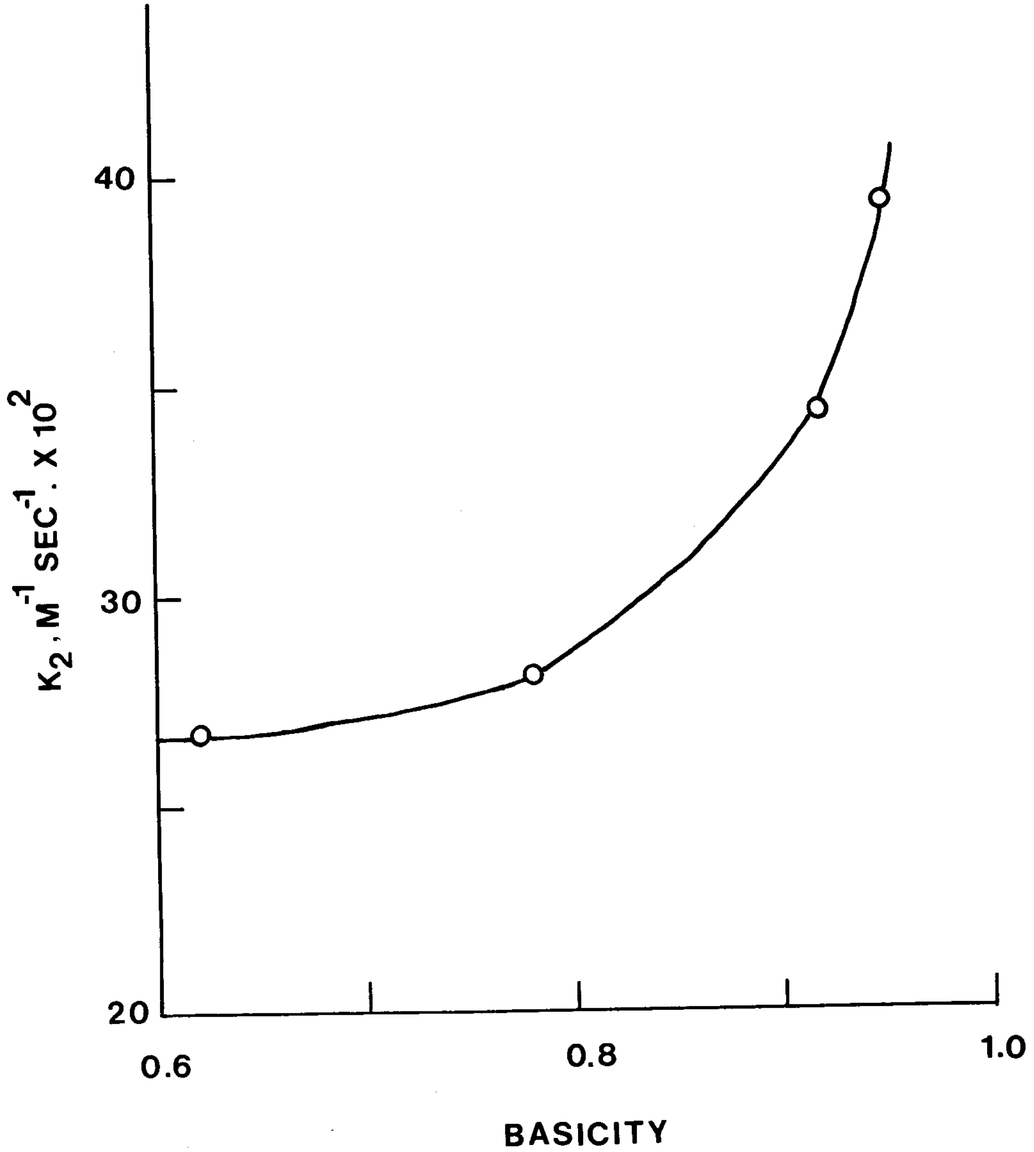

Figure 4. The plots of the second - order rate constant of the oxidation of Fe (11) - tartrate in aqueous solution of alcohols 10 % (v/v) vs. basicities of alcohols at 27.5 ± 0.1C.

Taking into consideration the reported mechanism (King and Davidson, 1958) for the oxidation of Fe(II)-complexes by O_2 in aqueous acidic media, the reaction in our case may be given by:

$$Fe^{II}(tart.)_X(H_2O)_Y(Alcoh.)_Z{}^{(2-2X)}+O_2$$

$$\rightarrow Fe^{III}(tart.)_X(H_2O)_Y(Alcoh.)_Z{}^{(3-2X)}+O_2{}^-$$

$$O_2{}^- + H^+ \rightleftharpoons HO_2.$$

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تأثير المذيبات على تاكسد متراكب الطرطرات للحديد الثنائي التكافؤ بواسطة الأكسجين في المحاليل المائية للكحولات

المتولي نور ـ حمادة كيلة ـ منير زكي ـ صديق عطية

تم دراسة تاكسد متراكب الطرطرات للحديد الثنائي في وسط مائي وفي وجود كحولات مثل الكحول الميثيلي والايثيلي والايزوبروبيلي وكذلك البيوتيلي الثلثي ونظراً لقدرة الطرطرات العالية كمحلول منظم فقد امكن دراسة التفاعل عند اس ـ هيدروجيني ثابت قيمة ٥ .

وقد وجد ان التفاعل هو من تفاعلات الرتبة الأولى بالنسبة للحديد كما وان ثابت التفاعل يزداد باضافة الكحولات إلى الوسط المائي وكذلك بزيادة تركيز الكحول المضاف وقد تبين ان الزيادة لثابت التفاعل تتمشى والزيادة في عدد ذرات الكربون للكحولات : البيوتيلي الثلثي > الايزوبروبيلي > الايثيلي > الميثيلي . وقد عينت قيم طاقة التنشيط وكذلك قيم انتروبي التنشيط للتفاعل في غياب وفي وجود الكحولات المختلفة .

ومن النتائج قد استنتج ان زيادة معدل التاكسد للحديد الثنائي في وجود الكحولات يرجع أساساً إلى احلال لجزئيات الماء بجزئيات الكحولات في متراكب الحديد وكذلك إلى زيادة القاعدية للكحولات بمقارنتها بالماء .