

SILVER CATALYSED OXIDATION OF AMIDES BY  
PEROXYDISULPHATE ION IN AQUEOUS MEDIUM

S Y N O P S I S

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Master of Philosophy in Chemistry

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The use of potassium peroxydisulphate as an oxidant is comparatively recent. It is not a strong oxidising agent. Although the standard redox potential of the system :



is 2.01 Volts ( Latimer<sup>1</sup>). The oxidation by peroxydisulphate ion generally takes place slowly.<sup>2</sup> Because of this fact, peroxydisulphate ion has been largely used for kinetic study of the oxidation of various class of the compounds, and with this oxidant it is very often possible to isolate and identify the intermediate products formed during the course of the reaction.

The work on the kinetic studies involving peroxydisulphate ion upto 1961 has been reviewed by House<sup>3</sup>, Wilmarth and Haim.<sup>4</sup>

The kinetic features of the reactions studied are summarized below :

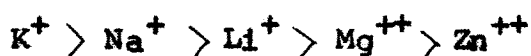
- 1) The reaction is first order in  $S_2O_8^{2-}$  and zero order in reductants.
- 2) The variation of peroxydisulphate ion concentration on the specific rate is governed by the expression :

$$k_c = k_{\min} \frac{\{ [S_2O_8^{2-}] + c \}}{[S_2O_8^{2-}]_0}$$

- 3) The effect of variation of reductant concentration on the specific rate follows the equation :

$$k_c = k_{\max} \frac{[\text{Reductant}]_0}{b + (\text{Reductant})_0}$$

- 4) The magnitude of inhibition of the specific ions is in the order :



- 5) Silver ion is an efficient catalyst for this reaction. The specific rate is related to  $AgNO_3$  concentration by the expression

$$k = k_0 + m C_{Ag^+}$$

Aminoacetamide	Acetylaminacetamide
Where $k_0 = 2.0 \times 10^{-3}$	$3.9 \times 10^{-3}$
and $m = 3.9$	3.3

- 6) The reaction exhibits a negative salt effect of primary exponential type, suggesting that the rate determining process is between two oppositely charged ions.
- 7) Copper sulphate has not been found to be an efficient catalyst for this reaction.
- 8) The reaction is retarded by the addition of allylacetate. This is due to the capture of sulphate radical ions by allyl acetate. Similarly addition of allyl alcohol also retarded the rate of reaction.



- 9) The effect of sulphuric acid is negative. Increase in the concentration of the acid decreases the rate.
- 10) Mole ratio has been found to be one mole of reductant to one mole of peroxydisulphate ion.
- 11) The final oxidation products obtained was formaldehyde and ammonia. These final products were detected by their spot tests as given in Feigl<sup>5</sup>.
- 12) The various activation parameters determined are recorded in Table-1.

TABLE - 1

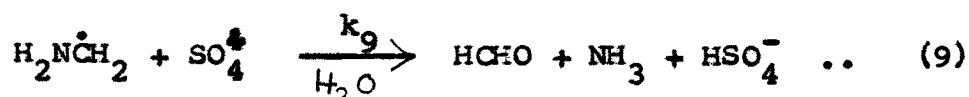
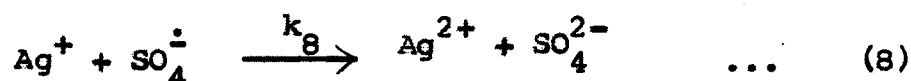
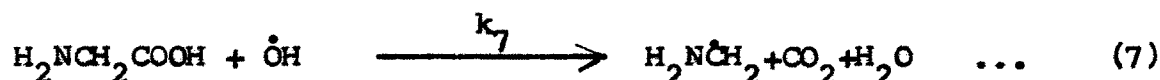
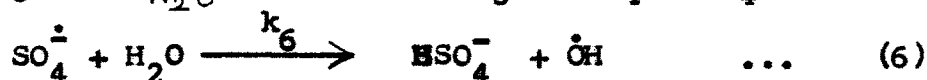
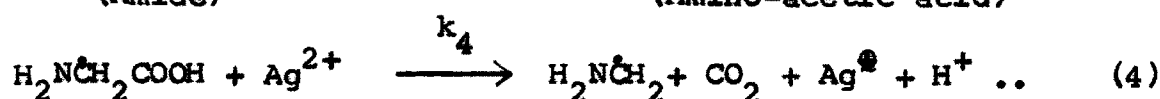
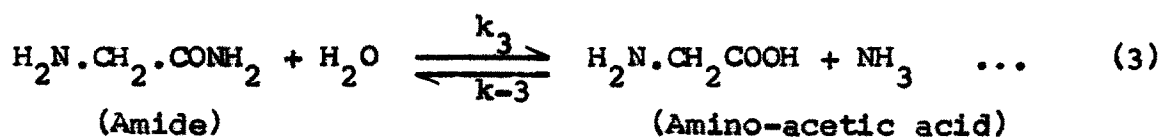
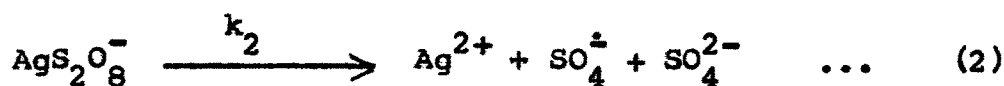
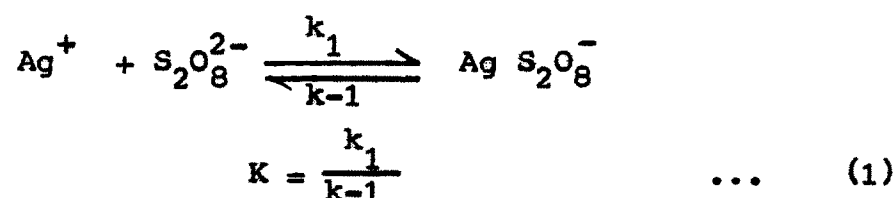
Amide	E K.Cals. mole <sup>-1</sup>	A litre mole <sup>-1</sup> Sec <sup>-1</sup>	$\Delta G^\ddagger$ K.Cals mole <sup>-1</sup>	$\Delta S^\ddagger$ e.u.	$\Delta H^\ddagger$ K.Cals mole <sup>-1</sup> (Graphically)
Amino- acetamide	12.613	7.956 X10 <sup>4</sup>	21.27	-29.77	12.170
Acetyl- -amino- acetamide	13.390	3.690 X 10 <sup>5</sup>	21.11	-26.21	11.745

From the kinetic results summarized above for the oxidation of amides, it can be concluded that the reaction follows first order behaviour with respect to  $S_2O_8^{2-}$  and  $Ag^+$  and zero order with respect to amides. The reaction is inhibited by the addition of allyl acetate pointing out to the existence of a radical mechanism. Further, the large negative value of entropy of activation suggests the formation of the complex between  $Ag^+$  and  $S_2O_8^{2-}$ , also proposed by Beckier and Kijowski<sup>6</sup> and later on supported by Chaltikyan and Beilerian<sup>7</sup>.

## REACTION MECHANISM

The first order with respect to  $S_2O_8^{2-}$  and  $Ag^+$ , zero order with respect to aminoacetamide and acetylaminoacetamide, inhibitory action of metal ions and allyl acetate together with the fact that the mole ratio is one, lead that the following mechanism may be operative.

We discuss here the mechanism for the oxidation of aminoacetamide. The same mechanism can be operative for acetylaminoacetamide. The steps involved in the proposed mechanism are presented in the scheme :



It may be pointed out that the first two steps have also been proposed by Bawn<sup>8</sup> and Margerison and other steps were suggested by Ram<sup>9</sup> Raddy and their Co-workers, in the  $\text{Ag}^+$  catalysed reactions by  $\text{S}_2\text{O}_8^{2-}$  ion.

Applying steady state treatments to the intermediates namely,  $\text{Ag}^{2+}$ ,  $\text{SO}_4^{\cdot-}$ ,  $\dot{\text{O}}\text{H}$  and amino acid radical. The following differential equations set up :

$$\begin{aligned} \frac{d}{dt} [\text{SO}_4^{\cdot-}] &= k_2 [\text{AgS}_2\text{O}_8^-] - k_6 [\text{SO}_4^{\cdot-}] - k_8 [\text{Ag}^+] [\text{SO}_4^{\cdot-}] \\ &\quad - k_9 [\text{H}_2\text{N}\dot{\text{C}}\text{H}_2] [\text{SO}_4^{\cdot-}] + k_5 [\text{H}_2\text{N}\dot{\text{C}}\text{H}_2] [\text{S}_2\text{O}_8^{2-}] = 0 \quad \dots (1) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} [\text{Ag}^{2+}] &= k_2 [\text{AgS}_2\text{O}_8^-] - k_4 [\text{Ag}^{2+}] [\text{H}_2\text{NCH}_2\text{COOH}] \\ &\quad + k_8 [\text{Ag}^+] [\text{SO}_4^{\cdot-}] = 0 \quad \dots (2) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} [\text{H}_2\text{N}\dot{\text{C}}\text{H}_2] &= k_4 [\text{H}_2\text{NCH}_2\text{COOH}] [\text{Ag}^{2+}] - k_5 [\text{H}_2\text{N}\dot{\text{C}}\text{H}_2] [\text{S}_2\text{O}_8^{2-}] \\ &\quad + k_9 [\text{SO}_4^{\cdot-}] [\text{H}_2\text{N}\dot{\text{C}}\text{H}_2] + k_7 [\text{H}_2\text{NCH}_2\text{COOH}] [\dot{\text{O}}\text{H}^-] = 0 \quad \dots (3) \end{aligned}$$

$$\frac{d}{dt} [\dot{\text{O}}\text{H}] = k_6 [\text{SO}_4^{\cdot-}] - k_7 [\text{H}_2\text{NCH}_2\text{COOH}] [\dot{\text{O}}\text{H}] = 0 \quad \dots (4)$$

Solving all the above differential equations we get ,


$$- \frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k' [\text{S}_2\text{O}_8^{2-}] [\text{Ag}^+] \quad \dots (5)$$

$$\text{Where } k' = \left[ \frac{k_2 k_4 k_8}{k_9} \right]^{\frac{1}{2}}$$

Thus the equation (5) shows that the reaction is first order in  $S_2O_8^{2-}$  and also in  $Ag^+$  and Zero order in substrate as found experimentally. The above rate expression does not account for the slight dependence of the first order rate constant on the concentration of peroxydisulphate or the organic substrate. Since the reaction involves a free radical mechanism, it is likely that this slight decrease in the rate constant with increase in the concentration of either of the reactants is due to the presence of trace impurity in them.

Thus the mechanism furnishes a sound explanation of the salient kinetic features of the data obtained in the oxidation of all the above reactions studied.

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[Dr. S. G. SanKpai]

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C E R T I F I C A T E

This is to certify that the  
dissertation entitled ' Silver Catalysed  
Oxidation of Amides by Peroxydisulphate ion  
in Aqueous medium' which is being submitted by  
Shri. Y. N. Bhojani for the award of Degree of  
Master of Philosophy in Chemistry to the Shivaji  
University, Kolhapur (India), is record of his  
own work under my supervision and guidance. The  
work has not been submitted for any other degree  
or diploma to any other University.



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