Co(II) catalyzed oxidation of organic compounds by peroxomonosulphate

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Received 25 November 2014; revised and accepted 28 February 2015

The Co(II) ion catalyzed decomposition of peroxomonosulphate (PMS) and the influence of organic substrates such as ethanol, t-butanol, α-hydroxy acids (AHA) and glycine is studied at pH ≤1.0 and 4.0−5.2. In strong acid medium, the reaction is inhibited by the organic compounds and the present results, in accordance with the earlier reports, suggest a redox process through the formation of sulphate radical intermediate. Ethanol and AHAs are more effective quenchers than t-butanol. However in buffered medium (pH 4.05−5.20), the substrate other than t-butanol catalyze the reaction and get oxidized quantitatively. Ethanol is oxidized in the presence of AHA and glycine, suggesting a molecular mechanism involving a complex intermediate EtOH-Co(II)-SO$_2^-$ and subsequent oxygen atom transfer from SO$_2^-$.

The catalytic effect of Co(II) is observed with concentrations of ppm or lower level.

Keywords: Kinetics, Reaction mechanisms, Oxidation, Decomposition, Peroxomonosulphate decomposition, Cobalt, Sulphate ion radicals

The peroxomonosulphate (PMS) is a versatile oxidant and is widely used in environmental applications such as the decontamination and disinfection treatment of water. The potential use of this compound in the removal of organic contaminants in waste water is due to its ability to generate free radicals of higher oxidizing strength. The transition metal ions in catalytic amounts activate the homolytic scission of peroxomonosulphate and favor the formation of sulphate ion radical or hydroxyl radical intermediates. Sulphate radical ($E^0$(SO$_4^-$/SO$_2^-$) 2.5−3.1 V)$^4,5$ and hydroxyl radical ($E^0$(OH /OH$^-$) 1.98 V)$^6$ or ($E^0$(OH /H$_2$O) 2.38V−2.72V)$^7,8$ have more oxidizing power than PMS ($E^0$(HSO$_4^-$/SO$_2^-$) 1.8 V).$^8$ Recently Anipsitakis and Dionysiou$^3$ have reported that the cobalt(II) ion is the most effective transition metal ion catalyst for the production of sulphate radical. Therefore, PMS in conjunction with Co(II) is widely used in Advanced Oxidation Technology for water remediation.$^9$−$^{13}$

M(II) + HSO$_5^-$ $\rightarrow$ M(III) + SO$_4^{2-}$ + OH$^-$
M(II) + HSO$_3^-$ $\rightarrow$ M(III) + OH$^-$ + SO$_2^-$

The earlier works by Edwards and co-workers$^{14}$−$^{16}$ suggest that the cobalt(II) catalyzed decomposition of PMS in the pH range 0.0−6.0 proceeds through radical mechanism involving sulphate radical and Co(III) intermediates. Recent experimental results also support the molecular mechanism. Wang and coworkers$^{17,18}$ have reported that the reactions of cobalt-peroxomonosulphate system in the presence of chloride ion may proceed through both (i) one electron process resulting chlorine radical (through the sulphate ion radical intermediate), and, (ii) two electrons transfer producing chlorine. The oxidation of hydroxy acids such as malic acid$^{19}$ and citric acid$^{20}$ by Co(II)-PMS at higher pH (4.0−5.2) is reported to proceed through the molecular mechanism involving oxygen atom transfer with the catalytic process observed at ~0.2 mM (10 ppm) or even lower concentration of the metal ion.

Aliphatic alcohols such as ethanol and t-butanol, react quickly with hydroxyl and sulphate ion radicals, but with different rates.$^{21}$−$^{23}$ This difference in reactivity was utilized to identify the radical intermediate, i.e., sulphate ion radical or hydroxyl radical, produced in the metal ion activation of PMS.$^3$ Burrows and co-workers$^{24}$−$^{28}$ extensively used ethanol and t-butanol quenching technique at pH ~7.0 to identify the primary radicals in Co(II)-PMS induced modification of RNA and DNA wherein a 500:1 molar ratio of alcohol versus PMS was used. However, preliminary results from this laboratory showed that the effect of ethanol on the rate of Co(II)-
PMS reaction depends upon the pH; in strong acidic $pH (~1.0)$ ethanol, as expected, quenched the reaction while at higher $pH$ (4.0 – 6.0) it enhanced the rate. Little information is available on Co(II)-PMS-ethanol system, especially in the $pH$ range 4.0–6.0. Therefore, a detailed investigation on Co(II)-PMS-ethanol system is of interest.

It is reported that $\alpha$-hydroxy acids (AHA), such as glycolic acid (GA), lactic acid (LA) and $\alpha$-hydroxy isobutyric acid (AHIBA) enhance the generation of hydroxyl radicals in Fenton reaction. Available literature shows that sulphate ion radical is the primary radical from Co(II)-PMS system. Since not much information is available on the formation of hydroxyl radical, it would be interesting to study the influence of $\alpha$-hydroxy acids on Co(II)-PMS reaction.

In the present study, the kinetics of Co(II)-PMS reaction and the effect of added organic compounds such as ethanol, $t$-butanol and AHAS has been investigated at $pH$ 1.0 and 4.0 – 6.0 and the results are presented herein. Zhang et al. observed that the Co(II) ion catalyzed decomposition of PMS was higher with cobaltous acetate than either with cobaltous sulphate or cobaltous nitrate. Therefore, cobaltous acetate was chosen as the source of Co(II) ion in the present study.

Materials and Methods

Cobalt(II) acetate ($\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$) was obtained from Merck, India. Peroxomonosulphate as its potassium salt was purchased from Sigma-Aldrich Chemie GmbH (Germany). The purity of the sample was estimated as >95% by cerimetry, and since further purification beyond this purity is not possible, the sample was used as such. Stock solution of $\text{HSO}_3^-$ was freshly prepared daily and standardized by iodometric titration. Commercial grade alcohol was purified by the method of Marcus. $t$-butanol (GR, Merck, India) was distilled from freshly prepared quicklime, through a fractionating column.

Glycolic acid (2-hydroxy acetic acid) (GLA), with a purity of ≥99% was supplied by Fluka (USA). Lactic acid (2-hydroxy propanoic acid) (LA), $\alpha$-hydroxy isobutyric acid (2-hydroxy-2-methyl propanoic acid) (AHIBA) and mandelic acid (2-hydroxy-2-phenyl acetic acid) (MA) were of highest purity (99%) from Aldrich (Germany). Absence of carbonyl impurities in these $\alpha$-hydroxy acids (AHA) was ensured by standard confirmatory tests and hence, all AHAs were used as received. Glycine (Gly) was the highest purity (>99%) sample from Merck, India. All other chemicals were of reagent grade and were used without further purification.

The kinetics were carried out in aqueous perchloric acid (0.12 $M$) medium and also at buffered condition ($pH$ 4.05–5.20). Sodium acetate/acetic acid buffer was used to adjust the $pH$. The $pH$ of the solutions was regulated to the predetermined values by adjusting the concentration of acetic acid, while keeping the $[\text{NaOAc}]$ always constant, usually at 0.32 $M$. The concentration of PMS was followed iodometrically at various times and the rate constants of the reactions were calculated from the first order kinetic equation. The reactions were monitored usually up to 75% decrease in PMS concentration. All the kinetic runs were carried out with $[\text{PMS}]_0 \approx 4.00 \times 10^{-3} \, \text{M}$. The kinetic experiments were initiated by pipetting out an appropriate aliquot of $\text{HSO}_3^-$ (usually 10 mL) into the solution containing the other reagents at the desired temperature. Duplicating the experiments shows that the results are reproducible within the error of ±5%.

The product analysis in the absence of organic compounds was carried out at kinetic conditions. The evolution of oxygen gas, at perchloric acid and higher $p$Hs, was identified by the color change with alkaline sodium dithionite activated with indigo carmine. The evolution of oxygen was highly diminished (as indicated by the intensity of the color) with added ethanol in perchloric acid medium and practically no oxygen evolution at higher $p$Hs. The oxidation product of ethanol at $pH$ 4.05–5.20 was confirmed as acetaldehyde, from spectroscopic identification of 2,4-dinitrophenyl hydrazone derivative as given by Wells. The stoichiometry of the reaction in the presence of ethanol (0.85 $M$) was carried out under kinetic conditions: $[\text{Co(II)}] = 5.0 \times 10^{-6} \, \text{M}$, $[\text{PMS}] = 4.20 \times 10^{-3} \, \text{M}$ at $pH$ 5.20 and 31.0 °C. The acetaldehyde was estimated by Wells method and also by hydroxylamine hydrochloride- pyridine method. The yield was found to be 90 (±5) % in terms of [PMS].

The stoichiometry and product analysis for AHA was carried out in aqueous perchloric acid (0.10 $M$) medium and at a higher $pH$ (~4.75) as well. The $pH$ was adjusted with $\alpha$- hydroxy acid and its carboxylate (AHA). A large excess of PMS (0.04 $M$) over AHA+ AHA$^-$ (0.01 $M$) and Co(II) (5.0 $\times 10^{-5} \, \text{M}$) were allowed to stand for 24 hours and the remaining PMS
was estimated. In all the cases, almost all PMS reacted and the remaining concentrations were negligible. This is due to the Co(II) catalyzed thermal decomposition of remaining PMS even after the completion of oxidation of AHA. However, the oxidation products from AHA were identified.

The product acetone from α-hydroxysobutyric acid was confirmed and estimated as 2,4-dinitrophenyl hydrazine derivative. The acetone produced at pH 4.75 was found to be 90(±5)% in terms of AHIBA concentration and was 65(±5)% in perchloric acid medium. Similarly, benzoic acid from mandelic acid was confirmed by the color test with rhodamine-B and also from the IR spectra. At pH 4.75, glycolic acid gave a mixture of formic acid and oxalic acid. Formic acid was confirmed by the reduction to formaldehyde and oxalic acid was detected by aniline blue test. Oxalic acid was estimated by permanganometry and found to be only~70(±5)% of GLA. The formation of acetic acid and oxalic acid. Formic acid was estimated from AHA+PMS in perchloric acid was found to be 10−50 mmoles/liter. Similarly, in buffered media, acetate ion concentration was equal to~10 mmoles/liter and thereafter remained constant. Perusal of the results shows that the organic substrates quench the reaction. Among the

Results and Discussion

In the absence of the metal ion catalyst, PMS was quite stable for 6–8 h under the experimental conditions. In presence of Co(II) ion, even in mM − µM concentrations, the loss of PMS was faster. It was found out that for the reactions to proceed at a measurable speed we had to decrease the metal ion concentration with increase in pH. The Co(II) concentration used at different pHs were: (i) pH 1.0 (aqueous perchloric acid): 2.50×10−4–3.50×10−3 M, (ii) pH 4.05: 1.25×10−5–1.5×10−4 M, (iii) pH 4.75: 1.25×10−6–2.00×10−5 M, and, (iv) pH 5.20: 1.25×10−7–4.0×10−6 M.

In general, the rate constant values were independent of ionic strength and sulphate ion concentration. However, all the kinetic studies were carried out with constant sulphate ion concentration (0.50 M). Similarly, in buffered media, acetate ion concentrations had no effect on the rate and thus it acts only as a buffer.

Decomposition of HSO₅⁻ catalyzed by Co(II) in perchloric acid medium

The rate of the reaction in 0.12 M perchloric acid followed first order kinetics with respect to [HSO₅⁻]. Plots of In[PMS] versus time are strictly linear for at least two half lives. First order kinetics was observed in the presence of organic substrates also. The first order rate constant, $k_{1obs}$, values are found to be independent of the initial [PMS] in the range 2.00×10⁻³ M to 8.00×10⁻³ M. The rate constant values increase with Co(II) concentrations (Eq. (1)) and the plots $k_{1obs}$ versus [Co(II)] are straight lines with regression coefficient (r) higher than 0.99 and passing through origin (Fig. 1).

\[ k_{1obs} = k_i[Co(II)] \]

The correlation between Co(II) ion concentration and $k_{1obs}$ was also determined in the presence of aliphatic alcohols, AHAs, glycine, AHAs+alcohols and glycine+alcohols also. Equation 1 is found to be valid in presence of organic substrates also (Fig. 1(b) & 1(c)).

The $k_i$ values were calculated using Eq. (1) at different organic substrate concentrations ([ethanol] = 8.50–850 mM, [t-Butanol] = 5.25–525 mM, [AHA] and [Glycine] = 10–50 mM). The $k_i$ value decreased rapidly, reached a limiting value when the alcohol concentration was equal to~10 mM and thereafter remained constant. Perusal of the results shows that the organic substrates quench the reaction. Among the
alcohols, ethanol is more effective than \( t \)-butanol. Comparison of the quenching results from AHAs, AHAs+alcohols and alcohols show that the degree of quenching of AHAs is almost equal to that of ethanol. Glycine showed the least quenching effect.

The \( k_{\text{obs}} \) values decreased with increase in \([H^+]\) (0.05–0.30 \( M \)) and the plots of \( k_{\text{obs}}^{-1} \) versus \([H^+]\) were straight lines passing approximately through the origin. When the data points with \([H^+] >0.30 \( M \) were included in the curve fitting, correlations of the type \( k_{\text{obs}} = A + B/[H^+] \) was obtained with \( A \) having a statistically insignificant negative value always. Therefore, at \([H^+] = 0.05–0.30 \( M \), \( k_{\text{obs}} \) can be expressed as in Eq. (2), which is identical with Eq. (1) if \( k_1 \) is replaced by \( k_1^{\text{Co}} /[H^+] \).

\[
k_{\text{obs}} = k_1^{\text{Co}} [\text{Co(II)}]/[H^+] \quad \ldots(2)
\]

Equation (2) was found to be satisfied in the presence of organic substrates also. The \( k_1^{\text{Co}} \) values were obtained from the correlations of \( k_{\text{obs}} \) versus \([\text{Co(II)}] \) and \( k_{\text{obs}} \) versus \([H^+]^3 \) and these two values were found to be almost equal. The average of these two, denoted as \( k_1^{\text{Co}} \), was used for further analysis. The \( k_1^{\text{Co}} \) value with ethanol (\( k_1^{\text{Co,EtOH}} \)) is almost half of that of \( t \)-butanol (\( k_1^{\text{Co,t-BuOH}} \)). The \( k_1^{\text{Co}} \) values for AHAs (\( k_1^{\text{Co,AHA}} \) in the presence and in the absence of alcohols were also calculated. The added alcohols did not change the \( k_1^{\text{Co,AHA}} \) values and they are approximately equal to that of \( k_1^{\text{Co,EtOH}} \).

In the presence of glycine, the \( k_1^{\text{Co}} \) values (\( k_1^{\text{Co,Gly}} \)) are slightly lower but the deviation is appreciable at the higher temperature 38 °C. The \( k_1^{\text{Co}} \) values for glycine+ethanol and glycine+\( t \)-butanol mixtures are equal to that of the corresponding alcohol.

The \( \text{Co(II)} \) ion catalyzed decomposition of PMS in aqueous acidic medium has been shown to obey Eq. (2) by earlier workers\(^{13,37} \) also. Zhang and Edwards\(^{15} \) proposed a detailed kinetic scheme (Scheme 1) involving sulphate ion radical and derived an expression for the first order rate constant. In the present investigation, the quenching study with aliphatic alcohols also supports the formation of sulphate ion radical intermediate. Therefore, the

Zhang and Edwards scheme can be used to explain the observed kinetics in the present study also.

\[
\text{Co}^{2+} + \text{H}_2\text{O} \stackrel{k_1}{\rightleftharpoons} \text{CoOH}^+ + \text{H}^+ \quad \ldots(3)
\]

\[
\text{CoOH}^+ + \text{HSO}_5^{-} \stackrel{k_{\text{obs}}}{\rightarrow} \text{CoO}^+ + \text{H}_2\text{O} + \text{SO}_4^{2-} \quad \ldots(4)
\]

\[
\text{CoO}^+ + 2\text{H}^+ \stackrel{k_2}{\rightarrow} \text{Co}^{3+} + \text{H}_2\text{O} \quad \ldots(5)
\]

\[
\text{Co}^{3+} + \text{HSO}_4^{-} \rightarrow \text{Co}^{2+} + \text{SO}_4^{2-} + \text{H}^+ \quad \ldots(6)
\]

\[
\text{Co}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} \quad \ldots(7)
\]

\[
2\text{SO}_4^{2-} \rightarrow 2\text{SO}_3^{2-} + \text{O}_2 \quad \ldots(8)
\]

\[
2\text{SO}_5^{2-} \rightarrow 2\text{SO}_3^{2-} + \text{O}_2 \quad \ldots(9)
\]

**Scheme 1**

\[
k_{\text{obs}} = (k_{\text{obs}} K_1)(3 + \frac{2k_5}{k_5}) \quad \ldots(10)
\]

Equation (10) is similar to Eq. (2) and therefore

\[
k_1^{\text{Co}} = (k_{\text{obs}} K_1)(3 + \frac{2k_5}{k_5}) \quad \ldots(11)
\]

The \( k_1^{\text{Co}} \) values at different temperatures are listed in Table 1.

The quenching effect of organic substrates in perchloric acid medium can be explained by incorporating reactions (12) and (13) with Eqs (3) to (9).

\[
\text{SO}_4^{2-} + \text{Quencher} \rightarrow \text{Products} \quad \ldots(12)
\]

\[
\text{Co}^{3+} + \text{Quencher} \rightarrow \text{Products} \quad \ldots(13)
\]

Sulphate ion reacts at a faster rate with ethanol and \( t \)-butanol.\(^{21,23} \) Limited information is available on the reaction of \( \text{Co(III)} \) with ethanol\(^{38,39} \) and \( t \)-butanol.\(^{40-43} \) However available data show that ethanol\(^{39} \) reacts with \( \text{Co(III)} \) at a faster rate than \( t \)-butanol. Therefore, we can presume that added ethanol would quench both the sulphate radical (Eq. (12)) and \( \text{Co}^{3+} \) ion (Eq. (13)). Thus the kinetic scheme in the presence of added ethanol can be represented by Eqs (3-5) as well as Eqs (12) and (13). The rate equation in the presence of ethanol simply becomes as in Eq. (14).

\[
-k_1^{\text{Co}} = k_{\text{obs}} [\text{CoOH}^+ ][\text{HSO}_5^{-}] \quad \ldots(14)
\]

\[
k_{\text{obs}} = k_{\text{obs}} K_1 [\text{Co}^{3+} ]/[H^+] \quad \ldots(15)
\]
Substituting for [CoOH\textsuperscript{+}], we get Eq. (15) which is similar to Eq. (2). Therefore, \( k_1^{\text{Co}} \) in Eq. (2), in the presence of ethanol is denoted as \( k_1^{\text{Co,EtOH}} \) and is given by Eq. (16).

\[
k_1^{\text{Co,EtOH}} = k_{1a} K_1
\]  

... (16)

Since the reaction between Co(III) and \( t \)-butanol (Eq. 13) may not be as effective as with ethanol, the rate equation in presence of \( t \)-butanol can be expressed as in Eq. (17). On applying steady state approximation for [Co\textsuperscript{3+}] and rearranging we get Eq. (18).

\[
\frac{-d[PMS]}{dt} = k_{1a}[\text{CoOH}\textsuperscript{+}][\text{HSO}_4^-] + k_{1b}[\text{Co}\textsuperscript{3+}][\text{HSO}_4^-]
\]  

... (17)

\[
k_{\text{obs}} = 2k_{1a}K_1[\text{Co}^{2+}]/[\text{H}^+] \]

... (18)

Therefore \( k_1^{\text{Co}} \) in the presence of \( t \)-butanol, \( k_1^{\text{Co,t-BuOH}} \) is given by Eq. (19).

\[
k_1^{\text{Co,t-BuOH}} = 2k_{1a}K_1
\]  

... (19)

The values of \( k_1^{\text{Co,EtOH}} \) and \( k_1^{\text{Co,t-BuOH}} \) are shown in Table 1. From Eqs 11, 16 and 24, the value of \( k_1^{\text{Co}} \) should be at least three to five times, greater than that of \( k_1^{\text{Co,EtOH}} \) and this is found to be true at all temperatures. Similarly \( k_1^{\text{Co,t-BuOH}} \) values should be twice that of \( k_1^{\text{Co,EtOH}} \). While this expectation holds good at 25 \( ^\circ \)C and 31 \( ^\circ \)C, the two values are almost equal at higher temperature 38 \( ^\circ \)C. This may be due to the fact that, at higher temperature, the rate of oxidation of \( t \)-butanol by Co\textsuperscript{3+} may be faster and become an effective quencher as that of ethanol. Therefore, both alcohols may have the same quenching mechanism at higher temperature.

If the added organic substrate quenches both Co\textsuperscript{3+} and sulphate radical ion effectively, then, according to the mechanism in Eqs (12) and (13), the rate constant values in the presence of quenchers (\( k_1^{\text{Co,Q}} \)) should be independent of the nature of the quenching molecule. The experimental observations in the presence of AHAs can be explained if we assume that they are also as effective quenchers as that of ethanol. Moreover, the stability constant values for the equilibria of Co(II)-AHAs\textsuperscript{44} and Co(II)-glycine\textsuperscript{45,46} suggest that the concentration of Co(II) ion is not affected by the added substrates in perchloric acid (~0.1 \( M \)) medium. Therefore, the rate equation should be equal to Eq. (14) and the first order rate constant values in the presence of AHAs (\( k_1^{\text{Co,AHA}} \)) should be equal to those with ethanol (\( k_1^{\text{Co,EtOH}} \)).

This is found to be true from the \( k_1^{\text{Co,AHA}} \) values over wide range of conditions (Table 2). Since AHAs seem to be as effective quenchers as ethanol in Co(II) catalyzed activation of PMS, we could not differentiate

<table>
<thead>
<tr>
<th>Temp. ((^\circ)C)</th>
<th>( k_1^{\text{Co}} \times 10^3 )</th>
<th>( k_1^{\text{Co,Gly}} \times 10^3 )</th>
<th>( k_1^{\text{Co,EtOH}} \times 10^3 )</th>
<th>( k_1^{\text{Co,t-BuOH}} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>23.5(±1.0)</td>
<td>17.5(±0.7)</td>
<td>3.8(±0.4)</td>
<td>7.1(±1.0)</td>
</tr>
<tr>
<td>31.0</td>
<td>38.8(±1.3)</td>
<td>29.2(±1.5)</td>
<td>7.0(±0.1)</td>
<td>16.6(±0.8)</td>
</tr>
<tr>
<td>38.0</td>
<td>81.1(±2.3)</td>
<td>52.2(±2.3)</td>
<td>16.8(±0.6)</td>
<td>22.8(±0.8)</td>
</tr>
</tbody>
</table>

\( ^a \) In presence of 0.05 \( M \) glycine.

<table>
<thead>
<tr>
<th>Temp. ((^\circ)C)</th>
<th>( k_1^{\text{Co,AHA}} \times 10^3 ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>4.9(±0.2) (4.3)(^b)</td>
</tr>
<tr>
<td>31.0</td>
<td>7.3(±0.2) (7.0)(^b)</td>
</tr>
<tr>
<td>38.0</td>
<td>13.5(±0.3) (13.3)(^b)</td>
</tr>
</tbody>
</table>

\( ^b \) In presence of 0.85 \( M \) ethanol; \( ^a \) With 0.53 \( M \) \( t \)-butanol.

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Table 1: The kinetic constants for Co(II) ion catalysed decomposition of PMS in perchloric acid medium

Table 2: The rate constants for Co(II) ion catalysed decomposition of PMS in the presence of AHAs and in perchloric acid medium
between the quenching due to ethanol and AHAs. Similarly, the AHAs are better quencher than t-butanol and hence the effect of t-butanol could not observed. This explains why the added ethanol and t-butanol have no effect on the rate of the reaction of Co(II)-AHA-PMS system in strong acidic medium.

Perusal of the values in Table 1 suggests that glycine is not an effective quencher as compared to aliphatic alcohols and AHAs. This observation is in accordance with the earlier report \(^{21}\) wherein sulphate radical reaction with glycine is slower than that of alcohols.

Edwards et al.\(^{16}\) calculated the values of \(k_1^\text{Co}\) and \(k_{1u}K_1\) at 25 °C as \(9.3\times10^{-3}\) s\(^{-1}\) and \(0.5\times10^{-3}\) s\(^{-1}\). Comparison of these data with the values in Table 1 shows that \(k_1^\text{Co}\) value from the present study is higher by a factor of two and \(k_{1u}K_1\) by a factor of ten. The large difference in \(k_{1u}K_1\) may be due to the experimental methods used; Edwards et al. obtained the \(k_{1u}K_1\) value from the chain length of the radical reactions (Eqs (3)–(9)). On the other hand, the values in Table 1 are calculated directly from the quenching studies with alcohols and AHAs and therefore may be more reasonable.

Co(II) catalyzed decomposition of PMS at higher pH

The Co(II) catalyzed decomposition of PMS shows some interesting results at pH 4.05. The rate of decomposition followed both first order and second order kinetics with respect to PMS concentration as shown in Eq. (20) or a simple second order depending on the concentration of Co(II) ion.

\[
\text{Rate} = \frac{-d[\text{PMS}]}{dt} = k_{1\text{obs}}[\text{PMS}]+k_{2\text{obs}}[\text{PMS}]^2 \quad \text{(20)}
\]

The mixed order was confirmed by the plots of \((\text{Rate}/[\text{PMS}])\) versus [PMS], which gave a straight lines with a positive intercept. When the concentration of the Co(II) ion was above a critical value, e.g. \([\text{Co(II)}] > 2.5\times10^{-5} \text{M}\) (25 °C), the rate followed simple second order kinetics. The kinetic studies were carried out with Co(II) concentration at which the rate followed second order only. The \(k_{2\text{obs}}\) values increase with increase in [Co(II)] and the plots \(k_{2\text{obs}}\) versus [Co(II)] were linear passing through the origin. Similar second order reaction has been reported by earlier workers \(^{4}\) also, but at pH ~6.0.

At pH 4.75 and 5.20, the rates of the reactions were simple first order only over a wide range of [Co(II)]. The correlation between \(k_{1\text{obs}}\) and [Co(II)] was also linear passing through the origin.

Kolthoff and Miller\(^{47}\) suggested that sulphate ion radical reacts with water to give hydroxyl radical (Eq. (21)), an equally strong oxidant.

\[
\text{SO}_4^-+\text{H}_2\text{O} \rightleftharpoons \text{OH}^+ + \text{SO}_4^{2-} + \text{H}^+ \quad \text{(21)}
\]

Therefore, we have considered the formation of hydroxyl radical intermediate also at higher pH. Similar to sulphate radical, hydroxyl radical also reacts fast and at almost equal rate as with the aliphatic alcohols, ethanol and t-butanol.\(^{21-23}\) Therefore, like perchloric acid medium, both ethanol and t-butanol, should quench the activation of PMS by Co(II). Contrary to this expectation, ethanol enhanced the reaction (Fig. 2) while t-butanol has no effect at all on the rate. The catalytic effect of ethanol and zero order kinetics with respect to t-butanol was observed at all the studied pHs and over the temperature range 25–38 °C as well. This clearly suggests that Co/PMS reactions at higher pHs do not involve alcohol quenchable radical intermediates. Therefore, a most probable mechanism in acetate buffer that can explain the experimental observations may be a molecular one involving oxygen atom transfer. A kinetic (Scheme 2) for the reactions at higher pHs can be formulated as in Eqs (22) to (25) and detailed mechanism is shown in Scheme 3.

![Fig. 2−Plot of \(k_{1\text{obs}}^E\) versus [ethanol] at two different Co(II) concentrations. \(p\text{H} = 4.05; \text{Temp.} = 25.0 \, ^\circ\text{C}; [\text{Co(II)}] \quad (\text{M});\) curve 1, \(1.00\times10^{-5} \text{M};\) curve 2, \([\text{Co(II)}] = 2.00\times10^{-5} \text{M}].\)
Co(H₂O)₆²⁺ + SO₅²⁻ $\xrightarrow{k_i}$ (SO₅)Co(H₂O)₆²⁺ + H₂O

(SO₅)Co(H₂O)₆²⁺ + HSO₅⁻ $\xrightarrow{k_{HSO}}$ Co(H₂O)₆²⁺ + 2SO₄²⁻ + H⁺ + O₂

(SO₅)Co(H₂O)₆²⁺ $\xrightarrow{k_{HSO}}$ HOOCo(H₂O)₆⁺ + H⁺ + SO₄²⁻

HOOCo(H₂O)₆⁺ + HSO₅⁻ $\xrightarrow{\text{fast}}$ Co(H₂O)₆²⁺ + SO₄²⁻ + O₂

Scheme 2

The proposed mechanism will also explain the experimental results (Eq. (20)), namely the reaction is both first and second order in [PMS] at pH 4.05, when [Co(II)] < 2.50×10⁻⁵ M. At higher Co(II) concentration, the contribution from reaction (23) may be more significant and the rate becomes second order in [PMS]. Fortuitously, the Co(II) concentrations used herein were such that we observed only second order kinetics. The calculated second order rate constants $k_{2\text{obs}}$ can be given by Eq. (26).

$$k_{2\text{obs}} = K_d K_f [\text{Co(II)}]/[\text{H}^+]$$

Therefore, $k_{2\text{obs}} = k_{2\text{obs}}^{\text{PH}} [\text{Co(II)}]$ (27)

In Eq. (26), $K_d$ is the dissociation constant of PMS. At pH 4.75 and 5.20, the observed rate is first order in the [PMS], indicating the reactions (24) and (25) are more dominant than reaction (23). The calculated rate constant, $k_{1\text{obs}}$, is given by Eq. (28).

$$k_{1\text{obs}} = K_d K_f [\text{Co(II)}]/[\text{H}^+]$$

$$k_{1\text{obs}} = k_1 [\text{Co(II)}]/[\text{H}^+] = k_1^{\text{PH}} [\text{Co(II)}]$$

The kinetic constants $k_2^{\text{PH}}$ and $k_1^{\text{PH}}$ calculated at different experimental conditions are given in Table 3.

**Oxidation of ethanol at higher pH**

Ethanol was oxidized to acetaldehyde by PMS only in the presence of Co(II). Added ethanol not only enhanced the rate but also changed the order of the reaction from second order (in its absence) to first order at pH 4.05. Therefore, the effect of ethanol concentration was studied with two different concentrations of Co(II) (Fig. 2) at which the rate (in the absence of ethanol) could be either second order or mixed order as in Eq. (20). When [Co(II)] = 1.00×10⁻⁴ M, the reaction was second order and as the alcohol concentration was increased the kinetics changed to a simple first order via mixed order (Eq. (20)). The oxidation of alcohol was also studied at lower concentration of Co(II) (2.00×10⁻⁵ M) at which the decomposition of PMS was originally a mixed order. However, the added ethanol changed the reaction to simple first order. This clearly shows that $k_{2\text{obs}}$ values in Eq. (20) decreases rapidly with ethanol concentration.

The first order rate constant, denoted as $k_{1\text{obs}}^{\text{ethanol}}$, increased and reached a limiting value (Fig. 2) with ethanol concentration. The correlation between $k_{1\text{obs}}^{\text{ethanol}}$ and [EtOH] obeys Eq. (30) and $k_{1\text{obs}}$ is first order rate constant in the absence of alcohol Eq. (20). The values of $K$ and $k_{1\text{obs}}^{\text{ethanol}}$ were calculated at different temperatures also (Table 4).
The other aliphatic alcohol, 2-butanol, had no effect either on the rate or on the order and we could not identify the products such as acetone or any other carbonyl compound. This clearly shows that 2-butanol is not oxidized by Co(II)-PMS.

Figure 2 suggests that ethanol, unlike in perchloric acid medium, catalyses the reaction at higher pH and the degree of enhancement depends upon the concentration of Co(II) ion. The product and stoichiometry analysis show that ethanol is oxidized to acetaldehyde. A molecular mechanism that can explain the correlation between the rate and ethanol concentration Eq. (30) is shown in Scheme 4.

\[
k_{\text{EtOH}}^{\text{obs}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)
\]

Reactions (33) and (34) represent the Co(II)-Ethanol complex catalyzed decomposition of PMS. The oxidation of ethanol is shown in reaction (35). In addition, Co(II) ion catalyzed decomposition of PMS (Eqs (24) and (25)) may also occur. The rate equation, in the presence of ethanol, can be written as in Eq. (36).

\[
-k_{\text{obs}}^{\text{EtOH}} \frac{d[\text{PMS}]}{dt} = k_{\text{obs}}^{\text{EtOH}} [\text{PMS}]= k_h [(\text{SO}_4^2-)\text{Co(H}_2\text{O)}^2_5] + (k_{H1} + k)(\text{C}_2\text{H}_5\text{OH})\text{Co(H}_2\text{O)}_4(\text{SO}_4^2)^+ \quad \ldots(36)
\]

Table 3 – The \(k_1^{\text{pH}}\) and \(k_2^{\text{pH}}\) values for Co(II) ion catalysed decomposition of PMS at higher pH

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(k_1^{\text{pH}}) (M(^{-1})s(^{-1})) at pH = 4.05</th>
<th>(k_2^{\text{pH}}) (M(^{-1})s(^{-1}))</th>
<th>(10^2 \times k_2^{\text{pH}}) (M(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>(3.5 ±0.2)(^a)</td>
<td>4.75</td>
<td>5.20</td>
</tr>
<tr>
<td>31.0</td>
<td>(5.4±0.7)(^a)</td>
<td>22.2 ±3.1</td>
<td>444.7±3.8</td>
</tr>
<tr>
<td>38.0</td>
<td>(24.3±2.6)(^a)</td>
<td>31.3±3.0</td>
<td>775.±6.2</td>
</tr>
</tbody>
</table>

\(^a\)In presence of 0.05 M glycine.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>4.05</th>
<th>4.75</th>
<th>5.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>18.2±0.7</td>
<td>83.9±6.0</td>
<td>444.7±3.8</td>
</tr>
<tr>
<td>31.0</td>
<td>32.5±1.7</td>
<td>160.1±5.1</td>
<td>596.6±22.0</td>
</tr>
<tr>
<td>38.0</td>
<td>(28.2±0.7)(^a)</td>
<td>(139.6±5.6)(^a)</td>
<td>977(±9.86)</td>
</tr>
</tbody>
</table>

Table 4 – The reaction parameters for the oxidation of ethanol by Co(II)-PMS at higher pH

\[k_{\text{obs}}^{\text{EtOH}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)\]

\[k_{\text{obs}}^{\text{EtOH}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)\]

\[k_{\text{obs}}^{\text{EtOH}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)\]

\[k_{\text{obs}}^{\text{EtOH}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)\]

\[k_{\text{obs}}^{\text{EtOH}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)\]

\[k_{\text{obs}}^{\text{EtOH}} = k_{\text{obs}} + \frac{k_{\text{EtOH}}^{\text{obs}} [\text{Co(II)}][\text{EtOH}]}{1 + K_{\text{[EtOH]}}^2} \quad \ldots(30)\]
Therefore better values for $k^{\text{obs}}$ and $K$ can be obtained by keeping $k^{\text{obs}}$ as known value in Eq. (37), that is, substituting the values from the previous section. The values of $k^{\text{obs}}$ and $K$ thus calculated are listed in Table 4. The plots $\log(k^{\text{obs}})$ versus $pH$ are linear with a positive slope of ~1.0 as also $k^{\text{obs}}$ versus $[H^+]^{-1}$. These observations support the proposed mechanism in Scheme 4.

**Oxidation of α-hydroxy acids**

As in ethanol, the oxidation of AHAs was observed only in the presence of Co(II) and the rate was first order in [PMS]. The first order rate constant values increase with [Co(II)] and the plots $k^{\text{obs}}$ versus [Co(II)] were straight lines ($r>0.99$) passing through the origin. The $k^{\text{obs}}$ values were found to be independent of [AHA]. The effect of $pH$ on the rate of the reaction may be inferred by calculating the slope ($k^{1\text{H A}}$) of $k^{\text{obs}}$ versus [Co(II)] at different $pH$ values.

The results showed that $k^{1\text{H A}}$ values increased with $pH$ and plots of $\log k^{1\text{H A}}$ versus $pH$ were linear with a slope of ~1.0. The plots of $k^{1\text{H A}}$ versus $[H^+]^{-1}$ were straight lines, almost passing through origin. This shows that Eq. (2) is valid in the $pH$ range of 4.05–5.20 also. The Co(II)-PMS-AHA reactions were studied in the presence of aliphatic alcohols. Ethanol enhanced $k^{\text{obs}}$ values but not significantly, and we could not correlate $k^{\text{obs}}$ versus [EtOH]. The effect of alcohol on the rate was studied by calculating $k^{1\text{H A}}$ values in varying [EtOH]. The results show that $k^{1\text{H A}}$ value in the presence of ethanol is higher than in its absence. This clearly shows that ethanol is oxidized in the presence of AHAs also. $t$-Butanol had no effect on the rate/rate constant values.

Studies on the effect of [AHA] on the rate in perchloric acid medium and at higher $pH$ shows that the reaction is catalyzed in the buffered medium in contrast to the quenching in aqueous perchloric acid. This suggest that the mechanism of oxidation at buffered medium may be different from the one at perchloric acid medium.

Based on the experimental results, we propose the kinetic scheme in Eqs 38 and 39 for the oxidation of AHAs by PMS in the presence of Co(II) ions.

\[
\text{CoL}^+ + \text{SO}_5^{2-} \xrightleftharpoons[K_{12}]{k_\text{f2}} \text{Co(L)(SO}_5^\text{2-}) \quad \ldots(38)
\]

\[
\text{Co(L)(SO}_5^\text{2-}) \xrightarrow[k_o]{\text{products}} \quad \ldots(39)
\]

The concentration of various Co(II)-AHA complexes are calculated at the higher $pH$s using the reported formation constant values. The Co(II) ion is complexed to the extent of 50% or greater even at 0.05 $M$ of AHA. The concentration of Co(II)-α-hydroxycaboxylate, CoL*, remains almost constant (40–60%) and is independent of both $pH$ and [AHA] but the concentrations of CoL$_2$ and CoL$_3$, if any, increase linearly with AHA concentration. If CoL$_2$ and/or CoL$_3$ is involved in the reaction, then rate should be first order or higher order in [AHA]. The reaction is zero order in [AHA] and this excludes the reactions of higher Co(II) complexes. The kinetic scheme in Co(II) ion catalyzed decomposition of PMS (Eq. (26)) and the oxidation of ethanol (Eq. (32)) shows that the prerequisite for Co(II) ion catalyzed reaction is a complex intermediate Co(II)-SO$_5^{2-}$ or Co(II)(EtOH)-SO$_5^{2-}$. Such intermediates are less favorable with CoL$_2$ and CoL$_3$. This explains why CoL* alone is involved in the oxidation of AHAs.

Effect of ethanol concentration suggests that uncomplexed, that is free Co(II) ion may react with ethanol and PMS as discussed earlier. Therefore, in the kinetic scheme for the oxidation of AHA we have to include the Co(II) ion catalyzed decomposition of PMS (Eqs (22) and (28)) also. The rate equation for the oxidation of AHA can be expressed as in Eq. (40).

\[
\frac{-d[\text{HSO}_5^-]}{dt} = k^{\text{obs}}[\text{PMS}] = k^{1\text{H A}}[\text{SO}_5^{2-}] + k_o[\text{Co(L)(SO}_5^\text{2-})] \quad \ldots(40)
\]

Substituting for the concentration of Co(L)(SO$_5^\text{2-}$) in Eq. (40), we get Eq. (41).

\[
k^{1\text{H A}} = \frac{k^{\text{obs}} + (k_o K_{12} K_{2c} [L^+][H^+])[\text{Co(II)]}}{1 + K_{1c}[L^+] + K_{2c}[L^+]^2 + K_{3c}[L^+]^3} \ldots(41)
\]

The term $K_{1c}[L^+] / (1 + K_{1c}[L^+] + K_{2c}[L^+]^2 + K_{3c}[L^+]^3)$ in Eq. (41) represents the fraction of [Co(II)]$^+$ that exists as CoL$^+$ and can be calculated for a given $pH$. 

---

**Table 4.** The plots $k^{\text{obs}}$ versus $[\text{Co(II)}]$ were straight lines ($r>0.99$) passing through the origin.
The $k_{\text{obs}}$ values (Eq. (28)) were determined independently from the Co(II) ion catalyzed decomposition of PMS. Values of $k_0K_fK_d/\lbrack\text{H}^+\rbrack$ in Eq. (41), denoted by $k_{\text{AHA}}^1$, were determined at different pHs.

$$k_{\text{AHA}}^1 = k_0K_fK_d/\lbrack\text{H}^+\rbrack = k_1/\lbrack\text{H}^+\rbrack \quad \text{...(42)}$$

The $k_1(\times10^3, \text{s}^{-1})$ values calculated from the plots of $k_{\text{AHA}}^1$ versus $[\text{H}^+]^{-1}$ at 25 °C are as follows: PMS: 0.5(±0.0); EtOH: 3.0(±0.5); LA: 4.0(±0.0); GLA: 2.8(±0.2); AHIBA: 3.6(±0.2); MA: 2.2(±0.4). Perusal of these results suggests that the presence of a methyl group at the alpha position favors the oxidative decarboxylation. The oxidative decarboxylation process may be a slightly non-concerted one in which the oxidation of hydroxyl group or the elimination of the carboxylate group may occur first (to a smaller extent) resulting in a partial positive charge on the α-carbon. If decarboxylation takes place first, then the oxidation product from glycolic acid would be mainly formic acid (through formaldehyde). However, herein the products are a mixture of oxalic acid (major yield) and formic acid, thus supporting the mechanism that oxidation of Co(II)-α-hydroxy carboxylate proceeds through oxidation of hydroxyl group. The oxidation of Ni(II)-α-hydroxy carboxylates such as Ni(II)-glycolate and Ni(II)-lactate by PMS also involve an interaction between the peroxide oxygen (of PMS) and the hydroxyl group.

Calculations shows that ≥50% of the Co(II) ion exists as various complexes of AHAs. The Co(II) concentrations used were small ($10^{-5}$–$10^{-7}$ M) and hence the free metal ion concentration was not sufficient to enhance the rate through the oxidation of ethanol. This may be the reason why we could not get a correlation between the rate and [EtOH].

As pointed out earlier AHAs may favor/enhance the hydroxyl radical generation. If it is so, then both the radical quenchers, ethanol and $t$-butanol, should retard the reaction as observed in the Co(II) ion catalyzed decomposition of PMS in perchloric acid medium. However, the influence of these two alcohols on the reaction was different; ethanol catalyzed the reaction and $t$-butanol had no effect. This suggests that radical intermediate is not produced in Co(II)-AHA-PMS system and AHAs are oxidized through molecular mechanism, probably through oxygen atom transfer from PMS.

**Glycine**

The reaction in presence of glycine followed simple first order kinetics only at pH 4.05 and 25 °C ([Co(II)] = 1.25×$10^{-5}$–6.25×$10^{-5}$ M and [Gly] = 0.025 M to 0.10 M) and was auto-catalyzed (Eq. (43)) at all other pHs and temperatures. In Eq. (43) the first term represents the loss of PMS due to the oxidation of glycine. The second term corresponds to the intermediate catalyzed oxidation and the intermediate concentration is approximated to glycine oxidized (equivalent to [PMS] consumed).

$$-\frac{d[\text{PMS}]}{dt} = k_{\text{obs}}1[\text{PMS}] + k_{\text{obs}}2([\text{PMS}]_0-[\text{PMS}]_1)[\text{PMS}]_0 \quad \text{...(43)}$$

The reactions were fast and auto-catalyzed at pH 5.20 and higher temperatures, even in the absence of Co(II) ion. Therefore, we have limited the kinetic study on the effect of [Gly], [EtOH], etc., only to pH 4.05 and 4.75 at 25 °C and 31 °C.

The effect of Co(II) concentration on the rate was studied with 0.05 M of glycine. One interesting observation was that the contribution from the intermediate catalyzed oxidation decreased with increasing [Co(II)] and finally the reaction became first order. The $k_{\text{obs}}$ values were found to increase with the metal ion concentrations and the plots of $k_{\text{obs}}$ versus [Co(II)] were straight lines with a small positive intercept.

The influence of glycine concentration (0.013–0.15 M) on the rate was also studied. The Co(II) concentration was chosen in such a way that the rate was simple first order at 0.05 M of glycine. As the concentration of glycine was increased, the first order reaction became auto-catalyzed. The $k_{\text{obs}}$ values increased slightly with [Gly] but could not be correlated. The plots of $k_{\text{obs}}$ versus [Gly] were straight lines with a negative intercept. These observations are in accordance with the earlier reports. The slope of the plots $k_{\text{obs}}$ versus [Gly] is independent of [Co(II)].

The role of ethanol (17.0–2550 mM) on the reaction was investigated at 31 °C. The reactions which were originally first order, were auto-catalyzed by the added ethanol. The $k_{\text{obs}}$ values were found to
increase and reached a limiting value with [EtOH] and gave a correlation similar to Eq. (30). The $k_{\text{obs}}$ values were independent of ethanol concentrations. $t$-butanol, had no effect on the order or on rate constant values. Earlier reports from this laboratory\textsuperscript{13} showed that $\alpha$-amino acids were oxidized by PMS ($pH$ 4.0–5.2) and the reactions were auto-catalyzed by the product aldehyde.

Under the experimental conditions with $[\text{Gly}] = 0.05 M$, Co(II)-glycine complex (Co(II)L\textsuperscript{2+}) is negligible at $pH$s 4.0 and 4.75 and is ~7.5% at $pH$ 5.2.\textsuperscript{45,46} Therefore, we can safely assume that Co(II) ion exists as the free metal ion and the concentration can be equated to the total analytical concentration, i.e., $[\text{Co(II)}] = [\text{Co(II)}]_T$. Therefore, in the presence of glycine, the metal ion and the substrate will react independently with PMS. The $k_{\text{obs}}$ in Eq. (43) can be expressed as in Eq. (44) and the first term corresponds to Co(II) ion catalyzed decomposition of PMS given by Eq. (28). If it is so, then the slope of the plots $k_{\text{obs}}$ versus $[\text{Co(II)}]$ in the presence of glycine (Eq. (44) should be equal to the values of $k_{\text{obs}}^{\text{ph}}$ obtained from the Co(II) ion catalyzed decomposition of PMS (Eq. (28)). This is found to be true from the values shown in Table 3.

$$k_{\text{obs}} = k_{1}^{\text{ph}} [\text{Co(II)}] + k_{1}^{\text{A}[\text{gly}]}$$

The kinetics changes from autocatalysis to first order one as the concentration of Co(II) ion is increased. This can be explained as follows: At lower $[\text{Co(II)}]$, $k_{1}^{\text{ph}} [\text{Co(II)}]$ may be small in comparison with the second term in Eq. (44) and can be neglected. Therefore the approximation made in Eq. (43), namely, the [PMS] reacted was equal to the concentration of aldehyde produced, holds good and the reaction follows autocatalysis. This approximation is not applicable at higher concentration of Co(II) and this will explain why the reaction changes to first order as the concentrations of Co(II) is increased.

The oxidation of glycine was studied in the presence of ethanol also. The cobalt(II) ion concentration was chosen such that the rate of the reaction was simple first order in [PMS] in the absence of ethanol. Even at this concentration, the added alcohol made the reaction auto catalyzed one (Eq. (43)). This is due to the Co(II) ion catalyzed oxidation of ethanol into acetaldehyde. Therefore, aldehyde is initially introduced into the reaction from ethanol instead of glycine and the reaction becomes auto catalyzed. Therefore $k_{\text{obs}}$ in Eq. (44) can be replaced by the rate constants in the presence of ethanol and glycine.

$$k_{\text{obs}} = k_{1}^{\text{EtOH}} + k_{1}^{\text{A}[\text{gly}]}$$

The $k_{1}^{\text{EtOH}}$ is obtained from Eq. (37) and hence the plot of $k_{1}^{\text{EtOH}}$ versus [EtOH] should be similar to the one observed in the oxidation of ethanol without glycine. This is found to be true and the kinetic constants, $K$ and $k_{1}^{\text{EtOH}}$, values for the oxidation of ethanol in the presence of glycine coincide with the values in its absence (Table 4). This clearly shows that the Co(II) ion catalyzed oxidation of ethanol is taking place in the presence of glycine also. The lower concentrations and the oxidation of glycine itself make it difficult to obtain any information on the reactivity of Co(II)-glycine complexes with PMS.

### Conclusions

The Co(II) ion catalyzed decomposition of PMS was studied in strong acidic (aqueous perchloric acid) $pH$ (~1.0) and in acetate buffer ($pH$ 4.05–5.2) as well. The reaction was also studied in the presence of simple organic compounds such as alcohols (ethanol and $t$-butanol), $\alpha$-hydroxy acids and glycine. The reaction shows $[H^{+}]^{-1}$ dependence over entire range of $pH$ in accordance with the earlier reports.\textsuperscript{14} In strong acid medium, the reaction was quenched by ethanol, $t$-butanol and AHAs in the order: ethanol > AHAs > $t$-butanol. This observation suggest that in strong acid, the redox process is operative resulting in the formation of sulphate radical intermediate. In acetate buffer medium ($pH$ 4.05–5.20) ethanol, AHA and glycine catalyse the reaction and get oxidized quantitatively, which $t$-butanol has no effect. This suggests that the radical mechanism is operative only at strong acid medium and not over the entire $pH$ range (1.0–6.0) as proposed by earlier workers.\textsuperscript{14,15} The catalytic effect of ethanol and AHAs can be explained by a molecular mechanism involving the oxygen atom transfer from PMS. At higher $pH$ catalyzed decomposition of PMS and the oxidation of organic substrate proceed through the same mechanism. The results also suggest that the organic compounds which can chelate with Co(II) are
oxidized readily at higher pHs and are catalyzed by the metal ion concentrations of ppm or lower level. One advantage of the Co(II) ion catalyzed reactions of PMS at higher pH may be the elimination of the adverse effect of Co(II) on the environmental systems.

Acknowledgement

CL and PA express their gratitude to University Grant Commission, New Delhi, India, for financial assistance through UGC-Meritorious fellowship.

References

36. Feigl F, *Spot Tests in Organic Analysis*. (Elsevier, New York) 1956, (a) p. 120; (b) p. 340; (c) p. 355; (d) p. 342.