

## Kinetics of the Reaction of Terphthalic Acid and Peroxodisulphate Catalysed by Ag(1)

G.M. KHAN and M.J. IOBAL\*

*National Physical & Standards Laboratories. 16, Sector H- 9, Islamabad, Pakistan*

*\*Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan.*

(Received 5th July, 1988)

**Summary:** The reaction of terphthalic acid with peroxodisulphate with and without the presence of Ag(1) catalyst has been studied kinetically. The reaction rates have been found to show first-order dependence on peroxodisulphate concentration. The reaction products have been identified and a free radical mechanism is proposed.

### Introduction

Peroxodisulphate is one of the strongest known oxidising agents. It has been used in the oxidation of a large number of organic compounds, especially organic acids whose kinetic studies have been of interest to many workers [1-6]. The electron spin resonance studies [2,4] of the reactions of organic acids with peroxodisulphate have shown that they are mediated through free radicals leading to a first-order law [1].

In a previous publication [6], we have reported that the reactions of cinnamic acid and acrylic acid with peroxodisulphate follow a zero-order kinetics in acid and first-order in peroxodisulphate concentrations. The reactions are found to be sensitive to surface area; various surfaces such as glass wool, porcelain, glass rods, BaSO<sub>4</sub> and glass beads were found to catalyse the reaction to different extent. These features are characteristic of the free radical chain reactions. Besides, the electron spin resonance study by Norman et. al.[4] on acrylic acid, crotonic acid and other similar organic acids indicate that their reactions with peroxodisulphate are mediated by the free radicals. For instance, the reaction of crotonic acid has been found to proceed via the free radicals of the type; HOCH (CH<sub>3</sub>CH) COO<sup>•</sup>, CH<sub>3</sub>CHCH(OH)COO<sup>•</sup> & (SO<sub>4</sub><sup>•</sup>) CH (CH<sub>3</sub>CH) (COO<sup>•</sup>). Similarly, the following radicals have been detected in the case of acrylic acid HOCH(HCH) COO<sup>•</sup> HCHCH (OH) COO<sup>•</sup> (SO<sub>4</sub><sup>•</sup>) CH (HCH) COO<sup>•</sup> and HCHCH(SO<sub>4</sub><sup>•</sup>)COO<sup>•</sup>. Peroxodisulphate on the thermal decomposition forms sulphate radical anions, SO<sub>4</sub><sup>•</sup> which are capable of forming other intermediate radicals on interaction with various organic substrates in the system [6].

In order to gain further insight into the reaction, the reaction of peroxodisulphate with terphthalic acid with as well as without the presence of AgNO<sub>3</sub> catalyst have been studied and the reaction products are identified. A free radical chain mechanism is proposed and the rate law has been deduced.

### Experimentation

The chemicals used in the present work were of BDH AnalaR Grade except terphthalic acid which was a highly pure sample supplied by Fisher Chemicals. In order to make solutions in water, terphthalic acid was converted to its sodium salt. Redistilled water was used throughout the experimentation. The preparation of various solutions, treatment of reaction vessels and the details of kinetic studies have been described elsewhere [5]. The residual peroxodisulphate estimation was done as has been described by Vasudeva and Wasif [2].

The reaction products were analysed as follows: A series of the reaction mixtures containing 0.1M terphthalic acid and 0.1 M potassium peroxodisulphate were dissolved in distilled water and heated with stirring on an oil bath at about 353K for ten half- life times. After acidifying, the mother liquors were extracted with ether, dried over MgSO<sub>4</sub> and then distilled. The resulting yellow crystalline products contained no sulphur and did not melt upto 613K. About 2.0g of this compound was heated strongly with 5.0g of lime for one hour. The mixture was cooled, acidified with dilute HCl and extracted repeatedly with ether. The combined

\*To Whom all correspondence should be addressed:-

ether fractions were washed with  $\text{NaHCO}_3$  solution, dried over  $\text{MgSO}_4$  and ether removed. The resulting yellow compound was not acidic in nature and was found to melt at 337K. Recrystallisation from petroleum ether, however, raised the melting point to 344K. The compound was thus identified as biphenyl produced by decarboxylation of biphenyl 4,4-dicarboxylic acid [7,8].

### Results

Table (1.A) includes the average rate,  $R$ , and the rate constant,  $k_0$ , of the uncatalysed reaction at 343K when peroxydisulphate concentration was varied from  $(10 \text{ to } 70) \times 10^{-3} \text{ mol}$ . It is observed that  $R$  varies linearly with peroxydisulphate concentration indicating a first order dependence of this reaction on peroxydisulphate concentration whereas  $k_0$  values are independent of the same (Fig. 1.A). Similar behaviour is observed for the reaction catalysed by  $\text{Ag}(1)$  at 313K when the concentrations of terphthalic acid ( $20 \times 10^{-3} \text{ mol}$ ) and of  $\text{AgNO}_3$  ( $5 \times 10^{-4} \text{ mol}$ ) were kept constant. (See Table 1.B and Fig. 1.B).

Table 2.A depicts the values of  $R$  and  $k_0$  for the uncatalysed reaction at 343K when terphthalic acid concentration was varied from  $(10 \text{ to } 70) \times 10^{-3} \text{ mol}$  and peroxydisulphate concentration was kept constant ( $2 \times 10^{-3} \text{ mol}$ ). Similarly the results obtained for the reaction catalysed by  $\text{Ag}(1)$  at 313K, where peroxydisulphate and  $\text{AgNO}_3$  concentrations were

kept constant at  $20 \times 10^{-3} \text{ mol}$  and  $5 \times 10^{-4} \text{ mol}$ , respectively, have been shown in Table (2.B). Clearly, both  $R$  and  $k_0$  are independent of the substance concentration and the reaction, therefore, follows zero-order kinetics in terphthalic acid concentration in both the catalysed as well as the uncatalysed processes.

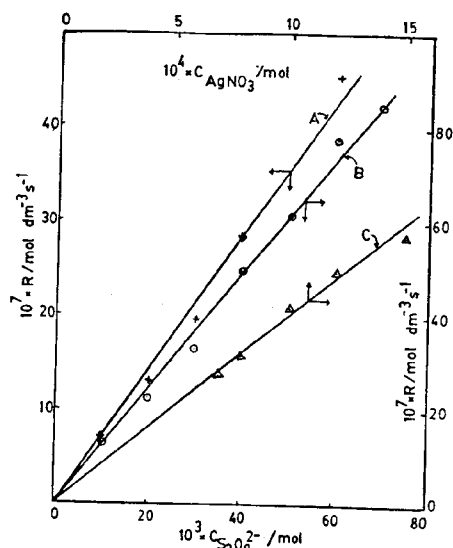


Fig. 1: Dependence of the reaction rate on the concentrations of: (A)-peroxydisulphate at 343K (uncatalysed); (B)-peroxydisulphate at 313K (catalysed) and (C)- $\text{AgNO}_3$  at 313K

Table 1: Rates  $R$ , and rate constant,  $k_0$ , data for the reaction of terphthalic acid with peroxydisulphate when the concentration of terphthalic acid was kept constant at  $20 \times 10^{-3} \text{ mol}$ .

A: The reaction at 343K without Catalyst.

	10	20	30	40	50	60	70
$10^7 R / \text{mol dm}^{-3} \text{ s}^{-1}$	7.2	12.8	19.5	28.4	34.0	45.4	-
$10^5 k_0 / \text{s}^{-1}$	14.1	11.9	13.9	12.0	12.3	13.4	-

B: The reaction at 313K catalysed by  $\text{Ag}(1)$  ( $[\text{AgNO}_3] = 5 \times 10^{-4} \text{ mol}$ )

$10^3 [\text{S}_2\text{O}_8^{2-}] / \text{mol}$	10	20	30	40	50	60	70
$10^7 R / \text{mol dm}^{-3} \text{ s}^{-1}$	13.2	22.5	32.5	49.3	61.5	77.3	84.8
$10^5 k_0 / \text{s}^{-1}$	32.8	32.5	34.2	33.7	32.2	34.0	32.5

Table 2: Rates R, and rate constant,  $k_0$ , data for the reaction of terphthalic acid with peroxodisulphate when the concentration of terphthalic acid was kept constant at  $20 \times 10^{-3}$  mol.

A: The reaction at 343K without Catalyst.

$10^3$ [Acid]/mol	10	20	30	40	50	60	80
$10^7$ R/mol dm <sup>-3</sup> s <sup>-1</sup>	18.1	18.1	18.0	17.0	18.0	18.0	18.1
$10^5$ $k_0$ /s <sup>-1</sup>	32.9	33.2	32.0	32.2	32.7	34.1	33.1

B: The reaction at 313K catalysed by Ag(1) ([AgNO<sub>3</sub>] =  $5 \times 10^{-4}$  mol)

$10^3$ [Acid]/mol	10	20	30	40	50	60	70
$10^7$ R/mol dm <sup>-2</sup> s <sup>-1</sup>	22.0	24.0	22.2	24.6	22.2	22.0	23.9
$10^5$ $k_0$ /s <sup>-1</sup>	34.2	32.5	34.0	32.2	33.8	32.8	34.0

Table 3 shows the values of R and  $k_0$  of the reaction when AgNO<sub>3</sub> concentration was varied from (7 to 15) $\times 10^{-4}$  mol keeping the concentrations of terphthalic acid and peroxodisulphate constant at  $20 \times 10^{-3}$  mol. The reaction is found to follow first-order kinetics in AgNO<sub>3</sub> concentration (Fig. 1.C).

The concentration of peroxodisulphate at different intervals of time in the case of uncatalysed reaction was analysed for several kinetic runs and half-lives were calculated graphically. The values are shown in Table 4.

## Discussion

### The Rate Law:

It is well known that peroxodisulphate decomposes thermally in the absence of a reducing substrate [1-3]. The rate constant for the decomposition of peroxodisulphate under experimental conditions similar to ours have been determined by Vasudeva and Wasif [2]. For the reaction of terphthalic acid with peroxodisulphate catalysed by Ag(1), the reaction rate and the rate constant  $k_0$  can be expressed as,

$$R = \frac{-dC_{S_2O_8^{2-}}}{dt} = k_0 C_{S_2O_8^{2-}} C_{Ag^+}$$

Since the concentration of the catalyst,  $C_{Ag^+}$ , is kept constant during the reaction, the above expression can be reduced to,

$$R = \frac{-dC_{S_2O_8^{2-}}}{dt} = k_0 C_{S_2O_8^{2-}}$$

$$k_0 = k + k_1$$

For both the uncatalysed reaction as well as for the reaction catalysed by Ag(1),  $k$  is the rate constant of the thermal decomposition of peroxodisulphate in the absence of substrate and  $k_1$  is the rate constant for the oxidation reaction.

In addition to the integration method, the order of the reaction was also confirmed by other methods: At various temperatures, the plots of log against time at equal reactant concentrations were found to be straight lines indicating that the order of the reaction is independent of the change in the temperature. The half-life for a first-order reaction is supposed to be independent of the initial concentration: Table 4 shows that the half-lives are almost independent of the acid concentration indicating therefore that the overall order of the reaction should be unity.

Table 3: Rate, R, and rate constant,  $k_0$ , data for the reaction at 313K of terphthalic acid with peroxydisulphate where the concentration of  $\text{AgNO}_3$  is varied and the concentrations of the reactants were kept constant ( $[\text{S}_2\text{O}_8^{2-}] = [\text{Terphthalic Acid}] = 20 \times 10^{-3} \text{ mol}$ ).

$10^4 [\text{AgNO}_3]/\text{mol}$	7	8	10	12	15
$10^7 R/\text{mol dm}^{-3} \text{ s}^{-1}$	27.2	31.5	42.0	49.7	57.5
$10^5 k_0/\text{s}^{-1}$	31.0	34.6	32.7	33.5	34.8

The energy of activation for the overall reaction (uncatalysed) was determined by plotting  $\log k_0$  against  $1/T$ . From the slope of the straight line obtained in this plot, a value  $113 \text{ KJ mol}^{-1}$  was computed for the energy of activation.

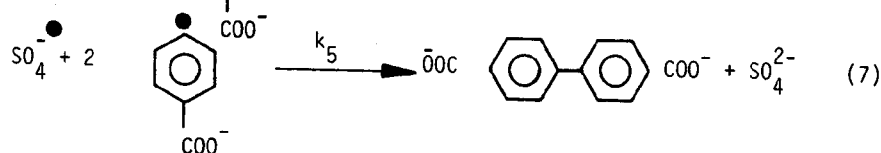
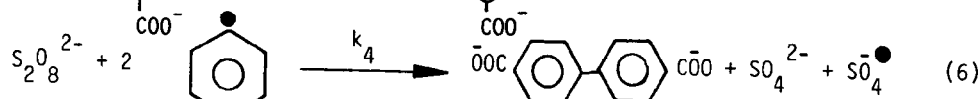
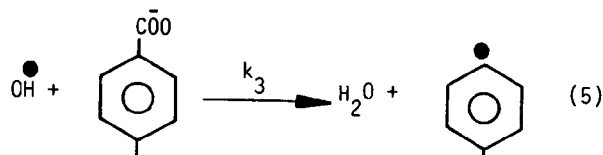
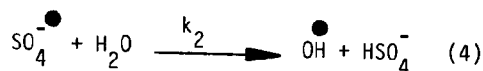
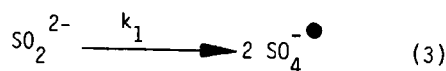
*Proposed Mechanism and Deduction of the Rate Law:*

Both uncatalysed and the catalysed oxidation of terphthalic is found to have zero-order dependence on the acid concentration and result in the formation of biphenyl 4,4'-dicarboxylic acid as reaction product. Also, the reaction is found to be sensitive

to the nature and area of the surface (see Introduction). A free radical chain mechanism for the reaction may be thought to be operative.

The peroxydisulphate furnishes sulphate radical anion,  $\text{SO}_4^{\cdot-}$  on thermal decomposition at its own or in the presence of organic substrate. The  $\text{SO}_4^{\cdot-}$  can attack the organic substrate directly or through an intermediate radical. On the basis of the above mentioned information, the following mechanism seems to be the most probable as it supports the kinetic results obtained for the reaction and also accounts for the products formed.

The Reaction without a catalyst:-



The Reaction Catalysed by Ag(1):-

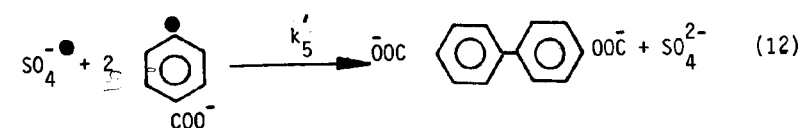
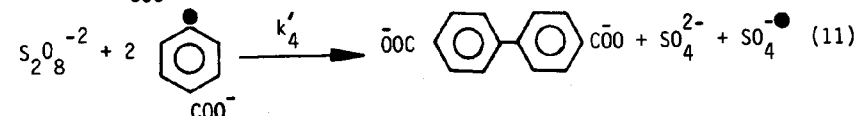
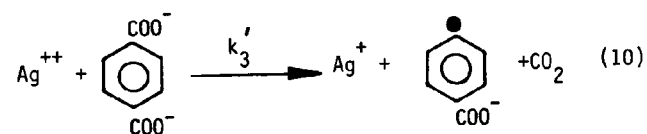
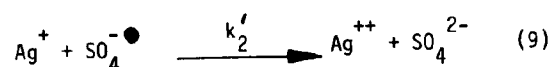
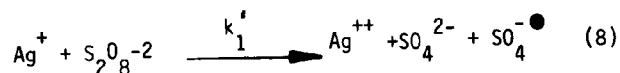


Table 4: The calculated half-lives of the reaction of terphthalic acid with peroxodisulphate at 313K for various initial concentrations of terphthalic acid. The concentration of  $\text{S}_2\text{O}_8^{2-}$  was kept constant at  $20 \times 10^{-3}$  mol.

$10^3$ [Acid]/mol	10	20	30	40	50	60	80
$t_{-1/2}/\text{min}$	34.5	33.7	32.9	35.1	35.3	34.5	32.6

On applications of the steady-state treatment to the above mechanisms, a rate law of the type proposed in equation (1) and (2) is obtained.

#### References

1. D.A. House, *Chem. Rev.*, **62**, 185, (1977).
2. W.C. Vasudeva and S. Wasif, *J. Chem. Soc. Perkin II*, **960**, (1970).
3. W.C. Vasudeva and S. Wasif, *J. Inorg. Nucl. Chem.*, **34**, 3153, (1972).
4. R.O.C. Norman, P.M. Storey and P.R. West, *J. Chem. Soc. Perkin II*, **1087**, (1970).
5. G.M. Khan and M.I. Khalil, *J. Chem. Soc. Pak.*, **3**(3), 125, (1981).
6. G.M. Khan and I.H. Hashmi, *Annali Chimica; Soc. Chim. Italiana*, **72**, 83, (1982).
7. F. Feigl, *Spot Test in Organic Analysis*, Elsevier, New York (1966).
8. H.T. Clarke, A. Handbook of Organic Analysis, E. Arnold, London (1975).