Silver Ion Catalysed Oxidation of Primary Aliphatic Amines by Potassium Peroxydisulfate — A Kinetic Study

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A detailed kinetic study of the oxidation of propyl-, isopropyl-, butyl- and isobutylamines by potassium peroxydisulfate in presence of silver ions has been carried out in aqueous medium. The effects of silver ion concentration and various neutral salts have been detected and the variation of the order of reaction with respect to amine had been explained. The activity of Ag^+ ion has been correlated with the amine structure and probable rate law and the mechanism has been proposed.

Marshall1) observed the catalytic action of silver ions in the oxidation by peroxydisulfate. Agrawal and Mushran2) and Srivastava and Hambir Singh3) reported the silver ion catalysed oxidation of certain amides by peroxydisulfate while Khare and Bhattacharya4) studied kinetically the morpholine–persulfate reaction. Beileryan *et al.*5) studied certain aspects of the peroxydisulfate oxidation of some simple primary and secondary amines and amino alcohols. In the present investigation silver ion catalysed oxidation of propyl-, isopropyl-, butyl-, and isobutylamines has been studied kinetically and the effect of amine structure on the catalytic activity of silver ions has been discussed.

Experimental

All the chemicals used were of AnalaR or E. Merck's G. R. quality. The amines were distilled before use. The solutions were always freshly prepared in redistilled water. The amine solution and peroxydisulfate solution along with other required solutions were separately thermostated to attain constant temperature (accuracy±0.1 °C). The amine solution is added to peroxydisulfate to start the reaction. Aliquots (5 ml) of the reaction mixture were pipetted out in ice cold water to quench the reaction. The progress of the reaction has been studied by estimating the unreacted peroxydisulfate with use of Kolthoff and Carr's6) iodometric method with necessary modifications.

Preliminary experiments showed that all the reactions follow pseudo first order kinetics in the presence of silver ion when the concentration of amine has been taken in excess. The self decomposition of peroxydisulfate was found to be negligible and therefore not taken into consideration. Since the boiling point of isopropylamine is 34 °C, all the results of the silver ion catalysed oxidation of isopropylamine have been given at 20 °C, while the oxidation of the other three amines have been carried out at 30 °C. The rate of uncatalysed oxidation was found to be quite small for all the four amines.

Results and Discussion

Effect of Silver Ion Concentration on the Rate of Oxidation. We see that the rate of reaction increases with increase in the concentration of Ag^+ ions for all the four reactions. Straight lines were obtained for the plots of pseudo first order rate constant k *versus* (Ag^+) and the values of intercepts are in good agreement with the rate of uncatalysed reaction (k_0).

Order with Respect to Each Reactant. Since the values of pseudo first order rate constants were found to be fairly constant during all the sets, the order with respect to peroxydisulfate is unity.

The values of order of reaction with respect to amine at different silver ion concentrations in each case are given in Table 2.

The order with respect to amine decreases with the increase in silver ion concentration.

According to Moelwyn-Hughes7) the uncatalysed and catalysed reactions proceed simultaneously in the presence of a catalyst, and the relation $k=k_0+k_c$ (catalyst), holds, where in k is observed overall pseudo first order rate constant in the presence of catalyst silver ion.

k_0 is pseudo first order rate constant for uncatalysed reaction and k_c, is catalytic constant.

The above relation holds for all the four amines, the k_c values for different concentrations of (Ag^+) being fairly constant within the limits of experimental error (Table 3).

Effect of Neutral Salts. The values of rate constants in the presence of different concentrations of

TABLE 1.
(Pot. peroxydisulfate) 0.005M (Amine) 0.20M

Isopropylamine		Propylamine		Butylamine		Isobutylamine	
$(Ag^+) \times 10^4$ M	$k\times 10^2$ min^{-1}	$(Ag^+) \times 10^5$ M	$k\times 10^2$ min^{-1}	$(Ag^+) \times 10^5$ M	$k\times 10^2$ min^{-1}	$(Ag^+) \times 10^5$ M	$k\times 10^2$ min^{-1}
—	0.1019	—	0.1300	—	0.1123	—	0.1327
2.5	0.6064	6.0	0.7196	5.0	0.6121	5.0	0.5058
5.0	1.156	10.0	1.141	10.0	1.131	10.0	0.8752
7.5	1.709	15.0	1.605	15.0	1.609	15.0	1.197
10.0	2.251	20.0	2.054	20.0	2.122	20.0	1.562
12.5	2.756	25.0	2.570	30.0	3.247	30.0	2.239

Table 2.
(Pot. peroxydisulfate) 0.005M

(Ag^+) M	Concn of amine C' (M)	Concn of amine C'' (M)	Rate Const. $\times 10^2$ k' min^{-1}	Rate Const. $\times 10^2$ k'' min^{-1}	Order of reaction n
Isopropylamine					
—	0.40	0.20	0.2023	0.1019	0.9897
2.5×10^{-4}	0.40	0.20	1.120	0.6064	0.8870
5.0×10^{-4}	0.40	0.20	2.002	1.156	0.7920
10.0×10^{-4}	0.40	0.20	3.736	2.251	0.7308
Propylamine					
—	0.40	0.30	0.2505	0.1876	1.007
6.0×10^{-5}	0.20	0.10	0.7196	0.4683	0.6192
20.0×10^{-5}	0.20	0.10	2.054	1.569	0.3880
25.0×10^{-5}	0.20	0.10	2.570	2.010	0.3528
Butylamine					
—	0.30	0.20	0.1586	0.1123	1.002
5.0×10^{-5}	0.20	0.10	0.6121	0.4030	0.6332
10.0×10^{-5}	0.20	0.10	1.131	0.8090	0.4833
15.0×10^{-5}	0.20	0.10	1.609	1.200	0.4011
Isobutylamine					
—	0.30	0.20	0.1991	0.1327	1.000
5.0×10^{-5}	0.20	0.10	0.5058	0.3163	0.6774
20.0×10^{-5}	0.20	0.10	1.562	1.168	0.4192
30.0×10^{-5}	0.20	0.10	2.239	1.718	0.3817

neutral salts are given in Table 4.

Table 4 indicates that the rate of oxidation decreases with the addition of neutral salts, *i.e.* with increase in ionic strength.

The order of reaction with respect of amine was found to change with the amine concentration as well as with the temperature and it was not possible to calculate the over all rate constant and hence the energy parameters.

Rate Laws and Discussion. The experimental results show that all the four amines behave similarly. Hence, the following general rate law is proposed for all the four amines.

$$\frac{-d(S_2O_8^{2-})}{dt} = \underbrace{k_s(Am)(S_2O_8^{2-})}_{\text{Uncatalysed path}} + \underbrace{k_c(Ag^+)(S_2O_8^{2-})}_{\text{Catalysed path}} \quad (8)$$

where k_s is second order rate constant for uncatalysed reaction and k_s (Am) $=k_0$ pseudo first order rate constant for uncatalysed reaction. The rate law suggests that in the presence of catalyst both uncatalysed and catalysed reactions proceed simultaneously. In the absence of a catalyst the reaction proceeds through the path involving the first term only and the order with respect to amine should be one. Similar results were reported by Chaltykyan and Beileryan,[8] during the course of their study of the uncatalysed oxidation of some simple primary and secondary amines. In the presence of high concentration of Ag^+ ions, k_0 is negligible as compared with k_c (Ag^+), *i.e.* the reaction proceeds entirely along the second path and the order with respect to amine would be zero. Naturally, at moderate concentrations of Ag^+ which have been used in the present investigation, the order with respect to amine is fractional. This was found to be actually the case. With further increase

Table 3.
(Pot. peroxydisulfate) 0.005M (Amine) 0.20M

Isopropyl- (Ag^+) $\times 10^4$ M	Isopropyl- k_c $l\cdot mol^{-1}\cdot min^{-1}$	Propyl- (Ag^+) $\times 10^5$ M	Propyl- k_c $l\cdot mol^{-1}\cdot min^{-1}$	Butyl- (Ag^+) $\times 10^5$ M	Butyl- k_c $l\cdot mol^{-1}\cdot min^{-1}$	Isobutyl- (Ag^+) $\times 10^5$ M	Isobutyl- k_c $l\cdot mol^{-1}\cdot min^{-1}$
2.5	20.18	6.0	98.26	5.0	98.96	5.0	74.62
5.0	21.08	10.0	101.10	10.0	101.87	10.0	74.25
7.5	21.42	15.0	98.33	15.0	99.78	16.0	70.95
10.0	21.49	20.0	96.20	20.0	100.48	20.0	71.46
12.5	21.43	25.0	97.60	30.0	104.45	30.0	69.88
Average	21.08		98.30		101.31		72.33
From graph	21.22		100.00		102.52		71.27

Table 4.
(Pot. peroxydisulfate) 0.005M

	Isopropyl-		Propyl-		Butyl-		Isobutyl-	
Amine Concn M →	0.20		0.10		0.20		0.20	
(Ag^+) M →	10.0×10^{-4}		20.0×10^{-5}		10.0×10^{-5}		10.0×10^{-5}	
Salt	Salt concn	$k\times10^2$ min^{-1}	Salt concn	$k\times10^2$ min^{-1}	Salt concn	$k\times10^2$ min^{-1}	Salt concn	$k\times10^2$ min^{-1}
—	—	2.251	—	1.569	—	1.182	—	0.8752
K_2SO_4	0.0075	2.004	0.015	1.271	0.010	0.8112	0.020	0.7399
K_2SO_4	0.0150	1.833	0.025	1.005	0.015	0.6997	0.025	0.7150
Na_2SO_4	0.0075	2.113	0.010	1.303	0.015	0.8015	0.004	0.8537
Na_2SO_4	0.0150	1.929	0.020	1.086	0.020	0.7187	0.008	0.8131
$NaClO_4$	0.0075	2.062	0.005	1.392	0.005	1.008	0.008	0.8220
$NaClO_4$	0.0150	1.871	0.030	1.112	0.012	0.8604	0.020	0.7511

in silver ion concentration the order should decrease, approaching zero. This is also in agreement with the observed data (Table 2).

The second term in the rate law also suggests that the reaction proceeding *via* catalysed path occurs between two oppositely charged ions, and negative salt effect should be observed. This was found also to be the case.

In the presence of excess amine as in the present study, Eq. 1 is reduced to

$$\frac{-\mathrm{d}(S_2O_8^{2-})}{\mathrm{d}t} = [k_o+k_c(Ag^+)](S_2O_8^{2-}) \qquad (2)$$

At particular Ag^+ concentration,

$$[k_o+k_c(Ag^+)] = k, \text{ the over all rate constant} \qquad (3)$$

Equation 3 is similar to that proposed by Moelwyn-Hughes, which has been experimentally found to hold good.

Effect of Amine Structure on the Oxidation Rate. Since the rate constants for the uncatalysed oxidation of all the four amines are of similar magnitude, the catalytic activity of Ag^+ ion has been compared for the values of k_c. To compare the results of isopropyl amine with propylamine, the value of k_c of propylamine was determined at 20 °C under identical conditions and found to be 47.52 l mol^{-1} min^{-1}.

Chaltykyan and Beileryan[9] suggested that the catalytic activity of silver ions in the oxidation of amines with peroxydisulfate increases with decreasing basicity of amines. Nikolaev and Sychev[10] and other workers have reported that the catalytic activity of the metal ion is directly proportional to the instability of metal amine complex.

The order of stability of the silver amine complex and P_{kb} values of the four amines are: butyl-<isobutyl-[11] and propyl-<isopropyl-. The catalytic activity of Ag^+ ions should therefore be in the reverse order which was actually the case.

Mechanism. Taking into consideration all the experimental evidences, the following mechanism has been proposed. Firstly Ag(III)[12,13] will form (rate determining step) which will readily oxidizes the amine to hydroxyl amine derivative

$$S_2O_8^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2SO_4^{\cdot-} \qquad (3a)$$

$$\frac{(SO_4^{\cdot-})^2}{(S_2O_8^{2-})} = k_e \text{ (Equilibrium constant)} \qquad (3b)$$

$$2SO_4^{\cdot-} + Ag^+ \xrightarrow[\text{Rate determining step}]{\text{slow}} 2SO_4^{2-} + Ag^{3+} \qquad (4)$$

$$Ag^{3+} + R\cdot NH_2 + H_2O \xrightarrow{\text{Rapid}} R\cdot NHOH + Ag^+ \qquad (5)$$

This explains the rate law proposed for the catalysed path,

$$\frac{-\mathrm{d}(S_2O_8^{2-})}{\mathrm{d}t} = k_2(Ag^+)(SO_4^{\cdot-})^2$$

from Eq. 3b.

$$(SO_4^{\cdot-})^2 = k_e(S_2O_8^{2-}), \text{ then}$$

$$\frac{-\mathrm{d}(S_2O_8^{2-})}{\mathrm{d}t} = k_2k_e(Ag^+)(S_2O_8^{2-})$$
$$= k_c(Ag^+)(S_2O_8^{2-})$$

where $k_c = k_2k_e$ is catalytic constant.

The stoichiometric ratio determined for all the four amines is 1 : 1, showing that one molecule each of the oxidant and reductant have been consumed in the reaction.

The oxidation products have been isolated from the reaction mixture using solvent extraction technique. The presence of two compounds other than the excess of amine have been found by thin layer chromatography. From the samples obtained hydroxyl amine derivative and oxime have been detected.[14,15] The oximes formed were due to autooxidation of hydroxylamine derivatives[16,17] as the pH of the systems is above 7. This might be due to reduction of catalyst Ag^+ ion left in the system to Ag by the hydroxylamine derivatives.[18] Black particles of silver were observed when the system was left for a long time.

Lebedev and Kazarnovskii[19] also found oximes, hydroxyl amines of hydroxyamic acids as end products in their study on the catalytic oxidation of aliphatic amines with hydrogen peroxide. Bacon and Stewart[20] also reported aldoximes as the products of oxidation of the silver catalysed peroxydisulfate oxidation of amine.

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