Kinetics and Mechanism of the Oxidation of Aliphatic Diamines by Peroxodisulphate

Sreekantha Babu Jonnalagadda *
Department of Chemistry, University of Nairobi, P.O. Box 30197, Nairobi, Kenya
Veena Choudary and A. K. Bhattacharya
School of Studies in Chemistry, Vikram University, Ujjain 456 010, India

The kinetics of the oxidation of two aliphatic diamines (1,2-diaminoethane and 1,3-diaminopropane) with potassium peroxodisulphate in aqueous medium were investigated under identical conditions. The rates of the uncatalysed reactions were not influenced by changing the ionic strength or by the presence of allyl acetate. An analysis of the dependence of the rates of oxidation shows that the reactions are second order, being first order in both diamine and peroxodisulphate ion. Activation parameters for uncatalysed reactions were reported. The catalytic effect of the cations Cu^{2+} and Ag^+ on the rate of oxidation of diamines is compared. On the basis of kinetic studies and product analysis the rate laws and reaction mechanisms for both uncatalysed and silver-ion catalysed reactions are proposed.

Although the oxidation of organic and inorganic substrates with peroxodisulphate has been studied extensively,[1-5] little attention has been paid to reactions with aliphatic amines,[6-9] particularly with respect to the oxidation kinetics of those diamines which form chelates with metal catalysts. The oxidation of diamines with different oxidising agents [10,11] and by electrocatalytic methods [12] has been reported earlier. This paper presents the results of kinetic studies of the oxidation of 1,2-diaminoethane (DAE) and 1,3-diaminopropane (DAP) with peroxodisulphate ion in aqueous solution.

Table 1. Dependence of reaction rate on the peroxodisulphate ion concentration. [diamine] 0.20M, 45 °C

[peroxodisulphate]/M	DAE	DAP
	10^4k_o/s^{-1}	10^4k_o/s^{-1}
0.004	1.494	2.838
0.005	1.502	2.857
0.006	1.505	2.877

Table 2. Pseudo-first-order (k_o) and second-order (k_s) rate constants for the oxidation reaction of 1,2-diaminoethane (DAE) and 1,3-diaminopropane (DAP) with potassium peroxodisulphate (0.005M) at different temperatures in aqueous solution

Temp. (°C)	[diamine]/ M	DAE		DAP	
		10^5k_o/s^{-1}	10^4k_s/dm^3 mol^{-1} s^{-1}	10^5k_o/s^{-1}	10^4k_s/dm^3 mol^{-1} s^{-1}
30	0.10	1.953	1.953	3.768	3.768
30	0.20	3.940	1.970	7.607	3.804
35	0.10	3.165	3.165	6.148	6.148
35	0.20	6.320	3.160	12.30	6.150
40	0.10	4.907	4.907	9.367	9.367
40	0.20	9.827	4.914	18.53	9.625
45	0.10	7.533	7.533	14.32	14.32
45	0.15	11.23	7.487	21.38	14.25
45	0.20	15.02	7.510	28.57	14.29
45	0.30	22.48	7.493	42.63	14.21

Experimental

All chemicals used were of AnalaR or Merck's G.R. quality. The diamines were distilled before use. The requisite solutions were freshly prepared in doubly distilled water, transferred into black bottles, and thermostatted separately to constant temperature (±0.1 °C). The reaction was started by the addition of peroxodisulphate to the amine solution. Its progress was followed by pipetting 5 cm^3 portions of reaction mixture at suitable intervals into flasks containing ice–water (50 dm^3), glacial acetic acid (2 dm^3), and 40% potassium iodide solution (8 dm^3) to quench the reaction. Unchanged peroxodisulphate was estimated using Kolthoff and Carr's iodometric method [13] after incubation for 2 h.

For the t.l.c. experiments silica gel 60F on 0.2 mm thickness plates activated for 15 min at 110 °C was used. Chromatograms were developed by the ascending method using methanol with a few drops of ammonia solution and visualized with iodine.

60-MHz ^{1}H N.m.r. spectra was taken for $CDCl_3$ solutions using tetramethylsilane as external standard on a Perkin-Elmer R12B spectrometer.

Preliminary kinetic experiments showed that for both diamines, catalysed and uncatalysed oxidations follow pseudo-first-order kinetics, when the concentration of amine is taken in excess. The self-decomposition rate of peroxodisulphate ion was found to be insignificant under these experimental conditions and therefore was not taken into consideration.

Results

Plots of log [peroxodisulphate] *versus* time yielded straight lines, from whose gradients the pseudo-first-order rate constants, k_o, were calculated. A plot of k_o against the initial concentration of diamine gave a good straight line passing through the origin in both cases. No significant change occurred in the value of k_o when the concentration of peroxodisulphate was varied while keeping the diamine in excess, showing that the order with respect to peroxodisulphate is unity (Table 1).

Thus, both reactions are of first order with respect to both oxidant and substrate.[14] The pseudo-first-order rate constant k_o and overall second-order rate constant k_s for different initial concentrations of DAE and DAP at different temperatures are summarised in Table 2.

Influence of Neutral Salts and Allyl Acetate on Oxidation Rate.—The k_o values determined in the presence of varying concentrations of neutral salts (Table 3) showed no marked change in the rate of oxidation, suggesting that the rate-limiting step does not involve two charged species. Further, the lack of effect by allyl acetate, an effective sulphate radical trap,[14,15] on the rate of disappearance of peroxodisulphate ion

Table 3. Effect of neutral salts and allyl acetate on the rate of oxidation. [diamine] 0.20M, [peroxodisulphate] 0.005M, 30 °C

Additive	Concn. (M)	DAE 10^4k_o/s^{-1}	DAP 10^4k_o/s^{-1}
No salt		0.394	0.761
Sodium sulphate	0.006	0.397	0.759
Sodium sulphate	0.012	0.391	0.755
Potassium sulphate	0.008	0.392	0.758
Potassium sulphate	0.016	0.390	0.751
Allyl acetate	0.008	0.390	0.755
Allyl acetate	0.016	0.385	0.748

Table 4. Influence of alkali and acid on the rate of oxidation. [diamine] 0.20M, [peroxodisulphate] 0.005M, 40 °C

Alkali or acid		DAE	DAP
Name	Concn. (M)	10^4k_o/s^{-1}	10^4k_o/s^{-1}
No alkali or acid		0.983	1.853
Potassium hydroxide	0.024	0.984	1.878
Potassium hydroxide	0.040	0.986	1.883
Hydrochloric acid	0.050	0.924	1.763
Hydrochloric acid	0.090	0.864	1.616
Hydrochloric acid	0.20	0.565	0.988
Hydrochloric acid	0.50	0.058	0.102
Hydrochloric acid	1.00		

Table 6. Dependence of order of reaction with respect to diamine on silver ion concentration and temperature

(i) Order in DAE, peroxodisulphate 0.005M

10^6[Ag$^+$]/	[DAE]/M				Order
M	C'	C''	$10^4k'$/s^{-1}	$10^4k''$/s^{-1}	n
At 30 °C					
	0.10	0.20	0.196	0.394	1.007
1.0	0.10	0.20	1.100	1.650	0.585
2.0	0.10	0.20	2.380	2.897	0.283
3.0	0.10	0.20	3.885	4.142	0.095
At 35 °C					
	0.10	0.20	0.317	0.632	0.996
1.0	0.10	0.20	1.855	2.208	0.251
2.0	0.10	0.20	3.406	3.754	0.140
3.0	0.10	0.20	5.008	5.316	0.086

(ii) Order in DAP, peroxodisulphate 0.005M

10^6[Ag$^+$]/	[DAP]/M				Order
M	C'	C''	$10^4k'$/s^{-1}	$10^4k''$/s^{-1}	n
At 30 °C					
	0.10	0.20	0.377	0.701	1.014
5.0	0.10	0.20	2.272	2.797	0.300
10.0	0.10	0.20	4.098	4.797	0.227
15.0	0.10	0.20	6.317	6.917	0.131
At 35 °C					
	0.10	0.20	0.615	1.23	1.00
5.0	0.10	0.20	3.482	4.098	0.235
10.0	0.10	0.20	6.345	6.966	0.135
15.0	0.10	0.20	9.219	9.834	0.093

Table 5. Influence of cations as catalyst on the oxidation rate and the catalytic constants (k_c). [diamine] 0.20M, [peroxodisulphate] 0.005M, 30 °C

	DAE			DAP		
Catalyst	10^6[cat]/M	10^4k/s^{-1}	k_c/dm^3 mol^{-1} s^{-1}	10^6[cat]/M	10^4k/s^{-1}	k_c/dm^3 mol^{-1} s^{-1}
No catalyst		0.394			0.761	
Copper sulphate	4.0	0.504	2.75	5.0	1.605	16.38
Copper sulphate	6.0	0.564	2.83	15.0	3.323	17.08
Copper sulphate	10.0	0.679	2.85	25.0	4.980	16.88
Silver nitrate	1.0	1.650	125.6	5.0	2.797	40.58
Silver nitrate	2.0	2.897	125.1	10.0	4.797	40.37
Silver nitrate	3.0	4.152	125.5	15.0	6.917	41.03
Silver nitrate	5.0	6.608	124.3	25.0	11.14	41.52

(Table 3) suggests that the rate-limiting step does not involve any radical species.

Dependence on Hydrogen-ion Concentration.—While the presence of different concentrations of alkali showed no effect on k_o, the addition of acid, *i.e.* H$^+$, retarded the reaction. In highly acidic solutions no reaction was observed (Table 4). This suggests that the protonated species of amine is not the reactive species during the oxidation reaction.[1,7,16] The decrease in value of k_o might also be attributed, to some extent, to the stabilizing effect by salt formation of the amine.

Cations as Catalysts for Oxidation.—Among the different cations examined only Cu^{2+} and Ag$^+$ were found to have a catalytic effect on the oxidation reaction between diamines and peroxodisulphate ion (Table 5). As Ag$^+$ showed a marked effect on the reaction rate, the silver-catalysed oxidation kinetics were studied in detail. A plot of [Ag$^+$] *versus* k, the pseudo-first-order rate constant for the catalysed reaction gave a straight line with k_c, the catalytic constant for Ag$^+$, as the slope and k_o, the pseudo-first-order rate constant for the uncatalysed reaction, as the intercept. The k_o values so obtained were in good agreement with those determined experimentally. Further, the k values were found to be fairly constant at different initial concentrations of $S_2O_8^{2-}$, showing a clear first-order dependence of the reaction on peroxodisulphate ion. However, the order with respect to amine as calculated by van't Hoff's method was found to decrease with increasing [Ag$^+$] and tends to zero at very high [Ag$^+$]. The order with respect to substrate was also found to decrease with increasing temperature (Table 6).

Effect of Addition of Neutral Salts and Allyl Acetate on the Silver-ion Catalysed Reaction.—The observed negative salt effect with neutral salts suggests that the rate-limiting step involves oppositely charged species, while the retardation of rate by allyl acetate points to the involvement of radical species (Table 7).

Activation Parameters.—The activation parameters for the uncatalysed oxidation of each diamine with peroxodisulphate ion were calculated using the mean k_s values from Table 2. The enthalpy of activation and entropy of activation were calculated at the mean experimental temperature, 310.5 K (Table 8).

The variation of order with respect to diamine with varying

Table 7. Effect of neutral salts on the rate of oxidation in the silver-ion catalysed reaction. [diamine] 0.20M, [peroxodisulphate] 0.005M, 30 °C

Salt		DAE + $[Ag^+]$ 4.0×10^{-6}M	DAP + $[Ag^+]$ 25.0×10^{-6}M
Name	Concn. (M)	$10^4k/s^{-1}$	$10^4k/s^{-1}$
No salt		5.512	11.14
Sodium sulphate	0.006	4.657	10.26
Sodium sulphate	0.012	4.002	9.047
Potassium sulphate	0.008	4.472	9.940
Potassium sulphate	0.016	3.907	8.827
Allyl acetate	0.016	2.298	5.191
Allyl acetate	0.050	1.395	3.152

Table 8. Activation parameters: energy, enthalpy, and entropy of activation and frequency factor

	E_a/ kJ mol^{-1}	$\Delta H^‡$/ kJ mol^{-1}	A/dm^3 mol^{-1} s^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
DAE	72.5	69.92	6.2×10^{10}	−46.95
DAP	71.3	68.72	7.5×10^{10}	−45.42

catalyst concentration and temperature conditions did not enable us to calculate the activation parameters for the Ag^+-catalysed reaction.

Stoicheiometric Ratio and Product Analysis.—Oxidation products from the uncatalysed and silver-ion catalysed reactions were isolated from the aqueous mixture by extraction with diethyl ether and hydroxylamine derivatives were identified as products for both the diamines by the methods described by Endres and Kaufmann [17] and Feigl and Silva.[18] The quantitative estimation of the hydroxylamine derivative for the silver-ion catalysed reaction by the indoxine complex method [sample (2 dm^3)–1% 8-hydroxyquinoline (2 dm^3) in ethanol + 1M-sodium carbonate (2 dm^3), incubation for 1 h, absorbance at 710 nm] as described by Berg and Becker [19] showed a 60% yield. The silver-ion catalysed reaction was repeated with a 1 : 1 molar ratio of DAE and peroxodisulphate. After 72 h the reaction mixture was slightly acidified (with HCl), and concentrated by fractional distillation at low pressure. Then from the neutralised concentrate water was completely removed by adding acetone (*ca.* 500 dm^3) and anhydrous magnesium sulphate. After removing the solvent, t.l.c. with methanol as eluant showed two products other than traces of DAE. The product with lower R_F was separated on a silica gel column using methanol as eluant, and showed ^{1}H δ ($CDCl_3$) 2.78 (m, CH_2–CH_2), 1.9, and 1.1. These latter peaks could be assigned the protons on the three hetero-atoms, indicating the product is a hydroxylamine derivative.

Discussion

Rate Laws.—In general both diamines behave similarly in uncatalysed and catalysed reactions. Hence an identical rate law (1) is proposed where k_s is the second-order rate constant

$$-d[S_2O_8^{2-}]/dt = \underset{\text{(uncatalysed path)}}{k_s[\text{diamine}][S_2O_8^{2-}]} + \underset{\text{(catalysed path)}}{k_c[Ag^+][S_2O_8^{2-}]} \quad (1)$$

for the uncatalysed reaction and k_s[diamine] = k_o. In the presence of catalyst, the reaction proceeds through both catalysed and uncatalysed pathways. The uncatalysed reaction follows second-order kinetics, being first order in diamine and in peroxodisulphate ion.

In the presence of the moderate concentrations of Ag^+ which were used in the present investigations, the order with respect to amine is fractional.[20] A further increase in catalyst concentration causes the order to decrease, finally approaching zero, making the value of k_o negligible compared with $k_c[Ag^+]$.[21] Then the reaction proceeds entirely along the second pathway. The second term in the rate law suggests that the reaction proceeding *via* the catalysed pathway occurs between two oppositely charged ions, as expected from the observed negative salt effect. In the presence of excess of amine, as in the present study, equation (1) reduces to (2). At a particular

$$-d[S_2O_8^{2-}]/dt = (k_o + k_c[Ag^+])\,[S_2O_8^{2-}] \quad (2)$$

silver ion concentration, $(k_o + k_c[Ag^+]) = k$, the overall pseudo-first-order rate constant for the catalysed reaction.

Mechanism.—(i) *Uncatalysed oxidation.* The rate-limiting step may be the initial formation of a oxidant–substrate adduct, the activated complex.[22] By nucleophilic attack of the lone-pair electrons of the amino-group on peroxodisulphate ion,[23,24] oxidation of substrate occurs within the adduct by electron transfer and it decomposes rapidly giving an $^-$N–O$^-$ species which readily undergoes subsequent steps, giving products (Scheme 1).

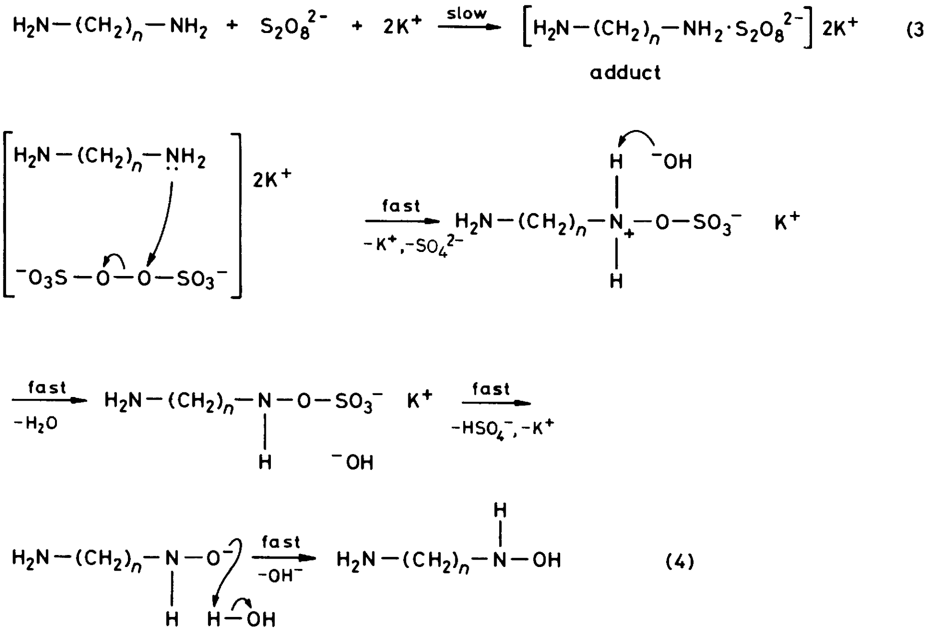
(ii) *Silver-ion catalysed reaction.* Reactions (5)—(10), consistent with the observed kinetics, involving Ag^{II} and Ag^{III} are proposed [5,25,26] for the diamine oxidation by $S_2O_8^{2-}$ in alkaline medium.

The observed rate law for the catalysed path can by obtained both by the rate-limiting reaction for the formation of Ag^{II} [equation (5)] and by the rapid equilibrium reaction (7) followed by the slow step of (8). However, consideration of the limited effect of allyl acetate (Table 6), an effective sulphate radical ion scavenger, which does not completely inhibit the catalysed path [interference with equation (7)] and the clean second-order kinetics [5] at higher concentrations of silver ion suggest an oxidation mechanism involving Ag^{II} (Scheme 2). However, since this mechanism involves aminyl as well as hydroxyl radicals, it is possible that it does not represent a major route to the hydroxylamine. An alternative mechanism involving a developing nitrenium ion due to interaction between the diamine and Ag^{III} is also proposed (Scheme 3).

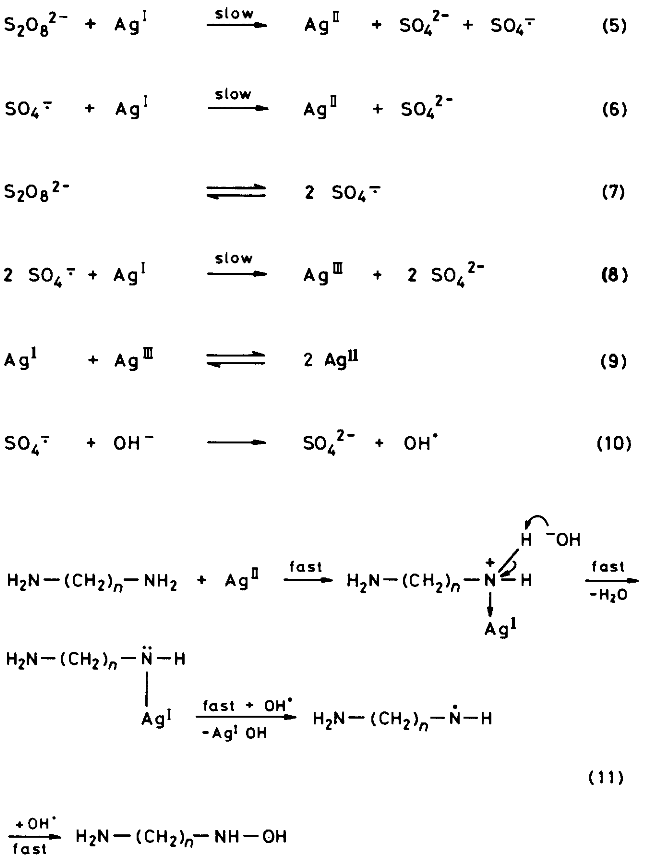
Hydroxylamine derivatives have been frequently reported as products of oxidation of aliphatic amines with hydrogen peroxide.[10,23,27] Lebedev and Kazarnovskii [27] have suggested the formation of an amine oxide intermediate species in amine–H_2O_2 reactions. Chaltykyan *et al.* during oxidation studies with $S_2O_8^{2-}$ and benzoyl peroxide also suggested the involvement of the lone pair electrons of the amino-group with the oxidising agent as the first step.

The proposed mechanism involving hydroxylamine formation through an N–O path is also supported by the reported mechanism of *N*-hydroxylation of amines by cytochrome P450 to their corresponding hydroxylamine. Pack and Loew have reported that the formation of an *N*-oxide intermediate would substantially lower the barrier to hydroxylamine formation and ruled out pathways to direct insertion of O into an NH bond or H abstraction followed by recombination of the OH species with N.[28]

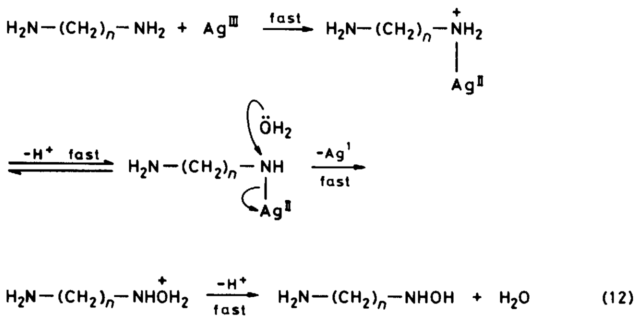
Amine Structure.—In the uncatalysed reaction the higher oxidation rate of DAP compared with that of DAE under identical conditions suggests that the increase in chain length between the two terminal amino-groups, *i.e.* the number of



Scheme 1. n = 2 or 3



Scheme 2.



Scheme 3.

CH_2 groups, from 2 to 3 facilitates the rate of oxidation. Similar kinetics were observed by Kahr and Berther while studying the oxidation of these amines with hydrogen peroxide.[10]

For the cation-catalysed reaction, a comparison of the catalytic activities of the cations Ag^+ and Cu^{2+} on the oxidation of DAE and DAP shows a greater catalytic activity for Ag^+ in the case of DAE, and Cu^{2+} in the case of DAP. Nikolaev and Sychev [29] have suggested that the lower the stability of the metal–reductant complex, the greater is the catalytic activity of the metal ion. The stability constant of the Ag^+–amine complex of DAE is less than that of DAP, whereas the reverse is true in case of the complex with Cu^{2+}.[30] The chelates of Cu^{2+} ion with DAP are significantly less stable than those with DAE. The large difference in stability of the chelates between these two amines with Cu^{2+} arises from a less favourable entropy change in formation of a six-membered ring.[29]

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