

Kinetics of Catalyzed Redox Reaction Between Acrylic Acid and Peroxydisulphate

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Summary: The redox reaction between acrylic acid and peroxydisulphate, catalyzed by Ag(1), has been studied kinetically over the range 35 to 55°C. The reaction products have been analyzed and a mechanism is proposed for the reaction. The rate law is deduced from this mechanism.

Introduction

The oxidation of carboxylic acids by peroxydisulphate has been extensively studied by many workers¹⁻⁴. The electron spin resonance studies of such reactions show that they are mediated through free radicals leading to a first order rate law.⁷ Attempts have also been made to correlate the proposed reaction mechanisms with the kinetic studies. In order to acquire further information the kinetics of the reactions of acrylic acid with peroxydisulphate has been studied using a catalyst.

Experimental

The reaction between acrylic acid and peroxydisulphate proceeds slowly below 60°C. In the presence of Ag(1) catalyst, however, the reaction can be conveniently studied in the range 35 to 55°C.

The kinetic studies were carried out as follows. The solution of the substrate in the reaction flask was kept at constant experimental temperature for about twenty minutes so that an equilibrium was established. The required volumes of potassium peroxydisulphate and AgNO₃ were then transferred to the reaction flask making a total volume of 100 ml each time. The samples were withdrawn at suitable time intervals and the residual peroxydisulphate was estimated by an iodometric method similar to the one used by Vasudeva and Wasif².

The solution to be analyzed consisted of (i) 5 ml of the reaction mixture, (ii) 5 ml of 4% sodium bicarbonate solution, (iii) 1 ml of 1 N sulphuric acid solution, and (iv) 5 ml of freshly prepared potassium iodide solution. The liberated iodine was titrated against sodium thiosul-

phate solution using starch as indicator. It was observed that the presence of unreacted reducing substrate did not interfere with this method of estimation.

Extreme care was taken in cleaning the reaction vessels since the reactions involving peroxydisulphate are sensitive to impurities resulting in misleading values. For this reason, the vessels were washed with chromic acid, rinsed with double distilled water, and kept in a steam bath before being dried in an oven.

The product analysis was done as follows. A reaction mixture containing (i) 40 ml 0.1 mol K₂S₂O₈, (ii) 20 ml 0.2 mol acrylic acid, (iii) 10 ml 0.01 mol/AgNO₃ and (iv) 30 ml double distilled water was heated with stirring under reflux for about 16 hours on an oil bath at 70±2°C till all the peroxydisulphate was consumed. The resulting mixture was distilled under reduced pressure and no distillate was obtained. The remaining material appeared to be a polymer which did not yield any detectable compound.

The above mentioned procedure was then repeated with cinnamic acid which contains -C₆H₅ group instead of -H in acrylic acid. The distillate thus obtained yielded stilbene detected by usual organic methods⁸. By analogy, it is inferred that acetylene is the possible product in the case of acrylic acid which cannot be detected by usual methods.

Results and Discussion

The Rate Law:

Table 1 A includes the values of the initial rates of reaction R and observed rate constants k_0 at 40°C when the concentrations of acrylic acid and AgNO_3 were kept constant at 20×10^{-3} mol and 5×10^{-4} mol, respectively, and that of peroxydisulphate varied from $(5 \text{ to } 80) \times 10^{-3}$ mol. The values of k_0 are almost constant while figure 1 A shows that the plot of R against $[\text{S}_2\text{O}_8^{2-}]$ is linear and the reaction follows first order in peroxydisulphate concentration.

Table 1 B includes the values of R and k_0 at 40°C when the concentrations of peroxydisulphate and AgNO_3 were kept constant at 20×10^{-3} mol and 5×10^{-4} mol, respectively, and that of acrylic acid varied from $(10 \text{ to } 80) \times 10^{-3}$ mol. Figure 1 B shows that the rates are independent of the substrate concentration and, therefore, the reaction follows zero order in acrylic acid concentration. The values of k_0 are again almost constant.

Table 1 C includes the values of R and k_0 at 40°C when the concentration of AgNO_3 was varied from $(7 \text{ to } 15) \times 10^{-4}$ mol, keeping peroxydisulphate and acrylic acid concentration as constant at 20×10^{-3} mol. Figure 1 C shows that the plot of R against AgNO_3 concentration is linear indicating that the reaction follows first order with respect to $\text{Ag}(1)$ concentration.

It is known that peroxydisulphate decomposes thermally in absence of a substrate¹⁻³. The rate constants for such a decomposition have been determined before². Keeping these facts in view, the reaction rate can be expressed mathematically by the following equations:

$$R = - \frac{d[\text{S}_2\text{O}_8^{2-}]}{dt}$$

$$= k_0 [\text{S}_2\text{O}_8^{2-}] [\text{Ag}(1)] = k_0 [\text{S}_2\text{O}_8^{2-}] \quad (1)$$

TABLE 1.

R and k_0 data of acrylic acid-Peroxydisulphate reaction at 40°C .

(A)							
$10^3 [\text{S}_2\text{O}_8^{2-}]$ (mol)	5	10	30	40	50	60	80
$10^7 R$ ($\text{mol}^{-1}\text{s}^{-1}$)	2.1	4.4	14.0	18.1	22.8	28.6	34.3
$10^5 k_0$ (s^{-1})	10.7	11.6	10.2	10.8	11.0	10.4	10.0
[Acrylic acid] = 20×10^{-3} mol; [AgNO_3] = 5×10^{-4} mol							
(B)							
10^3 [Acrylic acid] (mol)	10	20	30	40	50	60	80
$10^7 R$ ($\text{mol}^{-1}\text{s}^{-1}$)	8.5	7.9	8.1	8.9	8.6	8.0	7.8
$10^5 k_0$ (s^{-1})	10.7	11.1	11.6	10.8	10.6	11.0	10.8
$[\text{S}_2\text{O}_8^{2-}] = 20 \times 10^{-3}$ mol; [AgNO_3] = 5×10^{-4} mol							
(C)							
10^4 [AgNO_3] (mol)			7	8	10	12	15
$10^7 R$ ($\text{mol}^{-1}\text{s}^{-1}$)			8.4	9.9	13.2	15.0	18.8
$10^5 k_0$ (s^{-1})			16.8	15.4	16.0	18.0	19.2
$[\text{S}_2\text{O}_8^{2-}] = [\text{Acrylic acid}] = 20 \times 10^{-3}$ mol.							

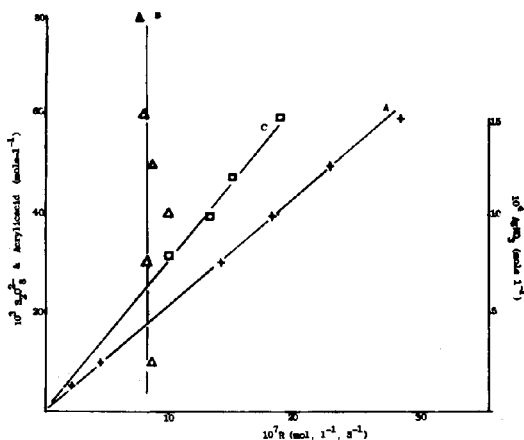


Fig. 1: Dependence of Rate on : A-[$S_2O_8^{2-}$]; B-[Acrylic Acid]; C-[$AgNO_3$]

$$k_0 = k + k_1 \quad (2)$$

where $Ag(1)$ is kept constant, k is the rate constant of the thermal decomposition of peroxydisulphate in absence of a substrate, and k_1 is the rate constant for the oxidation reaction.

Confirmation of the Rate Law:

In addition to the integration method, the order of reaction was confirmed by the following method.

The half-life for a first order reaction is supposed to be independent of the initial concentration⁵. The concentrations of the oxidant and the reductant at different intervals of time were plotted against time for various kinetic runs and half-lives calculated graphically. The half-life has been found to be almost independent of the acrylic acid concentration indicating that the overall order of the reaction should be unity.

Dependence of Rate Constant :

The variation of observed rate constant with temperature range studied are given in Table 2, showing a regular increase in the values of k_0 with rise in temperature.

Proposed Mechanism and the Rate Law:

The catalyzed reaction of acrylic acid with peroxy-

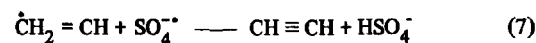
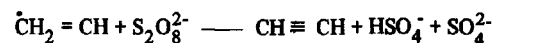
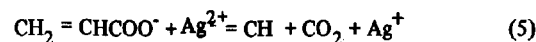
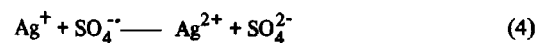
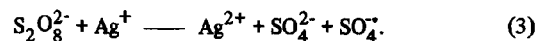
TABLE 2.

Rate constant, k_0 , values at different Temperatures

T^0 (K)	308	313	318	323	328
$10^5 k_0$ (S^{-1})	13.6	19.8	30.7	40.4	53.6

disulphate follows zero order in acrylic acid and first order in peroxydisulphate concentrations. The reaction is found to be sensitive to the surface added since the addition of varying amounts of $BaSO_4$, glass wool and porcelain increased the decomposition of acrylic acid appreciably. These characteristics indicate that it is a free radical chain reaction⁶. However, the absence of any lower hydroxy carboxylic acid as the product of reaction excludes the possibility of its mediation by the radicals mentioned by Norman et al.⁷

When heated, peroxydisulphate decomposes both alone and in presence of organic substrates¹⁻³ forming sulphate radical anions, $SO_4^{\cdot-}$, which form other intermediate radicals by interacting with the organic substrate in the system. The following mechanism, therefore, seems to be the most probable.



Equations (3) to (7) lead to a rate law

$$\frac{-d[S_2O_8^{2-}]}{dt} =$$

$$k_1 [Ag^+] [S_2O_8^{2-}] + k_4 [\dot{C}H_2 = CH] [S_2O_8^{2-}] \quad (8)$$

On applying the steady state treatment to the above mechanism the following equations are obtained:

$$(a) \quad \frac{d[SO_4^{\cdot-}]}{dt} = 0 \quad (9)$$

$$\begin{aligned} \text{or } k_2 [S_2O_8^{2-}] [Ag^+] + k_4 [\dot{C}H_2 = CH] [SO_4^{2-}] \\ = k_2 [Ag^+] [SO_4^{2-}] + k_5 [\dot{C}H_2 = CH] [SO_4^{2-}] \end{aligned} \quad (10)$$

$$(b) \quad \frac{d [Ag^{2+}]}{dt} = 0 \quad (11)$$

$$\begin{aligned} k_1 [Ag^+] [S_2O_8^{2-}] + k_2 [Ag^+] [SO_4^{2-}] \\ = k_3 [CH_2 = CH COO^-] [Ag^{2+}] \end{aligned} \quad (12)$$

$$(c) \quad \frac{d [\dot{C}H_2 = CH]}{dt} = 0 \quad (13)$$

$$\begin{aligned} \text{or } k_3 [CH_2 = CHCOO^-] [Ag^{2+}] \\ = k_4 [CH_2 = CH] [S_2O_8^{2-}] + \\ k_5 [CH_2 = CH] [SO_4^{2-}] \end{aligned} \quad (14)$$

from equations (10) and (12), by addition,

$$\begin{aligned} 2 k_1 [S_2O_8^{2-}] [Ag^+] + k_4 [CH_2 = CH] [S_2O_8^{2-}] \\ = k_3 [CH_2 = CHCOO^-] [Ag^{2+}] + \\ k_5 [CH_2 = CH] [SO_4^{2-}] \end{aligned} \quad (15)$$

From equation (14) and (15), by addition,

$$k_1 [S_2O_8^{2-}] [Ag^+] = k_5 [\dot{C}H_2 = CH] [SO_4^{2-}] \quad (16)$$

From equations (12) and (14),

$$\begin{aligned} k_1 [Ag^+] [S_2O_8^{2-}] + k_2 [Ag^+] [SO_4^{2-}] \\ = k_4 [CH_2 = CH] [S_2O_8^{2-}] + \\ k_5 [CH_2 = CH] [SO_4^{2-}] \end{aligned} \quad (17)$$

$$\begin{aligned} \text{or } k_1 [Ag^+] [S_2O_8^{2-}] - k_4 [\dot{C}H_2 = CH] [S_2O_8^{2-}] \\ = k_5 [CH_2 = CH] [SO_4^{2-}] \\ - k_2 [Ag^+] [SO_4^{2-}] \end{aligned} \quad (18)$$

On dividing equation (18) by (16),

$$\frac{k_1 [Ag^+] - k_4 [\dot{C}H_2 = CH]}{k_1 [Ag^+]}$$

$$= \frac{k_5 [\dot{C}H_2 = CH] - k_2 [Ag^+]}{k_5 [\dot{C}H_2 = CH]} \quad (19)$$

$$\begin{aligned} \text{or } [\dot{C}H_2 = CH] &= \frac{k_1 k_2}{k_4 k_5} \quad \frac{1}{2} \\ [Ag^+] &= k [Ag^+] \end{aligned} \quad (20)$$

From equations (8) and (20), therefore,

$$\begin{aligned} - \frac{d [S_2O_8^{2-}]}{dt} &= k_1 [Ag^+] [S_2O_8^{2-}] \\ &+ k_4 \frac{k_1 k_2}{k_4 k_5} [Ag^+] [S_2O_8^{2-}] \end{aligned} \quad (21)$$

$$= k_0 [Ag^+] [S_2O_8^{2-}] \quad (22)$$

Equation (22) suggests that the reaction should follow first order in $[S_2O_8^{2-}]$ and $[Ag^+]$ and should be independent of acrylic acid concentration. It also explains the possible formation of C_2H_2 during the oxidation.

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References:

1. D.A. House, *Chem. Rev.*, **62**, 185 (1962).
2. W.C. Vasudeva and Saad Wasif, *J. Chem. Soc. (B)* 960 (1970).
3. W.C. Vasudeva and Saad Wasif, *J. Inorg. Nucl. Chem.*, **34**, 3153 (1972).
4. W.C. Vasudeva, Z. Sherif, and A. Hossady, *Libyan J. Sci.*, **7B**, 27 (1977).
5. S.W. Benson, *Foundations of Chemical Kinetics*, McGraw-Hill, New York (1960).
6. F.S. Dainton, *Chain Reactions*, Methuen, London (1956).
7. R.O.C. Norman, P.M. Storey, and P.R. West, *J. Chem. Soc. (B)*, 1087 (1970).
8. F. Feigl, *Qualitative Analysis by Spot Tests*, Elsevier, New York, (1954).