CHAPTER VI

DISCUSSION
In the present chapter, it is proposed to interpret and discuss the results obtained in the foregoing chapters.

DETECTION OF OXIDATION PRODUCTS:

The qualitative analysis in each case revealed the presence of hydroxylamine derivative and oxime. It may, however, be pointed out that hexamethylenetetramine on oxidation gave a fainter indication of these groups in comparison to the other three amines whose oxidation has been studied by the present author. The methods applied for the prementioned identifications were those used by Jayson, Scholes and Weiss in their study of the action of X-rays on some aliphatic amines in aqueous solution. They detected the presence of hydroxylamine and oxime by methods described by Endres and Kaufman which in substance are given below:

(1) Detection of hydroxylamine:

2 ml. of sulphanilic acid solution (5.25 gms. in 100 ml. of 20% v/v acetic acid) and 0.2 ml. of iodine reagent (0.6 gm. in 100 ml. of glacial acetic acid) were added to 10 ml. of the aliquot portion of reaction mixture obtained after oxidation of amine by peroxydisulphate. After 15 minutes at room temperature, the excess of iodine was removed with a few drops of aqueous sodium thiosulphate (2% w/v) and the solution immediately treated with α-naphthylamine (0.6 gm. in 100 ml. of 5% acetic acid). A more or less
pronounced red colour appears according to the amount of hydroxylamine.

(2) Detection of oxime:

0.2 ml. of iodine reagent was added to 10 ml. of the aliquot portion of the reaction mixture obtained after oxidation by peroxydisulphate. The solution was brought quickly to boil and cooled at once in running water. 2 ml. of sulphanilic acid and a further 0.1 ml. of iodine reagent were added. The qualitative analysis was then continued as described above for hydroxylamine.

The difference between the tests for hydroxylamine and oxime is that the former involves oxidation to nitrite by iodine at room temperature, whereas the latter at a higher temperature and therefore the method of detection for oxime is known as the "hot iodine oxidation" method.

It has been reported in literature\(^3\) that persulphuric acid, hydrogen peroxide, peracetic acid and perbenzoic acid bring about the addition of oxygen to amines. Lebedov and Kazarnovskii\(^4\) in their study of the catalytic oxidation of aliphatic amines with hydrogen peroxide have reported that primary and secondary amines yielded oximes, hydroxylamines or hydroxamic acids. Of the four amines the kinetics of oxidation of which have been studied by the present author,
three viz., morpholine, 2-methylaminoethanol, 2-ethylaminoethanol contain the secondary amino group \(\text{\(\geq\)}\text{NH}\text{\(\geq\)}\). Morpholine has the chemistry of a typical secondary aliphatic amine.\(^5\) Henry and Dehn\(^6\) have reported that morpholine on oxidation by hydrogen peroxide yields N-hydroxymorpholine which as seen from the structure is a hydroxylamine derivative of morpholine.

\[
\begin{array}{c}
\text{OH} \\
\text{H}_2\text{C} \\
\text{N} \\
\text{H}_2\text{C} \\
\text{CH}_2 \\
\end{array}
\]

\(\text{N - HYDROXYMORPHOLINE}\)

The detection of hydroxylamine by the present author in the oxidation of morpholine by peroxydisulphate at room temperature is thus in accord with the formation of a hydroxylamine derivative of morpholine on oxidation by hydrogen peroxide. The detection of hydroxylamine during the oxidation of all the secondary amines at room temperature as described earlier shows that the initial product in the oxidation is a hydroxylamine derivative formed as a result of conversion of secondary amino group \(\text{\(\geq\)}\text{NH}\text{\(\geq\)}\) to \(\text{\(\geq\)}\text{N - OH}\). The hydroxylamine derivatives thus formed are easily oxidised\(^7\) and yield products such as oxime.

The faint red colouration observed in the tests for
hydroxylamine and oxime in the oxidation of hexamethylene-
diamine which does not contain a primary or secondary amino
group may be due to the presence in small amounts of certain
intermediate products containing these groups such as
trimethylenetriamine, and pentamethylenetetramine or alterna-
tively mono-, di-, and trimethylolamines. These may be formed
as a result of hexamethylenetetramine undergoing hydrolytic
breakdown to some extent.8

\[ \text{TRIMETHYLENETERIAMINE} \]

\[ \text{PENTAMETHYLENETERIAMINE} \]

**EFFECT OF INITIAL CONCENTRATION OF AMINE**

The experimental data recorded in chapters II, to
V show that the rate of reaction increases with the increase
in the concentration of amine. The value of pseudo unimolecu-
lar rate constant is directly proportional to the concentra-
tion of amine except in the case of hexamethylenetetramine.
A plot of \(k_1\) versus the concentration of amine is linear
(Figures 2, 10, 14) and the straight line passes through
the origin. In the case of hexamethylenetetramine, however,
all the points do not lie on or near the straight line. With
increase in the concentration of hexamethylenetetramine, the points move further and further away from the straight line (Fig. 6 ) as pointed out in chapter III. This deviation suggests that the reaction is attended with some complications and may be due to the hydrolytic breakdown of hexamethylenetetramine to some extent forming intermediate products mentioned in the previous section of this chapter. Simultaneous oxidation of the products of hydrolytic breakdown may be responsible for the value of $k_1$ not being directly proportional to the concentration of hexamethylenetetramine.

**EFFECT OF INITIAL CONCENTRATION OF PEROXYDISULPHATE :**

The experimental results recorded in chapters II to V (Tables 1.16, 2.18, 3.17, 4.16 ) show that variation in the initial concentration of oxidant, peroxysulphate when the concentration of amine is in excess does not appreciably alter the rate of reaction and confirms the conclusion that the order with respect to peroxysulphate is unity. Edwards and Fortnum⁹ in their study of the kinetics of oxidation of thiodiethanol by t-butylhydroperoxide found that the observed first order slopes were independent of the concentration of the oxidant which means that in their study the value of the rate constants did not alter on varying the concentration of the oxidant. Mishra and Ghosh¹⁰ in their study of the oxidation of lactic acid by peroxysulphate catalysed by
silver ions found that there was no significant effect of the initial concentration of peroxydisulphate and concluded that the order with respect to peroxydisulphate was unity. Benzvi and Allen\textsuperscript{11} verified first order dependence on peroxydisulphate concentration by changing the concentration of peroxydisulphate and found that the value of rate constant did not alter significantly.

The observations and conclusions of the present author are in agreement with those of Edwards and Fortnum\textsuperscript{9}, Mishra and Ghosh\textsuperscript{10}, Benzvi and Allen\textsuperscript{11}.

**ROLE OF ACIDS ON THE REACTION RATE:**

The experimental data recorded in Chapters II to V (Table Nos. 1.23, 2.23, 3.22, 4.21) show that the rate of oxidation of amines is retarded by acids. The resistance to oxidation of amines in presence of acids is due to the stabilizing effect of salt formation\textsuperscript{12} Littler and Waters\textsuperscript{13} have also pointed out that oxidation of amines was noticeably acid dependent, being stopped when the acid was too concentrated. Chaltykyan and Beileryan\textsuperscript{14} have also reported that protonated species of the amines such as \((R_2NH_2H)^+\) formed in acid solution are inactive. The retarding effect of acids on the rate of oxidation observed by the present author is in agreement with the observations of the above workers.
ROLE OF ALKALI ON THE REACTION RATE:

The experimental data recorded in chapters II, IV, and V (Tables Nos. 1.27, 3.26, 4.24) show that addition of potassium hydroxide does not significantly alter the rate of oxidation under the experimental conditions of study by the author.

The role of potassium hydroxide in not appreciably affecting the rate of oxidation of morpholine, 2-methylaminoethanol and 2-ethylaminoethanol is similar to its behaviour on the rate of catalytic oxidation of di-isopropylamine by hydrogen peroxide observed by Tyagi.\(^{15}\)

Beileryan and co-workers\(^ {16}\) in their study of the oxidation of amines with hydroperoxides found that the rate of reaction between triethanolamine and cumene hydroperoxide is affected by potassium hydroxide when the amine is not in excess. This means that in the presence of excess of amines, potassium hydroxide did not affect the rate of reaction. The present author has followed pseudo unimolecular kinetics and the concentration of amine taken was always in excess compared to that of the oxidant, peroxydisulphate. Therefore the results obtained by the author under the experimental conditions of study are in accord with the observations of Beileryan and co-workers.
In the case of hexamethylenetetramine (Chapter II, table 2.24), however, it was observed that in the presence of potassium hydroxide the values of \( k_1 \) were not reasonably constant and increased with time. This may be due to the fact that hexamethylenetetramine besides behaving like a tertiary amine, also reacts as formaldehyde as pointed out by Walker.\(^{17}\) It is also reported in literature that formaldehyde is rapidly oxidised by hydrogen peroxide in presence of alkali\(^ {18}\) and also undergoes Cannizzaro reaction\(^ {19}\) in alkaline medium. Behaviour of hexamethylenetetramine as formaldehyde associated with its oxidation in alkaline medium and the possibility of undergoing Cannizzaro reaction as pointed out above may be responsible for introducing complications, resulting in the values of \( k_1 \) not being reasonably constant.

**EFFECT OF NEUTRAL SALTS ON THE RATE OF UNCATALYSED OXIDATION**

The effect of salts such as potassium sulphate and sodium sulphate on the rate of all the four reactions, in the absence of catalyst, has been studied. The observed results show that change in ionic strength of the reaction mixture introduced by the addition of salts has no effect on the rate of uncatalysed reaction. LaMer\(^ {20}\) curve shows that if one of the reactants is a neutral molecule then the rate constant, at least in dilute solutions, should be independent of the ionic strength of the medium. Hammett\(^ {21}\) has pointed out that if the reaction is between an ion and an uncharged
molecule addition of salt has little effect upon the rate. This is the case with uncatalysed oxidation of the four amines under investigation. Thus it is confirmed that the rate-determining process in the uncatalysed oxidation of all the four amines is between a neutral molecule and an ion, i.e., amine and $\text{S}_2\text{O}_8^{2-}$.

**EFFECT OF ZINC SULPHATE AND MANGANOUS SULPHATE:**

Experimental data in chapters II to V (Tables 1.37, 2.34, 3.34, 4.32) show that the addition of zinc sulphate does not significantly alter the velocity of oxidation, though in the case of hexamethylenetetramine there is some decrease in the rate of oxidation on the addition of 0.0001 M zinc sulphate but further addition of zinc sulphate does not bring about any significant change in the rate constant.

Tables 1.40 (Chapter III), 2.37 (Chapter III), 3.37 (Chapter IV) and 4.35 (Chapter V) show that the addition of manganous sulphate does not significantly alter the rate of oxidation and therefore it may be concluded that manganous ions do not possess any catalytic activity so far as the four reactions studied by the author are concerned.

Beileryan et al. have reported that zinc and cadmium ions do not affect the rate of oxidation of diethyl-ethanolamine and diethylamine. They did not investigate the
effect of manganous ions. The present author finds that zinc ions and manganous ions have no catalytic effect on the rate of oxidation of four amines under investigation.

**EFFECT OF COPPER SULPHATE AND SILVER NITRATE**

Addition of copper sulphate and silver nitrate accelerates the rate of oxidation of all the four amines under investigation. The catalytic effect of silver ions is, however, more marked than that of cupric ions in all the four reactions. Beileryan and Chltykyan \(^{23,24}\) in their study of the kinetics of the reaction of persulphate with amines and ethanolamines, e.g., diethylamine, di- and tri-ethanolamines have reported that the catalytic activity of silver ions was greater than that of cupric ions. The observations of the present author regarding catalytic activity of cupric and silver ions are, therefore, similar to those of Beileryan and co-workers.

Of the two heterocyclic amines viz., morpholine and hexamethylenetetramine the oxidation of which has been studied by the present author, it is found that under similar conditions of temperature and concentration of amines, 10 x 10\(^{-5}\) M silver nitrate increased the value of \(k_1\) from 0.5631 min\(^{-1}\) (Table 1.7) to 1.7514 min\(^{-1}\) (Table 1.56) i.e., approximately 3.11 times in the case of morpholine, whereas in the case of hexamethylenetetramine the same concentration
of silver nitrate increased the value of $k_1$ from $1.5024 \text{ min}^{-1}$ (Table 2.10) to $2.1918 \text{ min}^{-1}$ (Table 2.45) i.e., about 1.46 times. This shows that the catalytic activity of silver ions for the reaction between morpholine and peroxydisulphate is greater than that for a similar reaction with hexamethylenetetramine. The reason for lower catalytic activity of silver ions in the case of hexamethylenetetramine may be due to the higher complex forming affinity of hexamethylenetetramine for silver ions as compared to that of morpholine, as pointed out by Bjerrum, resulting in lower concentration of free silver ions in solution.

Of the two aliphatic amines the oxidation of which has been studied by the author, it is found that under similar conditions of concentration of amines and temperature, $10 \times 10^{-5} \text{ M}$ silver nitrate raised the value of rate constant $k_1$ from $1.4078 \text{ min}^{-1}$ (Table 3.1) to $4.922 \text{ min}^{-1}$ (Table 3.49) i.e., by about 3.5 times in the case of 2-methylaminoethanol whereas in the case of 2-ethylaminoethanol the same concentration of silver nitrate under similar conditions increases the value of $k_1$ from $0.3021 \text{ min}^{-1}$ (Table 4.1) to $1.4052 \text{ min}^{-1}$ (Table 4.45) i.e., about 1.75 times. This shows that the catalytic activity of silver ions is greater for 2-methylaminoethanol than for 2-ethylaminoethanol.

It has also been found that the observed rate constant $k_1$ is directly proportional to the concentration of silver ions.
ORDER OF REACTION (uncatalysed reaction):

The experimental data in chapters II to V show that the total order of reaction in the uncatalysed oxidation of amines under study is two i.e., one with respect to peroxysulphate and one with respect to amine. Chaltykyan and Beileryan\textsuperscript{26} in their study of the kinetics of oxidation of some secondary amines e.g., diethylenamine, piperidine and diethanolamine found that all the reactions were of second order. The experimental results of the present author are also in agreement with the views of Waters\textsuperscript{27} who has pointed out that all heterolytic reactions of peroxo compounds are bimolecular.

It has, however, been pointed out in chapter III that the order of reaction with respect to hexamethylenetetramine varies from 1.04 to 1.38 and has been taken to be one. Variation in the order of reaction with respect to the organic substrate has also been observed by other workers. Mishra and Ghosh\textsuperscript{28} in their study of the kinetics of oxidation of ethylalcohol and dioxane by peroxysulphate observed that the order of reaction with respect to ethyl alcohol varied from 0.15 to 0.28 and of dioxane from 0.09 to 0.4. Beileryan and co-workers\textsuperscript{23} in their study of the kinetics of peroxysulphate - diethylethanalamine reaction found that the order of
reaction with respect to diethylethanolamine was between 0.7 to 0.9.

The variation in the order of reaction with respect to hexamethylenetetramine suggests that the reaction is attended with some complication and may be due to some extent, to the formation of intermediate products as a result of hydrolytic breakdown of hexamethylenetetramine as pointed out in the earlier parts of this chapter. Though the hydrolytic breakdown of hexamethylenetetramine may take place only to a small extent, the formation of intermediate products and their simultaneous oxidation may introduce variation in the order of reaction observed.

**EFFECT OF INCREASING THE CONCENTRATION OF SILVER IONS ON THE ORDER OF REACTION WITH RESPECT TO AMINE**

Experimental data in chapters II to V show that the order of reaction with respect to the organic substrate i.e., amine falls with the increase in the concentration of silver ions. This suggests that as the concentration of silver ions increases, the order of reaction with respect to amine tends towards zero i.e., the rate of reaction tends to become independent of amine concentration. In other words, if the concentration of silver ions were very high the total order of reaction will be one, i.e., one with respect to peroxydisulphate and zero with respect to amine.
Chakravarty and Ghosh in their study of the oxidation of oxalate by hexavalent chromium (K₂Cr₂O₇) catalysed by manganous ions observed that the order of reaction with respect to oxalate had a tendency to fall down to zero with increasing concentration of the catalyst and pointed out that a changed mechanism of the reaction in presence of the catalyst, manganous sulphate was expected. Their observation that the order of reaction with respect to the substance that is being oxidised falls with increase in concentration of the catalyst is similar to the observation made by the present author.

It may be pointed out here that the order of reaction with respect to peroxodisulphate in the silver ion catalysed reactions studied by the author is one because the values of k₁ obtained from the first order rate equation at a particular temperature were always constant within limits of experimental error.

**CATALYTIC CONSTANT FOR THE SILVER-ION CATALYSED REACTIONS**

Experimental results obtained by the author in Chapter II to V show that (i) the observed pseudo unimolecular rate constants, k₁ determined in the presence of silver ions are directly proportional to the concentration of silver ions and (ii) the value of n, i.e., the order with respect to the organic substrate falls with increase in the concentration of
silver ions. As pointed out in chapter II, this second observation suggests a changed mechanism in the presence of catalyst silver ion. According to Moelwyn-Hughes, in the presence of a catalyst, the uncatalysed and the catalysed reactions proceed simultaneously so that

$$k = k_0 + K_c \text{ (catalyst)}^x \quad (1)$$

If successive additions of a catalyst bring about proportionate increases in the observed velocity i.e., if the observed velocity is directly proportional to the concentration of the catalyst, $x$ is unity and $K_c$ becomes a bimolecular constant. In the present study of all the four reactions, it has been found that the value of observed rate constant is directly proportional to the concentration of the catalyst silver ion (Figures 3, 7, 11, 15) and therefore $x$ in the above equation is unity and the relation:

$$k_1 = k_0 + K_c \text{ (Ag}^+) \quad (2)$$

where $k_1$ is the observed pseudo unimolecular rate constant in the presence of catalyst silver-ion, $k_0$ is the pseudo unimolecular rate constant for the uncatalysed reaction and $K_c$ the catalytic constant, should hold good in the case of all the four reactions studied by the author. It has actually been found to be so. The values of $K_c$ obtained from the above equation were constant within limits of experimental error. The value of $K_c$ may also be obtained from the slope of the
plot of $k_1$ vs (catalyst) as was done by Overberger and Cummins in their study of the acid catalysed oxidation of p-p-dichlorobenzylsulphide by hydrogen peroxide. The values of $K_c$ calculated from the equation and obtained from the slope of the figures (3,7,11,15) for each reaction are fairly in agreement.

**EFFECT OF NEUTRAL SALTS, POTASSIUM SULPHATE AND SODIUM SULPHATE ON THE RATE OF REACTION CATALYSED BY SILVER IONS:**

The experimental data in Chapters II to V show that the value of overall rate constant of the reaction catalysed by silver ions decreases with increase in the concentration of salts. (Tables 1.63, 2.56, 3.58, 4.56). The negative salt effect observed by the present author in the case of all the four reactions catalysed by silver ions suggests that the mechanism involves ions of opposite charges. It has been pointed out earlier that the addition of neutral salts has no effect on the rate of uncatalysed oxidation. The observed decrease in the value of the overall rate constant with increase in the concentration of salt in the silver ion catalysed reaction strongly suggests that the rate law consists of a term involving oppositely charged ions.

**RATE LAWS AND MECHANISMS:**

(1) **Uncatalysed oxidation**:

The experimental evidence obtained by the present
author shows that in the uncatalysed oxidation of each amine by peroxysulphate total order of the reaction is two, one with respect to amine and one with respect to peroxysulphate and therefore the rate law is given by the following equation:

\[
-\frac{d\left[S_2O_8^{2-}\right]}{dt} = K_s \left[\text{amine}\right] \left[S_2O_8^{2-}\right] \tag{1}
\]

where \(K_s\) is the second order rate constant.

In the presence of excess amine,

\[
K_s \times \left[\text{amine}\right] = \text{Constant} = k_1
\]

So that

\[
-\frac{d\left[S_2O_8^{2-}\right]}{dt} = k_1 \left[S_2O_8^{2-}\right] \tag{2}
\]

(2) **Silver ion catalysed oxidation:**

Experimental evidence obtained by the present author in the study of silver ion catalysed reaction shows that:

(i) Overall rate constant or observed rate constant in the presence of silver ions is directly proportional to the \([\text{Ag}^+]\).

(ii) The value of the order of reaction with respect to the organic substrate, that is amine, falls with the increase in the concentration of silver ions.

(iii) The value of observed rate constant decreases on the addition of neutral salts i.e., negative salt effect
is observed in the catalysed reaction.

The following rate law is suggested for the reaction of all the amines with peroxydisulphate in presence of silver ions.

\[
\frac{-d[S_2O_8^{2-}]}{dt} = K_s [\text{amine}][S_2O_8^{2-}] + K_c [\text{Ag}^+][S_2O_8^{2-}] \quad (3)
\]

(Uncatalysed path) (Catalysed path)

In the absence of silver ions, the reaction proceeds via the first path i.e., the uncatalysed one which as is seen from equation (3) involves a neutral molecule of amine and \(S_2O_8^{2-}\) ion and is similar to equation (1). The second term in equation (3) shows that the reaction proceeding via the catalysed pathway or mechanism is independent of the amine concentration. If the concentration of silver ions is very high so that \(K_s\) becomes very much less or negligible in comparison to \(K_c [\text{Ag}^+]\), then the reaction will proceed via the second path only and the order of reaction with respect to amine will be zero and with respect to peroxydisulphate one.

In the presence of low silver ion concentrations, however, such as those employed in the present investigations, both the uncatalysed and catalysed reactions proceed simultaneously. Thus, it will be seen that if the reaction proceeds entirely by the uncatalysed path, the order of reaction with respect to
amine is one and with respect to peroxydisulphate also one, i.e., total order of reaction is two. On the other hand, if the reaction proceeds entirely via the catalysed path which happens at higher concentrations of silver ions, then the order of reaction with respect to amine is zero and with respect to peroxydisulphate one. At lower concentration range of silver ions, however, the order of reaction with respect to amine will be between 1 and 0, though with respect to peroxydisulphate it is one. As the concentration of silver ions is increased gradually the order with respect to amine tends towards zero.

The above rate-law also explains the decrease in the value of the observed rate constant on the addition of neutral salts in the silver ion catalysed reaction of each amine. The first term as seen from equation (3) involves a neutral molecule and an ion which do not affect the rate as pointed out earlier. The second term involves oppositely charged ions viz., \((\text{Ag}^+)\) and \((\text{S}_2\text{O}_8^{2-})\) which as has already been referred to are responsible for negative salt effect i.e., decrease in the rate. The overall rate constant decreases because of the decrease in the second term produced on the addition of neutral salts.

When the amine is in excess, equation (3) can be written as:
\[
- \frac{d \left[ S_{2}O_{8}^{2-} \right]}{dt} = k_{o} \left[ S_{2}O_{8}^{2-} \right] + k_{c} \left[ Ag^{+} \right] \left[ S_{2}O_{8}^{2-} \right]
\]  \hspace{1cm} (4)

where \( k_{o} = k_{3} \times [Am] \) is the pseudo unimolecular rate constant for the uncatalysed reaction, so that one obtains:

\[
- \frac{d \left[ S_{2}O_{8}^{2-} \right]}{dt} = \left\{ k_{o} + K_{d}[Ag^{+}] \right\} \left[ S_{2}O_{8}^{2-} \right]
\]  \hspace{1cm} (5)

or

\[
- \frac{d \left[ S_{2}O_{8}^{2-} \right]}{dt} = k_{1} \left[ S_{2}O_{8}^{2-} \right]
\]  \hspace{1cm} (6)

where \( k_{1} \) is the overall or observed pseudo unimolecular rate constant in the presence of silver ions and is equal to \( \left\{ k_{o} + K_{d}[Ag^{+}] \right\} \).

Comparison of equation (5) and (6) shows that \( k_{1} = k_{o} + K_{d}[Ag^{+}] \). This equation is similar to the one suggested by Moelwyn - Hyghes.²⁰

**MECHANISMS:**

1. The probable mechanism of reaction proceeding via the uncatalysed path suggested on the basis of experimental evidence obtained by the author is given below:

\[
Am + S_{2}O_{8}^{2-} \xrightarrow{\text{Slow}} \left\{ Am \left( S_{2}O_{8}^{2-} \right) \right\} \xrightarrow{\text{Rate-determining step}} (\text{Activated complex})
\]

\[
Am \left( S_{2}O_{8}^{2-} \right) + H_{2}O \xrightarrow{\text{Rapid}} AmO + 2H_{3}O^{+}
\]
(2) Probable mechanism of the reaction proceeding via the catalysed path is:

\[ S_2O_8^{2-} \xrightarrow{\text{Rapid}} 2SO_4^{2-} \quad (1a) \quad \frac{[SO_4^{2-}]}{[S_2O_8^{2-}]} = K_e \quad (1b) \quad \text{equilibrium constant.} \]

\[ 2SO_4^{2-} + Ag^+ \xrightarrow{\text{Slow}} 2SO_4^{2-} + Ag^{3+} \quad (2) \quad \text{rate-determining step.} \]

\[ Ag^{3+} + Am + H_2O \xrightarrow{\text{rapid}} Ag^+ + 2H^+ + AmO \quad \text{Further oxidation} \]
\[ \quad \quad \quad \downarrow \quad \quad \quad \quad \quad \text{other products e.g., oxime.} \]

\[ -\frac{d[S_2O_8^{2-}]}{dt} = k_2 [Ag^+] [SO_4^{2-}]^2 \]

But from equation (1b) \[ [SO_4^{2-}]^2 = K_e [S_2O_8^{2-}] \]

\[ -\frac{d[S_2O_8^{2-}]}{dt} = k_2 K_e [Ag^+] [S_2O_8^{2-}] \]
\[ = k_c [Ag^+] [S_2O_8^{2-}] \]

where \[ k_c = k_2 K_e \]

An alternative mechanism suggested for the catalysed path is:

\[ Ag^+ + S_2O_8^{2-} \xrightarrow{\text{Slow}} \{AgS_2O_8\} \quad \text{rate-determining step.} \]
\[ \{AgS_2O_8\} \xrightarrow{\text{Rapid}} Ag^{3+} + 2SO_4^{2-} \]
\[
\text{Ag}^{3+} + \text{Am} + \text{H}_2\text{O} \xrightarrow{\text{rapid}} \text{Ag}^{+} + 2\text{H}^+ + \text{AmO}
\]
Further oxidation
Other products e.g., oximes.

\[
\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = K_c [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}]
\]

**ENERGY OF ACTIVATION, FREQUENCY FACTOR, ENTROPY FACTOR, AND ENTROPY OF ACTIVATION:**

The values of second order rate constants \( K_s \) (litres mole\(^{-1}\) min\(^{-1}\)) at 25\(^\circ\) C, energy of activation \( E_a \) (cal. mole\(^{-1}\)), frequency factor \( A \) (litres mole\(^{-1}\) sec\(^{-1}\)), entropy factor \( \Delta S/R \) and entropy of activation \( \Delta S^\ddagger \) (cal. deg\(^{-1}\) mole\(^{-1}\) or e.u.) obtained in chapters II to V for the four reaction are given in the table below:

<table>
<thead>
<tr>
<th>AMINE</th>
<th>( K_s )</th>
<th>( E_a )</th>
<th>( A )</th>
<th>( \Delta S/R )</th>
<th>( \Delta S^\ddagger )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morpholine</td>
<td>11.275</td>
<td>16100</td>
<td>( 1.185 \times 10^9 ) 7.023x10(^{-5} )</td>
<td>- 19.00</td>
<td></td>
</tr>
<tr>
<td>Hexamethylene-</td>
<td>35.907</td>
<td>12720</td>
<td>( 1.274 \times 10^7 ) 7.551x10(^{-7} )</td>
<td>- 28.02</td>
<td></td>
</tr>
<tr>
<td>tetramine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methylamino-</td>
<td>14.078</td>
<td>14710</td>
<td>( 1.414 \times 10^8 ) 8.379x10(^{-6} )</td>
<td>- 23.24</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Ethylamino-</td>
<td>8.021</td>
<td>15370</td>
<td>( 2.024 \times 10^8 ) 11.99 x10(^{-6} )</td>
<td>- 22.52</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td></td>
<td></td>
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The transition state or activated complex theory expresses the rate constant in terms of the expression:
\[ k = e^{\frac{KT}{h}} \cdot e^{\frac{\Delta S^+}{R}} \cdot e^{-\frac{E_a}{RT}} \] where K is the Boltzmann constant and h the Planck's constant.

It is seen from the above equation that the value of rate constant depends not only on the energy of activation but also on the entropy of activation. Glasstone has pointed out that "if the entropy of activation is large and positive, the reaction will be normal or fast, but if \( \Delta S^+ \) is negative or small, actually it should be less than -7 units, then the reaction will be 'slow'." A perusal of the above table shows that the values of the entropy of activation for all the four reactions studied by the present author are less than -7 e.u. and therefore these reactions come in category of 'slow' reactions.

One thing which strikes notice is that the value of \( \Delta S^+ \) is lowest for hexamethylenetetramine. This is understandable because hexamethylenetetramine has a polycyclic structure made up of methylene groups bridged by nitrogen atoms in to a crossed-linked six-membered ring as shown below:

![Diagram]

and lower value of \( \Delta S^+ \) compared to other amines reflects a more crowded transition state. The faster rate of reaction, however, is due to low energy of activation, (12720 cals).