

Kinetic Studies of the Oxidation of Maleic and Fumaric Acids by Fenton's Reagent

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ABSTRACT. The kinetics and mechanism of the oxidation of maleic and fumaric acids by hydrogen peroxide in the presence of ferrous sulphate has been studied. The oxidation rate of fumaric acid is faster than that of maleic acid. The reaction is first order with respect to maleic acid or fumaric acid and first order with respect to ferrous sulphate but zero order with respect to hydrogen peroxide. The energies of activation have been calculated to be 24.36 and 38.29 kJ mol⁻¹ for maleic and fumaric acids, respectively. A reaction mechanism has also been proposed.

The combination of hydrogen peroxide and ferrous salt is frequently referred to as Fenton's reagent. It has been well established (Walling 1975) that the action of ferrous sulphate on hydrogen peroxide in acidic aqueous solution brings about the formation of hydroxyl radicals:



The Fenton's reagent has been used in the initiation of vinyl polymerisation, in the oxidation of alcohols (Merz and Water 1949, Walling and El-Taliawi 1973). Recently, we have studied the kinetics of the deamination of amino acids by this reagent (Ashraf *et al.* 1980, Ahmad *et al.* 1982). A survey of the literature (Nofre *et al.* 1964) indicates that the products have been identified for the oxidation of maleic and fumaric acids by hydrogen peroxide in the presence of ferrous sulphate as catalyst.

Experimental

All the chemicals used were of Analar (B.D.H.) grade. The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate solution. The concentration of hydrogen peroxide in kinetic runs was measured colorimetrically as described elsewhere (Reichert *et al.* 1939). Measured quantities of maleic acid or fumaric acid, ferrous sulphate, perchloric acid, sodium perchlorate (to maintain ionic strength) and distilled water were taken in a stoppered round bottom flask and placed in thermostated water bath at $40 \pm 0.1^\circ\text{C}$ unless mentioned otherwise. After the reactants had reached thermostated temperature, the reaction was started by addition of temperature equilibrated hydrogen peroxide. The kinetics were followed by examining 5 cm^3 aliquots of the reaction mixture for hydrogen peroxide content. The aliquots were added to 5 cm^3 of titanium sulphate solution to stop the reaction. Optical density was measured at 420 nm, and the concentration of hydrogen peroxide was read from the calibration graph.

Identification of Products

For the identification of products the reaction mixture, in which the concentrations of all the reagents were ten times those reported in Table 1, were heated at 60°C for about six hr. The reaction mixture was treated with acidified 2,4-dinitrophenylhydrazine solution which yielded a hydrazone. The IR spectrum of the hydrazones obtained from the reaction mixture of maleic acid and fumaric acid

Table 1. Variation of rate with hydrogen peroxide concentration.

$[\text{HClO}_4] = 1.50 \times 10^{-2}\text{ M}; [\text{FeSO}_4] = 5.00 \times 10^{-4}\text{ M}; \text{Temp.}, 40^\circ\text{C}$				
Maleic acid			Fumaric acid	
$[\text{H}_2\text{O}_2] \times 10^3$ (M)	$k_{\text{obsd}} \times 10^7$ ($\text{mol l}^{-1}\text{sec}^{-1}$)	$k' \times 10^2$	$k_{\text{obsd}} \times 10^7$ ($\text{mol l}^{-1}\text{sec}^{-1}$)	$k' \times 10^2$
3.00	4.33	1.73	6.76	2.12
3.50	4.38	1.75	6.80	2.16
4.00	4.45	1.78	6.67	2.12
4.50	4.38	1.75	6.80	2.16
5.00	4.45	1.78	6.78	2.15
$k' = (1.76 \pm 0.019) \times 10^{-2}$			$k' = (2.14 \pm 0.018) \times 10^{-2}$	
$[\text{Maleic acid}] = 5.00 \times 10^{-2}\text{ M}; [\text{Fumaric acid}] = 6.30 \times 10^{-2}\text{ M}$				

were superimposed on the spectrum of a corresponding hydrazone of the product obtained by the oxidation of tartaric acid with Fenton's reagent (Fenton 1896). The melting points of these hydrazones were also the same, *i.e.* 182°C. The mixed melting point did not show any depression. Thus, the presence of hydroxyoxaloacetic acid is confirmed. Moreover, the reaction mixture gave a violet colour with the addition of ferric chloride in excess alkali for both maleic and fumaric acids, which confirms the presence of hydroxyoxaloacetic acid (Fenton 1896).

Results and Discussion

The progress of the reaction was observed by measuring the disappearance of hydrogen peroxide in the presence of high concentration of maleic acid or fumaric acid. Trial and error plots of the rate data for runs indicate that the reaction is zero order in hydrogen peroxide. The plot of concentration of hydrogen peroxide versus time was a straight line, and its slope yields k_{obsd} . The pseudo-zero-order rate constants (k_{obsd}) were found to be independent of the concentration of hydrogen peroxide. The results are summarised in Table 1.

The order of the reaction with respect to catalyst (ferrous sulphate) was determined by varying its concentration and keeping other variables constant. The plot of k_{obsd} against the concentration of ferrous sulphate was a straight line (Fig. 1)

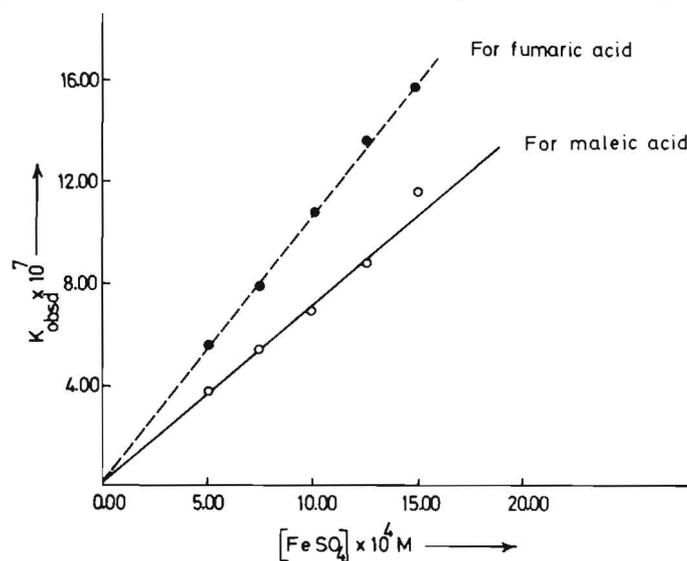


Fig. 1. Variation of rate with the concentration of ferrous sulphate

- For fumaric acid ○ For maleic acid
- [HClO₄] in fumaric acid = 1.50×10^{-2} M
- [HClO₄] in maleic acid = 1.80×10^{-2} M
- [Maleic acid] = [Fumaric acid] = 5.00×10^{-2} M

Table 2. Variation of rate with substrate concentration.

$[\text{H}_2\text{O}_2] = 4.50 \times 10^{-3} \text{ M}; [\text{FeSO}_4] = 5.00 \times 10^{-4} \text{ M}; \text{Temp.}, 40^\circ\text{C}$			
[Maleic acid] $\times 10^2$ (M)	$k_{\text{obsd}} \times 10^7$ (mol $l^{-1}\text{sec}^{-1}$)	[Fumaric acid] $\times 10^2$ (M)	$k_{\text{obsd}} \times 10^7$ (mol $l^{-1}\text{sec}^{-1}$)
5.00	3.75	5.40	5.55
7.50	5.53	5.85	5.83
10.00	7.08	6.30	6.25
12.50	9.00	6.75	6.72
15.00	10.71	7.20	7.08

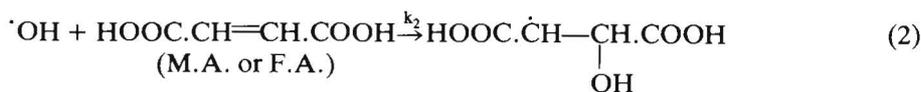
$[\text{HClO}_4]$ in maleic acid = $1.80 \times 10^{-2} \text{ M}$; $[\text{HClO}_4]$ in fumaric acid = $1.75 \times 10^{-2} \text{ M}$

which passes through the origin for both maleic and fumaric acids. This shows first order dependence of rate on catalyst concentration and it also confirms that there is no reaction in the absence of ferrous sulphate. k_{obsd} is directly proportional to the concentration of substrate (maleic acid or fumaric acid). This is indicative of first order dependence of rate on substrate concentration. The results are presented in Table 2.

All the experiments have been carried out in the presence of aqueous perchloric acid. The concentration of this acid used in all experiments was $\geq 0.015 \text{ M}$ which was sufficient to prevent the hydrolysis of Fe (II) ions and the self decomposition of hydrogen peroxide as well. Preliminary studies have shown that under our experimental conditions, hydrogen peroxide does not bring about oxidation of maleic and fumaric acids without ferrous sulphate. Also ferrous sulphate alone without hydrogen peroxide did not oxidise either maleic acid or fumaric acid. It has been well established that the action of ferrous ion on hydrogen peroxide in aqueous acidic solution brings about the formation of hydroxyl radical as shown in step (1)

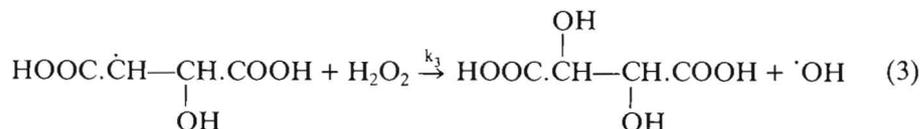


Hydroxyl radicals generated by this single electron transfer have been used in the oxidation of organic compounds. In these reactions, hydroxyl radical abstracts a hydrogen from the organic substrate and generates a free radical on carbon atom but in the present case hydroxyl radical attacks the double bond of maleic or fumaric acid and generates free radical on the carbon atom as shown below:

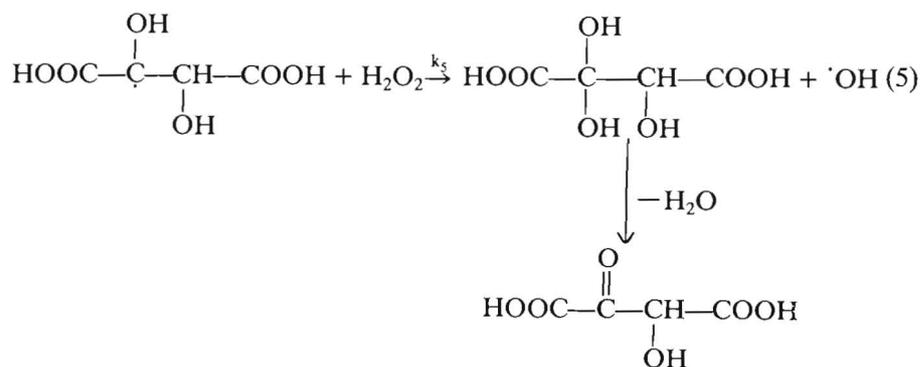
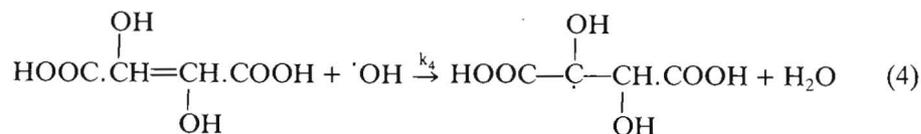


M.A. represents maleic acid and F.A. represents fumaric acid. The formation of free radical, $\text{HOOC}\cdot\text{CH}-\underset{\text{OH}}{\text{CH}}\cdot\text{COOH}$, was also confirmed by Dixon *et al.* (1964)

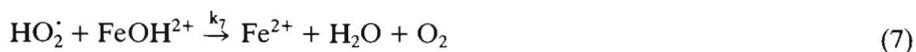
by the e.s.r. studies and generating $\cdot\text{OH}$ with hydrogen peroxide and titanous ions. The organic free radical generated in step 2 may be able to react with molecular hydrogen peroxide, as in step (3)



by a process which involve an electron transference somewhat similar to reaction (1). The presence of tartaric acid as an intermediate was detected in the reaction mixture and its form was identified by Buchanan's chromatographic method (Buchanan *et al.* 1950). The R_f values suggest that maleic and fumaric acids gave dl and meso forms of tartaric acid, respectively. The probable steps of conversion of tartaric acid into product are as follows:



The probable chain termination steps for hydroxyl free radicals are



The rate of reaction in given scheme is given by eq. (8),

$$-\frac{d[\text{M.A. or F.A.}]}{dt} = k_2[\text{M.A. or F.A.}][\cdot\text{OH}] \quad (8)$$

Applying the steady-state approximations for the concentrations of $\cdot\text{OH}$, $\text{HOOC}-\underset{\text{H}}{\text{C}}-\text{CH}(\text{OH})\text{COOH}$, and $\text{HOOC}-\underset{\text{OH}}{\text{C}}-\text{CH}(\text{OH})\text{COOH}$, we obtain eq. (9)

$$[\cdot\text{OH}] = \frac{k_1[\text{Fe}^{2+}]}{k_6} \quad (9)$$

Substituting the concentration of $\cdot\text{OH}$ from eq. (9) into eq. (8), we get eq. (10),

$$-\frac{d[\text{M.A. or F.A.}]}{dt} = \frac{k_1 k_2 [\text{M.A. or F.A.}][\text{Fe}^{2+}]}{k_6} \quad (10)$$

or,

$$-\frac{d[\text{M.A. or F.A.}]}{dt} = k'[\text{M.A. or F.A.}][\text{Fe}^{2+}] \quad (11)$$

Where,

$$k' = \frac{k_1 k_2}{k_6} \quad (12)$$

The eq. (11) can also be written as

$$-\frac{d[\text{M.A. or F.A.}]}{dt} = k_{\text{obsd}}[\text{H}_2\text{O}_2]^0 \quad (13)$$

Where,

$$k_{\text{obsd}} = k'[\text{M.A. or F.A.}][\text{Fe}^{2+}] \quad (14)$$

Equation (11) clearly explains the observed order of reaction with respect to substrate (maleic acid or fumaric acid), Fe (II) ions and hydrogen peroxide concentrations.

The rate constants, k' , were calculated for maleic and fumaric acids by substituting the concentrations of ferrous sulphate and the concentration of individual

Table 3. Variation of rate with temperature.

Temperature	$k_{\text{obsd}} \times 10^7 \text{ (mol l}^{-1}\text{sec}^{-1}\text{)}$	
	Maleic acid	Fumaric acid
303	3.33	4.05
308	3.75	5.00
313	4.45	6.80
318	5.23	8.82
323	6.38	10.33

acid from Table 1, which are $(1.76 \pm 0.019) \times 10^{-2} \text{ l mol}^{-1} \text{ sec}^{-1}$ and $(2.14 \pm 0.018) \times 10^{-2} \text{ l mol}^{-1} \text{ sec}^{-1}$, respectively. The value of k' is dependent on k_1 , k_2 and k_6 . The value of k_1 and k_6 are the same for maleic and fumaric acids but k_2 is different. The value of k_1 and k_6 are reported in the literature (Walling 1975) which are $76 \text{ l mol}^{-1}\text{sec}^{-1}$ for k_1 and $(1.2 \text{ to } 4.5) \times 10^7 \text{ l mol}^{-1} \text{ sec}^{-1}$ for k_6 . In our calculations $2.75 \times 10^7 \text{ l mol}^{-1} \text{ sec}^{-1}$ has been used as the average value of k_6 . Substituting the values of k_1 and k_6 in eq. (12), k_2 has been calculated to be $6.37 \times 10^3 \text{ l mol}^{-1} \text{ sec}^{-1}$ for maleic acid and $7.74 \times 10^3 \text{ l mol}^{-1} \text{ sec}^{-1}$ for fumaric acid. The value of k_2 is lower in the case of maleic acid than that of fumaric acid which clearly suggests that the second step in the proposed scheme is faster for fumaric acid than maleic acid. The two carboxylic groups on the same side of the double bond offer hindrance for the attack of $\cdot\text{OH}$ and this explains why the oxidation rate of maleic acid is slower than fumaric acid.

The ionic strength of the reaction mixture was varied from $3.20 \times 10^{-2} \text{ M}$ to $5.20 \times 10^{-2} \text{ M}$ by the addition of sodium perchlorate solution. No significant change in the rate of the reaction was observed. These observations indicate that the reaction does not follow an ionic mechanism.

The same reaction was performed at different temperatures from 30 to 50°C, and the results are given in Table 3. The plots of $\log k_{\text{obsd}}$ against reciprocal of temperature gives a straight line, and the energy of activation calculated from the slopes of these lines are 24.36 ± 0.01 and $38.29 \pm 0.01 \text{ kJ mol}^{-1}$ for maleic and fumaric acids, respectively and pre-exponential factors were also calculated from their intercepts which were 4.90×10^{-5} and 1.22×10^{-4} for maleic and fumaric acids, respectively.

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دراسات كيناتيكية أحماض الماليك والفوماريك بوساطة كاشف الفيتون

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في هذا البحث تمت دراسة كيناتيكية وآلية التفاعل لأكسدة حمض الماليك وحمض الفوماريك بوساطة فوق أكسيد الهيدروجين في وجود كبريتات الحديدوز.

إن سرعة أكسدة حمض الفوماريك أكبر من سرعة أكسدة حمض الماليك. إن التفاعل بالنسبة لحمض الماليك وحمض الفوماريك هو من الدرجة الأولى، وأيضا تفاعل من الدرجة الأولى بالنسبة لكبريتات الحديدوز ولكنه من الدرجة الصفر بالنسبة لفوق أكسيد الهيدروجين.

ولقد حسبت الطاقة التنشيطية ووجدت قيمتها ٣٦، ٢٤ و ٢٩، ٣٨ كيلو جول/مول لحمض الماليك وحمض الفوماريك على التوالي، ولقد اقترحت آلية لهذا التفاعل.