

REACTION BETWEEN ACRYLIC ACID AND PEROXYDISULPHATE A KINETIC STUDY

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The uncatalyzed reaction between acrylic acid and peroxydisulphate has been studied kinetically over the range 60 – 80°. The reaction is found to follow an overall first order. The products of the reaction have been analyzed and the rate law deduced.

INTRODUCTION

A large number of oxidation reactions of carboxylic acids with peroxydisulphate have been studied kinetically by various workers [1-3]. It has been shown that such reactions are mediated through radicals. Attempts have been made in this connection to correlate the proposed mechanisms with the rate laws by identifying the products of the reactions. In order to gain further information, the oxidation of acrylic acid by peroxydisulphate has been studied, and reported in the present communication.

EXPERIMENTAL

(a) *Kinetic Studies.* The use of conventional titrations was made to study the kinetics of the reaction in the temperature range 60 to 80°; the reaction was too slow at room temperature. The general procedure employed is given below:

The reaction flask containing the substrate was placed in thermostat for 20 min before transferring the required volume of potassium peroxydisulphate, making a total vol of 100 ml each time. At suitable time intervals, the samples were withdrawn and estimated for the residual peroxydisulphate by an iodometric method similar to the one used by Bartlet and Cotman [4]. A buffer solution of sodium bicarbonate and sulphuric acid was used to maintain a pH of 7.1 – 7.2.

A 5 ml solution containing (i) 5 ml of 4% of sodium bicarbonate solution, (ii) one ml of 1 N sulphuric acid solution, and (iii) 5 ml of approximately 40% potassium iodide solution was analysed each time for residual peroxydisulphate. The liberated iodine was titrated against sodium thiosulphate solution using freshly prepared starch solution as indicator.

Extreme care was taken in cleaning the reaction vessels since the reactions involving peroxydisulphate are sensitive to impurities. They were thoroughly washed with chromic acid, rinsed with double – distilled water, and kept in a steam bath for some time before drying.

(b) *Analysis of the Products.* The reaction products were analyzed as follows: 20 ml 0.2 M acrylic acid, and 30 ml double-distilled water was heated with stirring under reflux on an oil bath for more than ten half-lives at 70° ± 2° till all the peroxydisulphate was consumed. The resulting mixture was distilled under pressure. The distillate was found to contain 2,3-dihydroxy propionic acid which was detected by the usual methods. The remaining insoluble material appeared to be a polymer which did not yield any other detectable compound.

RESULTS AND DISCUSSION

The Rate Law and its Confirmation. Table 1 shows the evaluation of the average rates R and the observed rate constants k_o of the reaction.

Table 2A includes the values of R and k_o against peroxydisulphate concentration varying from (10 to 80) $\times 10^{-3}$ M at 70°, when the concentration of substrate (acrylic acid) was kept constant at 20×10^{-3} M. It is observed that the variation of R with $[S_2O_8]^{2-}$ is linear and the reaction follows first order in peroxydisulphate concentration.

Table 2B presents the values of R and k_o against substrate concentration varying from (10 to 80) $\times 10^{-3}$ M at 70°, when the peroxydisulphate concentration was kept fixed at 20×10^{-3} M. Both R and k_o are independent of the substrate concentration indicating that the reaction follows zero order in acrylic acid concentration.

Similar results were obtained at other temperatures in the range 60 to 80°.

Table 1. Average rates (R) and rate constants (k_0) of reaction between acrylic acid and potassium peroxydisulphates.

[Acrylic acid] = $40 \times 10^{-3} \text{M}$						
Time t (sec)	Titre (ml)	$M \cdot 10^3 [S_2O_8]^{2-}$ (M-lit $^{-1}$)	$\Delta M \cdot 10^3 [S_2O_8]^{2-}$ (M-lit $^{-1}$)	Δt (sec)	$10^7 R$ (M-lit $^{-1}$ -sec $^{-1}$)	$10^5 k_0$ (sec $^{-1}$)
0	9.9	20.0				
1800	9.1	18.4	1.6	1800	8.9	4.6
3600	8.7	17.6	0.8	1800	4.4	3.6
5400	8.4	16.7	0.9	1800	5.0	3.3
7200	7.9	16.0	0.7	1800	3.9	3.1
9000	7.5	15.2	0.8	1800	4.4	3.0
10800	7.0	14.1	1.1	1800	6.1	3.2
12600	6.6	13.3	0.8	1800	4.4	3.2
14400	6.3	12.7	0.6	1800	3.3	3.2

Temperature = 70° ; $[S_2O_8]^{2-} = 20 \times 10^{-3} \text{M}$

Table 2.

(A) Values of R and K_0 Vs peroxydisulphate concentration at constant concentration of acrylic acid.

$10^3 [S_2O_8]^{2-} (\text{M})$	5	10	20	30	40	50	60	80
$10^7 R (\text{M-lit}^{-1} \text{-sec}^{-1})$	1.2	2.5	4.4	8.0	10.1	12.9	16.8	21.4
$10^5 k_0 (\text{sec}^{-1})$	2.8	3.4	2.6	2.8	3.2	2.9	3.8	3.5

[Acrylic acid] = $20 \times 10^{-3} \text{M}$; temperature = 70° .

(B) Values of R and K_0 Vs concentration of acrylic acid at constant concentration of peroxysulphate.

$10^3 [\text{Acrylic acid}] (\text{M})$	10	30	40	50	60	80
$10^7 R (\text{M-lit}^{-1} \text{-sec}^{-1})$	5.0	4.2	4.1	4.9	4.8	4.7
$10^5 k_0 (\text{sec}^{-1})$	3.0	3.6	3.2	2.9	2.9	2.7

$(S_2O_8^{2-}) = 20 \times 10^{-3} \text{M}$; temperature = 70° .

The thermal decomposition of peroxydisulphate in the absence of a substrate is well known [1]. The rate constants for such a decomposition under similar experimental conditions have been determined before [5]. The observed rate of reaction and rate constant can be expressed mathematically as

$$R = - \frac{d [S_2O_8]^{2-}}{dt} = k_0 [S_2O_8]^{2-} \quad (1)$$

$$\text{and } k_0 = k_1 + k$$

where k is the rate constant for the oxidation reaction and k_1 is the rate constant of the thermal decomposition of peroxydisulphate alone.

The plots of $\log [S_2O_8]^{2-}$ against time, at equal reactant concentration of $20 \times 10^{-3} \text{M}$ and at various temperatures, are straight lines indicating that the order of reaction has no correlation of the change in temperature.

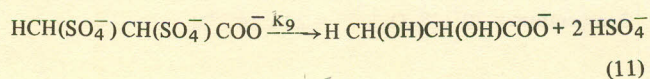
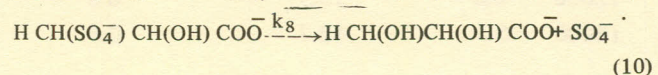
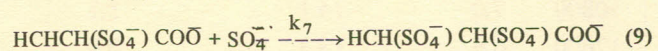
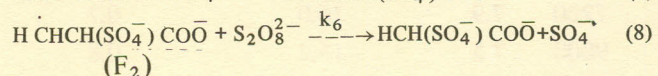
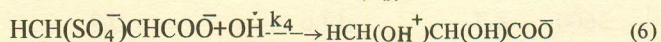
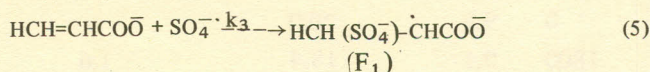
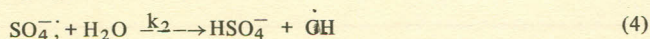
The rate law was confirmed by two methods. The peroxydisulphate concentration at different intervals of time was plotted against time for various kinetic runs and the half-life calculated. The half-life is almost independent of the terphthalic acid concentration indicating a first order reaction (Table 3). Likewise the values of $(t_{3/4} - t_{1/2})/t_{1/2}$ are almost the same (Table 4) at different temperatures confirming that the reaction follows the first order [6].

The energy of activation, as calculated from the plots of $\log k_0$ against $1/T$ was found to be approximately 28 KCal at 70° which lies between the activation energy of the simple decomposition (~ 30 KCal) and the oxidation reaction (~ 27 KCal).

It was also observed that surfaces such as glass, wool, porcelain, glass rods, BaSO_4 and glass beads catalyzed the reaction. The catalytic effect of glass wool was found to be the largest since the reaction was complete in less than 2 hrs at 70° .

Proposed Mechanism and the Deduction of the Rate Law. The oxidation of acrylic acid by peroxydisulphate is found to have zero order dependence on substrate concentration resulting in the formation of 2, 3 - dihydroxy propionic acid. The ESR study showed that the reactions of carboxylic acids have been mediating through free radicals [7,8,9]. On this basis, the following mechanism seems most probable as it supports the kinetic results of the reaction and accounts for the products formed.

By decomposing thermally in solution, both singly and in the presence of organic substrates [1,3] peroxydisulphate gives sulphate radical anions, which can attack the substrate directly or through an intermediate OH^- radical. Thus,



the rate of decomposition of peroxydisulphate in presence of acrylic acid can be expressed as

$$-\frac{d[\text{S}_2\text{O}_8]^{2-}}{dt} = k_1 [\text{S}_2\text{O}_8]^{2-} + k_6 [\text{F}_2] [\text{S}_2\text{O}_8]^{2-} \quad (12)$$

Table 3. Calculated half-lives of peroxidisulphate (A) and acrylic acid (B)

(A)							
$10^3 [\text{S}_2\text{O}_8]^{2-}$ (M)	10	30	40	50	60	80	
$t_{1/2}$ (min)	323	312	312	282	251	318	
(B)							
10^3 [Acrylic acid] (M)	5	20	30	40	50	60	80
$t_{1/2}$ (min)	285	282	300	264	264	264	264
$[\text{S}_2\text{O}_8]^{2-} = 20 \times 10^{-3}\text{M}$; temperature = 70°							

Table 4. Values of $(t_{3/4} - t_{1/2})/t_{1/2}$ vs Temperature.

Temperature $^\circ\text{C}$	60	70	75	80
$(t_{3/4} - t_{1/2})/t_{1/2}$	0.5	0.5	0.5	0.5

On application of the steady state treatment to the above mechanism, the following equations are obtained:

$$(a) \frac{d[\text{SO}_4^-]}{dt} = 0$$

$$\text{or } k_1[\text{S}_2\text{O}_8]^{2-} + k_6[\text{F}_2][\text{S}_2\text{O}_8]^{2-} = k_2[\text{SO}_4^-] + k_3[\text{SO}_4^-][\text{acrylic acid}] + k_5[\text{acrylic acid}][\text{SO}_4^-] + k_7[\text{F}_2][\text{SO}_4^-] \quad (13)$$

$$(b) \frac{d[\text{OH}^-]}{dt} = 0$$

$$\text{or } K_2[\text{SO}_4^-][\text{H}_2\text{O}] = k_4[\text{F}_1][\text{OH}^-] \quad (14)$$

$$(c) \frac{d[\text{F}_1]}{dt} = 0$$

$$\text{or } k_3[\text{acrylic acid}][\text{SO}_4^-] = K_4[\text{F}_1][\text{OH}^-] \quad (15)$$

$$(d) \frac{d[\text{F}_2]}{dt} = 0$$

$$\text{or } k_5[\text{acrylic acid}][\text{SO}_4^-] = k_6[\text{F}_2][\text{S}_2\text{O}_8]^{2-} = k_7[\text{F}_2][\text{SO}_4^-] \quad (16)$$

From equation (13) to (16)

$$k_1[\text{S}_2\text{O}_8]^{2-} = 2k_2[\text{SO}_4^-][\text{H}_2\text{O}] + 2k_7[\text{F}_2][\text{SO}_4^-]^{2-} \quad (17)$$

From equations (14) to (16)

$$k_6[\text{F}_2][\text{S}_2\text{O}_8]^{2-} = \frac{k_2 k_5}{k_3} [\text{SO}_4^-][\text{H}_2\text{O}] - k_7[\text{F}_2][\text{SO}_4^-] \quad (18)$$

Dividing equation (17) by (18) and re-arranging according to the powers of $[\text{F}_2]$,

$$2K_6 k_7 k_3 [\text{F}_2] + [\text{F}_2] 2k_2 k_3 k_6 [\text{H}_2\text{O}] + k_1 k_3 k_7 - k_1 k_2 k_5 [\text{H}_2\text{O}] = 0 \quad (19)$$

In other words, in the presence of excess of water the value of F_2 is constant; Therefore, equation (12) reduces to

$$\frac{d[\text{S}_2\text{O}_8]^{2-}}{dt} = k_1[\text{S}_2\text{O}_8]^{2-} + k_6 k [\text{S}_2\text{O}_8]^{2-} = k_0[\text{S}_2\text{O}_8]^{2-} \quad (20)$$

which is the same as the observed rate law.

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