KINETICS OF OXIDATION OF MALEIC ACID BY PERSULPHATE

Maleic acid has been subjected to oxidation by many oxidising agents. The most commonly employed oxidising agents, *e.g.*, the alkaline permanganate, potassium chlorate in presence of osmium tetra oxide as catalysts[1] have been used. Oxidation of maleic acid by cobaltic sulphate has also been studied by M. Aziz Beg and Firoz Ahmad[2]. The silver catalysed oxidation of maleic acid by $K_2S_2O_8$ has not been studied so far. The present communication deals with this problem and the study has been conducted in detail from the kinetics points of view.

Experimental

The maleic acid used was of Reidal grade. $K_2S_2O_8$ and $AgNO_3$ were of Analar grade. Other chemicals employed were of the highest purity and were prepared in distilled water. The kinetic study has been conducted at temperature 35° C, 40° C, 45° C and 50° C in a thermostat. The requisite amounts of acid and $K_2S_2O_8$ were taken in thoroughly cleaned bottles which were kept in a thermostat (within the range $\pm 0.01^\circ$ C) at the desired temperature already fixed. When the bottles had attained the temperature of the bath then the requisite volume of $K_2S_2O_8$ were added into the acid solution bottles. The time was noted when $K_2S_2O_8$ was half way down the pipette. 10 cc of the reaction mixture was withdrawn and poured in cold water to arrest the reaction. The change in the hydrogen ion concentration which was estimated by CO_2-free NaOH, using phenolphthalein as an indicator, gave the relevant data for the kinetic study of this reaction in which the acid produced was found to be of the same basicity as the acid oxidised. The order of the reaction has been determined by integration and isolation methods.

Observations

Table I
Effect of temperature

Concentration of maleic acid $=0.05$ M			
$K_2S_2O_8$ $=0.05$ M			
$AgNO_3$ $=0.0005$ M			
Temperature :	35° C	40° C	45° C	50° C
$k \times 10^3$ min.$^{-1}$	0.699	0.826	1.16	1.39

Table II
Effect of $K_2S_2O_8$ concentration

	Temperature 40° C
Concentration of acid $=0.05$ M	
$AgNO_3=0.0005$ M	
$K_2S_2O_8=0.035$ M	0.025 M
$K \times 10^3$ min^{-1} 0.681	0.496

Table III
Effect of acid concentration

		Temperature 40° C
Concentration of $K_2S_2O_8=0.05$ M		
$AgNO_3=0.0005$ M		
Concentration of acid : 0.04 M	0.03 M	0.02 M
$K \times 10^3$ min^{-1} 0.948	1.63	2.04

Table IV
Effect of catalyst concentration

Concentration of maleic acid $=0.05$ M		
$K_2S_2O_8$ $=0.05$ M		
Concentration of $AgNO_3$: 0.0004 M	0.003 M	0.0002 M
$K \times 10^3$ min^{-1} : 0.804	0.664	0.462

Table V
Effect of salts

| Concentration of maleic acid $=0.05$ M | | | | | | |
$K_2S_2O_8$ $=0.05$ M						
$AgNO_3$ $=0.0005$ M						
Salts :	KNO$_3$	Conc.	K$_2$SO$_4$	Conc.	MgSO$_4$	Conc.
$K \times 10^3$ min^{-1}	0.108	0.15 M	0.113	0.10 M	0.105	0.125 M
,,	0.104	0.10 M	0.115	0.05	0.115	0.075 M

DISCUSSION

The uncatalysed reaction of maleic acid with $K_2S_2O_8$ was very slow. A trace of catalyst (Ag^+ ions) greatly increases the rate. The rate has been directly proportional to Ag^+ ions concentration. The order of the reaction has been found to be one. The reaction is first order with respect to peroxydisulphate and zero order with respect to acid.

The energy of activation, frequency factor, and entropy of activation have been found to be 9.022 Kcals, 2.49×10^1 sec^{-1}, and -53.4 E.u. respectively. The presence of salts like KNO_3, $K_2S_2O_8$ and $MgSO_4$ slightly increases the reaction velocity. The silver catalysed oxidation depends upon the silver ion concentration. Thus the reaction is essentially bimolecular but for the given concentration it conforms to unimolecular reaction. The change in salt concentration did not change reaction so there is no salt effect on reaction.

The oxidation of maleic acid takes place in presence of silver (I) and the acid is oxidised to mesotartaric acid which is a dicarboxylic acid, *i.e.*, an acid of the same basicity as the original acid. Prolonged oxidation yields two molecules of formic acid (faint test given by chromotropic acid test). Because of the lack of dependence in rate law on the reductant concentration it has been suggested that the reaction has a rate determining step :

$$Ag^+ + S_2O_8^= \longrightarrow Ag^{++} + 2SO_4^=. \quad (1)$$

For the derivation of the rate law the following equations are to be taken into consideration.

$$S_2O_8^= \xrightarrow{K_1} 2SO_4^- \text{ rapid} \quad (2)$$

and

$$2SO_4^- + Ag^+ \xrightarrow{K_2} 2SO_4^= + Ag^{+++}. \quad (3)$$
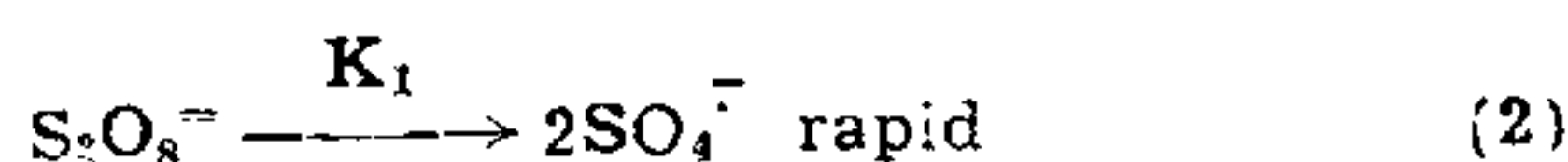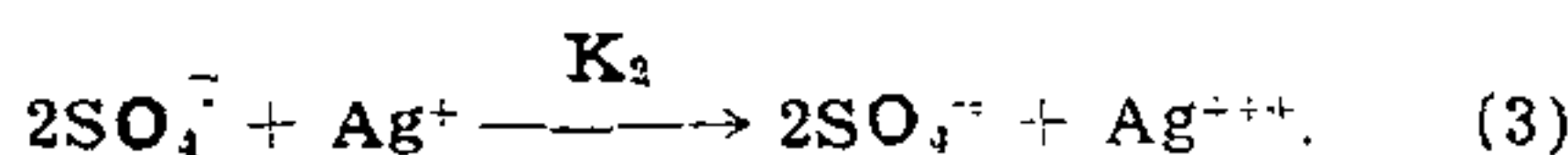
Rate is given by

$$-\frac{d\,(S_2O_8^=)}{dt} = K_2\,[SO_4^=]^2\,[Ag^+] \quad (4)$$

and from the equilibrium of equation (1)
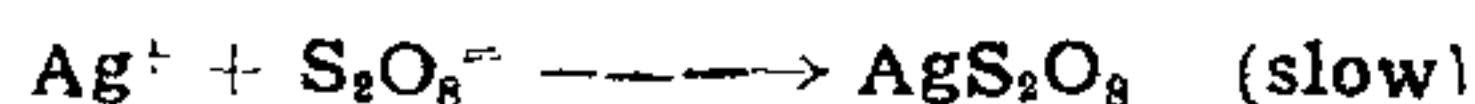
$$K = \frac{[SO_4^-]^2}{[S_2O_8^=]} \quad (5)$$

where K is the equilibrium constant. Substitution of (5) in (4) gives :

$$-\frac{d\,(S_2O_8^=)}{dt} = K_2K\,[S_2O_8^=]\,[Ag^+]$$
$$= K_{obs}\,[S_2O_8^=]\,[Ag^+]$$

where

$$K_{obs} = K_2K$$
$$K_2 = \frac{K_{obs}}{K}.$$

Another alternative mechanism to the same rate law is given by[3,4] :

$$Ag^+ + S_2O_8^= \longrightarrow AgS_2O_8 \quad (slow)$$

followed by either :

$$AgS_2O_8^- \longrightarrow Ag^{+++} + 2SO_4^= \quad (fast)$$

$$AgS_2O_8^- \longrightarrow Ag^+ + SO_4^- + SO_4^=.$$

Therefore it can be concluded that the above oxidation reactions conform to the above rate law obtained, as the practical data give the reaction to be of the first order with respect to peroxydisulphate concentration and independent of the reductant concentration.

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QUANTITATIVE ESTIMATION OF THE FRACTION OF CALCITE PRESENT IN A BINARY MIXTURE OF CALCITE AND VATERITE

INTRODUCTION

DURING the course of investigations on the kinetics and mechanism of the transformation of anhydrous vaterite to calcite, it became necessary to devise a method for the estimation of calcite in a mixture of calcite and vaterite. Except a passing mention that mixtures of calcite and vaterite could be estimated by I.R. spectrophotometry[1], there was no other report of any direct method for the quantitative estimation of mixtures of calcite and vaterite. Unlike in the case of aragonite and calcite, the I.R. spectra of calcite and vaterite are very much alike and there are no suitable absorption bands which are composition dependent. Hence X-ray powder diffraction technique was resorted to for the estimation of calcite and vaterite in mixtures.

EXPERIMENTAL METHOD AND RESULTS

The sample of vaterite was prepared by employing the method reported by McConnell[2]. The specimen of calcite was obtained by heating "pure aragonite"[3] at 480° C for 48 hours. Mixtures of vaterite and calcite were prepared at 10% calcite intervals. X-ray powder diffraction patterns of all