Journal of Molecular Catalysis A: Chemical xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Effect of metal ions on acetone dicarboxylic acid catalyzed peroxomonosulphate reactions

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A R T I C L E I N F O

Article history:
Received 31 July 2013
Received in revised form 20 February 2014
Accepted 22 February 2014
Available online xxx

Keywords:
Metal citrate
Peroxomonosulphate
Acetone dicarboxylic acid
Oxidation
Autocatalysis

A B S T R A C T

The oxidation of Fe(III), Ni(II) and Co(II) citrates by peroxomonosulphate (PMS) in the pH range 3.0–6.0 follows autocatalysis mechanism. The acetone dicarboxylic acid (ADC), the oxidative decarboxylation product from citrate, is found to catalyze the reaction. The added metal ions switch the reaction from the ADC catalyzed decomposition of PMS to the oxidation of citrates. Based on the results from alcohol quenching, a mechanism involving oxygen atom transfer is proposed.

1. Introduction

Citric acid (2-hydroxy propane-1,2,3-tricarboxylic acid), a weak organic acid, is an important intermediate in the tricarboxylic acid cycle, a metabolic pathway involved in the conversion of carbohydrates, fats and proteins to generate energy [1]. Its versatility as ligand for transition metal ions in chemical reactions of biological and analytical interest is widely known. Citric acid is used as a masking reagent for most metal ions [2] and buffering agent in the universal buffer solution, Mcllavaine's buffer [3]. The reactions involving citric acid are used to determine the ultra trace quantities of metal ions [4,5]. Citric acid plays an important role in food and pharmaceutical industries as acidulent, flavoring and preservative agent [6]. Citric acid and citrate are the reagents used in the environmental friendly nickel electroplating baths [7–10]. The biological and industrial importance of citric acid results in an increased attention on its oxidation and no report is available on the reaction with peroxomonosulphate, an inorganic peroxide.

Peroxomonosulphate ion (PMS), commercially available as OXONE® is a powerful oxidant with a reduction potential of +1.8 V [11]. PMS in the presence of transition metal ions generates radical intermediates of high oxidizing capacity. Anipsitakis and Dionysiou [12] studied the activation of PMS by various transition metal ions with special reference to the catalytic efficiency and the nature of radical intermediates generated. Cobalt(II), nickel(II) and ferrous ions produce sulphate radical intermediate and Co(II) is more efficient catalyst. The sulphate radical, with a redox potential of 2.5–3.1 V [13], is a better oxidizing agent than its precursor PMS. Therefore, Co(II)–PMS system is one of the methodologies used in advanced oxidation technology (AOT) for environmental technology such as removal of organic pollutants in water remediation [14–19] and degradation of dyes [20–25]. Wang and co-workers [24,25] observed that the reaction Co(II)-PMS with chloride ion proceed through both one electron transfer (resulting chlorine radical through sulphate radical intermediate) and two electrons transfer (producing chlorine). Results on the oxidation of cobalt(II) malate complexes by PMS [26] show that in the pH range 4.0–5.9 the probable mechanism may be a molecular (oxygen atom transfer) one. These observations suggest that the reactions Co(II)–PMS system under favorable conditions can proceed through molecular mechanism also.

The α-hydroxy carboxylates undergo oxidative decarboxylation to corresponding aldehydes or ketones [27]. It has been shown that the oxidative decarboxylation proceeds mainly through two-electrons process if the carboxylate contains both alpha hydrogen and alpha hydroxyl groups [28,29]. Citric acid/citrate has no hydrogen at hydroxyl carbon but the earlier reports [28,30–33] suggest that the oxidation leads to carbon dioxide elimination giving acetone dicarboxylic acid (ADC). Aliphatic ketones catalyze the decomposition of PMS [34,35] through a stable intermediate oxirane [36] which is also a powerful oxidizing agent [37–39]. Not only the simple ketones, but also alpha keto acids/esters such as

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http://dx.doi.org/10.1016/j.molcata.2014.02.023
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pyruvates [40,41] are also reported to give oxirane type intermediates. These ketone catalyzed reactions were observed only at neutral or weakly alkaline medium. Preliminary experiments from our laboratory shows that the ADC catalyzes the decomposition of PMS in moderate acidic pH (3.0) also. Results from this laboratory on the oxidation of metal(II)-α-hydroxy carboxylates by PMS [26,42] show that the reactions follow auto catalysis. The intermediate between α-hydroxy carboxylate and its oxidative decarboxylation product aldehyde is responsible for autocatalysis. Similar to this, the product acetone dicarboxylic acid may catalyze the oxidation of metal citrates or it can enhance the decomposition of PMS. Therefore, to explore the actual role of ADC it has been studied that the oxidation of citric acid by PMS in the presence of Fe(III), Ni(II) and Co(II) in the pH range 3.0–6.0 and the results are discussed in this report.

2. Materials and methods

All the chemicals used were of the highest purity commercially available and were used as received. The peroxide under the name OXONE®, monopersulphate compound was from Sigma–Aldrich GmbH (Germany). $Ni(NO_3)_2 \cdot 6H_2O$ (Extrapure, SD FINE-CHEM, India), $Co(OAC)_2{\cdot}4H_2O$ (Merck, India) and $NH_4Fe(SO_4)_2 \cdot 12H_2O$ (GR, Merck, India) were the source of metal ions. Acetone dicarboxylic acid (3-oxo glutaric acid) was 96% pure and from Sigma–Aldrich GmbH (Germany). This compound was recrystallized repeatedly from ethyl acetate to get a sharp melting point of 135 °C [43]. The peroxide solution was freshly prepared daily and standardized by iodometry. The pH of the reaction mixture was adjusted with citric acid-phosphate buffer. The pH values were adjusted to the predetermined values by adjusting the concentration of disodium hydrogen phosphate while keeping the citric acid concentration at a predetermined value, usually at 0.05 M. The rates of the reaction were calculated by following the concentration of unreacted PMS iodometrically at various times.

The stoichiometry of the reaction was determined at pH 4.8. A large excess of PMS (0.05 M) over citric acid (0.01 M) and the metal ion (0.002–0.0002 M) were allowed to stand for 6–8 h and the unreacted PMS was estimated. The unreacted oxidant concentration was very small in Ni(II) and Co(II) ions and this may be due to the self decomposition of PMS catalyzed by the metal ions. Therefore the stoichiometry was determined with equal concentration (0.01 M) of PMS and citric acid. The evolution of carbon dioxide from this mixture was confirmed with freshly prepared lime water. The oxidation product from citric acid gave 2,4-dinitro phenylhydrazone derivative which decomposed on heating. The formation of acetone dicarboxylic acid (3-ketoglutaric acid) was confirmed by the color test with sodium nitroprusside [44]. Acetone dicarboxylic acid was converted into acetone by the addition of aniline [45] and acetone was estimated as 2,4-dinitro phenylhydrazone (m.pt 126–127 °C, lit. 128 °C [46]). The quantitative estimation indicated that ~95–97% of the keto compound is produced per mole of PMS. Therefore, the oxidation of citric acid can be represented as in Eq. (1).

$$\text{Citric acid} + HSO_5^- \xrightarrow{M(II)/M(III)} \underset{(ADC)}{\text{Acetone dicarboxylic acid}} + CO_2 \uparrow \tag{1}$$

The stoichiometric determinations were also made in the presence of acetone dicarboxylic acid also. One interesting observation was that in the absence of metal ions, the evolution of oxygen gas was observed and was confirmed by the color test with alkaline sodium dithionite activated with indigo carmine [47]. Also the evolution of carbon dioxide was inhibited and could not be detected with lime water. The change in the concentration of acetone dicarboxylic acid, estimated as acetone, was practically negligible. Moreover, the turn over number, the number of moles of PMS decomposed per mole of ADC, was greater than six. These observations clearly show that in the absence of metal ions the decomposition of PMS is observed as in Eq. (2).

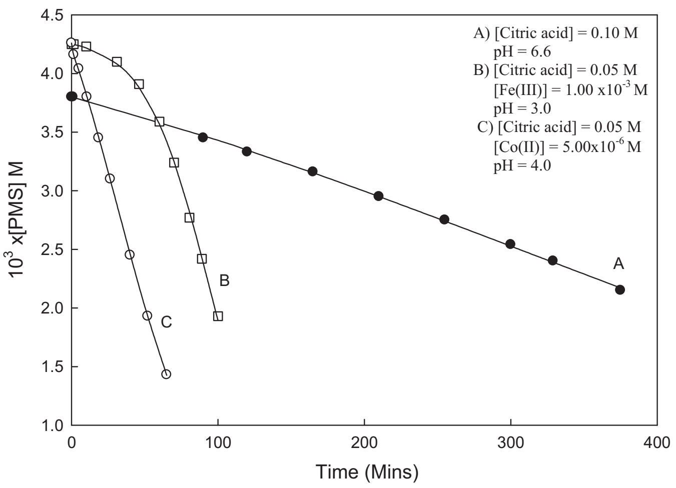

Fig. 1. Plot of [PMS] vs. time at 31.0 °C.

$$\text{Citric acid} + \text{ADC} + HSO_5^- \rightarrow \text{Citric acid} + \text{ADC} + O_2 \uparrow \tag{2}$$

However, in the presence of metal ions, the reaction reverted to the oxidation of citric acid as confirmed by the formation of carbon dioxide, absence of oxygen gas evolution and an increase in ADC concentration equal to that of PMS concentration. Thus the reaction in the presence of metal ions can be represented by Eq. (3).

$$\text{Citric acid} + \text{ACD} + HSO_5^- \xrightarrow{M(II)/M(III)} 2\text{ADC} + CO_2 \uparrow \tag{3}$$

3. Results and discussion

The oxidation of citric acid was observed only at pH ≥6.0 and that too at a slow speed. The conversion of [PMS] was ~25% at pH 6.0 and ~50% at pH 6.6 (Fig. 1A) for 6 h. In the presence of metal ions with the concentration range $\sim 10^{-5}$ M to 10^{-3} M, the oxidation of citric acid/citrate proceeded smoothly at a measurable rate even at pH 3.0 (Fig. 1B and C). This clearly shows that the metal ions catalyzed the oxidation of citric acid/citrate by PMS. The $[PMS]_t$–time profile for Fe(III) ion catalyzed reaction at pH 3.0 is shown in Figs. 1B and 2A. The reaction shows an induction period, usually 10–20 min after which the rate becomes fast. This feature

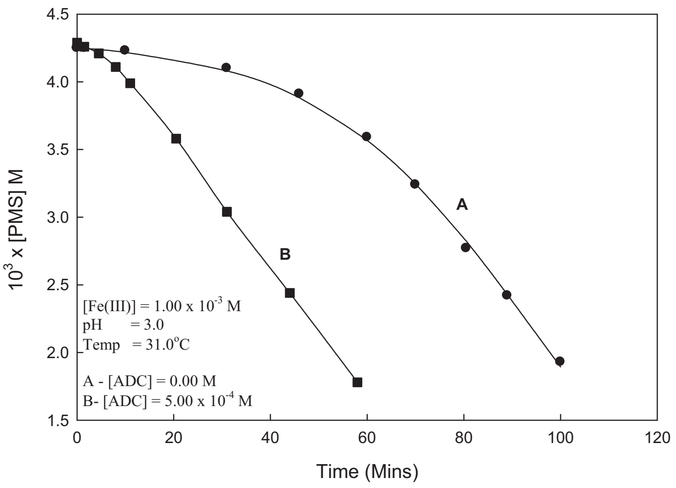

Fig. 2. PMS–time profile for Fe(III) ion catalyzed reaction.

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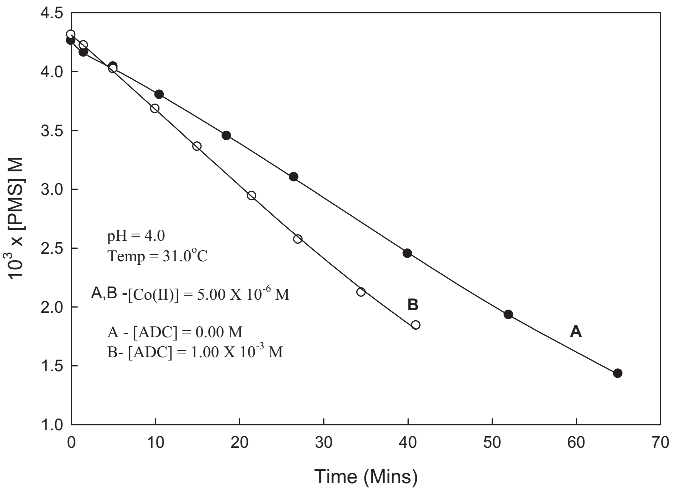

Fig. 3. PMS–time profile for Co(II) ion catalyzed reaction.

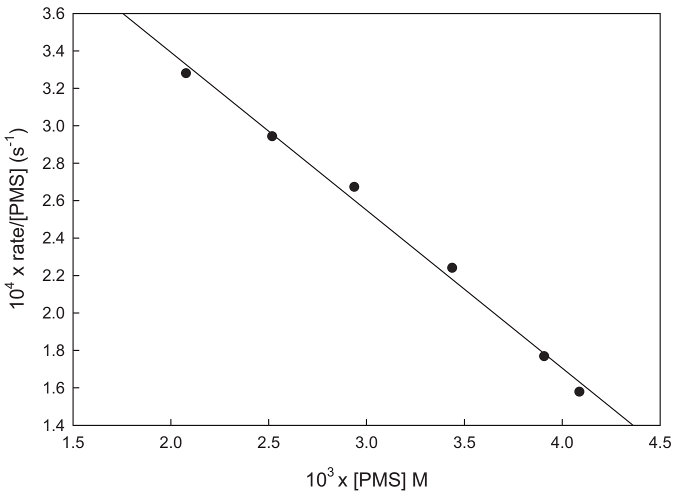

Fig. 4. Plot of (rate/[PMS]) vs. [PMS] for Co(II) ion catalyzed reaction in A.

is observed at all pH values (3.0–6.0) employed in this study. However no such induction period was observed in the Ni(II) and Co(II) (Figs. 1C and 3A) ions catalyzed reactions. The Co(II) catalyzed oxidation at pH 3.0 can be represented by simple first order kinetics with respect to [PMS] but at higher pH values and for Ni(II) (pH 3.0–6.0) the rate can not be expressed by the simple rate equations. Analysis of the results suggests that the metal ion catalyzed oxidation of citric acid can be explained by simple autocatalysis mechanism shown in reactions (4) and (5).

$$O + S \xrightarrow{k_1} C + P \tag{4}$$

$$S + C + O \xrightarrow{k_2} 2C + P \tag{5}$$

The oxidant PMS (O) reacts with the substrate (S) to yield the products C and P. One of the products (C) accelerates the reaction. The rate in terms of the decrease in [PMS] is given in Eq. (6).

$$\text{rate} = \frac{-[\text{PMS}]}{dt} = k_1[\text{S}][\text{PMS}]_t + k_2[\text{C}]_t[\text{PMS}]_t \tag{6}$$

If the catalyst (C) leakage is negligible, then $[\text{C}]_t$ can be replaced by the term $[\text{C}]_0 + [\text{PMS}]_0 - [\text{PMS}]_t$ where $[\text{C}]_0$ is the concentration of the catalyst at the start and ($[\text{PMS}]_0 - [\text{PMS}]_t$) represent the catalyst produced in the reaction. Since $[\text{S}] \gg [\text{O}]$ Eq. (6) can be simplified as in Eq. (7) where $k_{1\text{obs}} = k_1 \cdot [\text{S}]$ and $k_{2\text{obs}} = k_2 \cdot [\text{S}]$.

$$\text{rate} = k_{1\text{obs}}[\text{PMS}]_t + k_{2\text{obs}}([\text{C}]_0 + [\text{PMS}]_0 - [\text{PMS}]_t)[\text{PMS}]_t \tag{7}$$

According to Eq. (7) the plot rate/$[\text{PMS}]_t$ vs. $[\text{PMS}]_t$ should be in a straight line with a negative slope and positive intercept. This is found to be true (Fig. 4) and this confirms that all the reactions follow autocatalysis even though PMS-time profiles for Co(II) and Ni(II) sans the initial induction period.

The better values of $k_{1\,\text{obs}}$ and $k_{2\,\text{obs}}$ can be obtained from Eq. (8), the integrated form of Eq. (6).

$$[\text{PMS}]_t = \frac{k_{1\text{obs}} + k_{2\text{obs}}([\text{PMS}]_0 + [\text{C}]_0)}{k_{2\text{obs}} + ((k_{1\text{obs}} + k_{2\text{obs}}[\text{C}]_0)/[\text{PMS}]_0)\exp(t \times (k_{1\text{obs}} + k_{2\text{obs}}([\text{PMS}]_0 + [\text{C}]_0)))} \tag{8}$$

The kinetic constants $k_{1\,\text{obs}}$ and $k_{2\,\text{obs}}$ can be obtained from Eq. (8) by non-linear regression analysis. The $k_{1\,\text{obs}}$ and $k_{2\,\text{obs}}$ values calculated from Eqs. (7) and (8) are agreeable. However, as a rule the $k_{1\,\text{obs}}$ and $k_{2\,\text{obs}}$ have been calculated from non-linear regression analysis of Eq. (8) using the values from the derivative plots (Eq. (7)) as the approximate initial inputs for non-linear regression.

The product analysis (Eq. (1)) shows that the oxidation product from citric acid is acetone dicarboxylic acid. This is in accordance with the earlier reports [28,30–33]. Therefore, one would expect that the catalyst 'C' in Eq. (4) may be acetone dicarboxylic acid. The proposed kinetic scheme (Eqs. (4) and (5)) can be verified by calculating kinetic constants $k_{1\,\text{obs}}$ and $k_{2\,\text{obs}}$ with the added acetone dicarboxylic acid. Before that, the interaction of acetone dicarboxylic acid with PMS and citric acid has to be studied. The product analysis and stoichiometric determination (Eq. (2)) show that only the self decomposition of PMS takes place and this reaction is observed even at pH 3.0. One such result on the loss of PMS in the absence of metal ions is shown in Fig. 5A. Perusal of the result shows that the rate of [PMS] loss follows first order kinetics, as in Eq. (9), over

$$\frac{-d[\text{PMS}]}{dt} = k_{\text{obs}}[\text{PMS}] = k^{\text{ADC}}[\text{ADC}][\text{PMS}] \tag{9}$$

the pH range 3.0–6.0 and the plots k_{obs} vs. [ADC] (Fig. 6) are in straight lines passing through the origin. The k^{ADC} values calculated at different pH values are shown in Table 1.

The [PMS]–time profile in the presence of metal ion is shown in Fig. 5(B). Comparison of the curves in Fig. 5 shows that the mechanism of the reaction in the presence of the metal ion (Fig. 5B) may be different from its absence (Fig. 5A). This is also supported by the product analysis (Eqs. (2) and (3)). Careful analysis such as the plot of (rate/$[\text{PMS}]_t$) vs. $[\text{PMS}]_t$ for the curve 5B shows that the reaction with added ADC also follows autocatalysis. This can be verified by

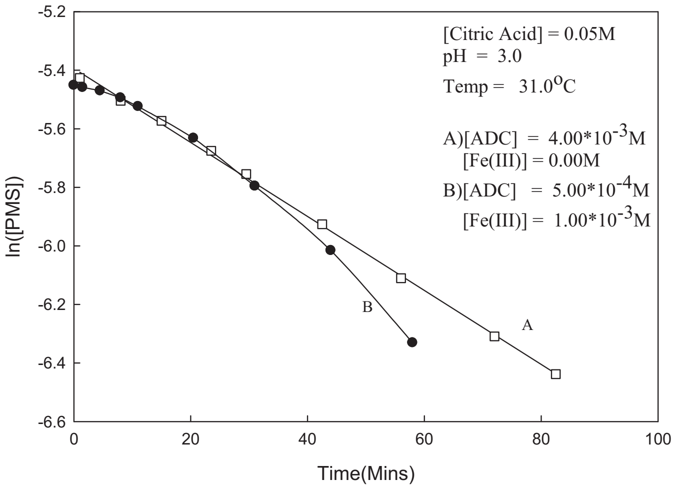

Fig. 5. The ln([PMS])–time plot at 31.0 °C.

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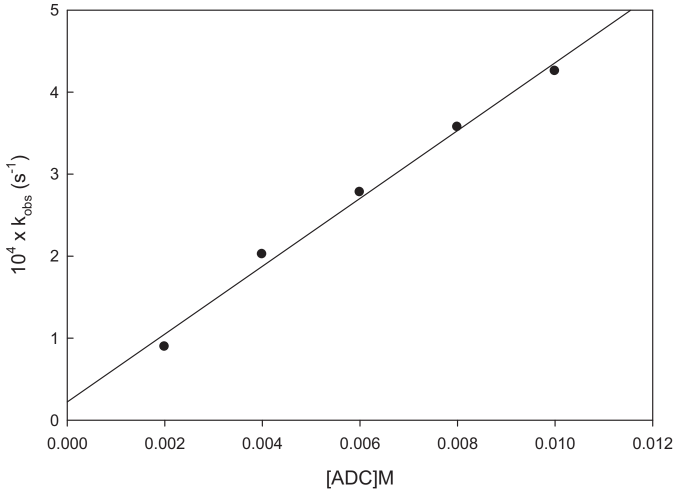

Fig. 6. Plot of k_{obs} vs. [ADC] at 31.0 °C.

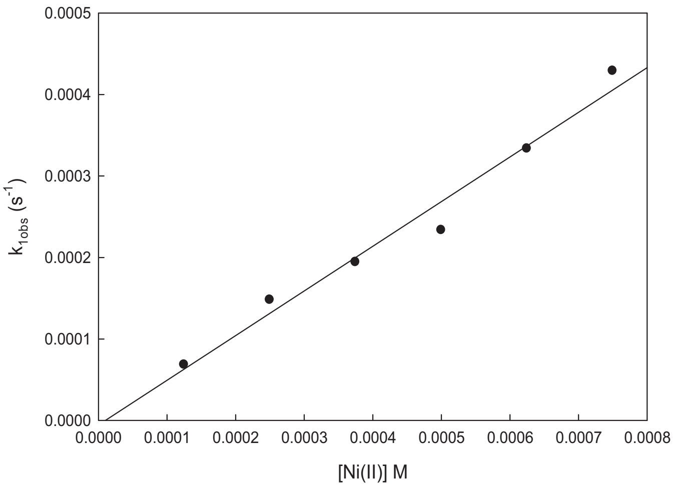

Fig. 7. Plot of k_{1obs} vs. [Ni(II)] at pH = 6.0, temp. = 31.0 °C.

Table 1
Kinetic constants k^{ADC} for the decomposition of PMS.

Temp. (°C)	$10^2 \times k^{ADC}$ (M^{-1} s^{-1})			
	pH			
	3.0	4.0	4.8	6.0
31.0	4.14 ± 0.23	9.92 ± 0.73	13.14 ± 0.63	14.67 ± 1.34
	(4.0)[a]	(8.25)[a]	(15.0)[a]	(14.0)[a]
	–	(8.5)[b]	(11.7)[b]	(13.0)[b]

Values in the parenthesis from the metal ion catalyzed oxidation in the absence of ADC.
[a] Ni(II) ion.
[b] Co(II) ion.

calculating the kinetic constants $k_{1\,obs}$ and $k_{2\,obs}$ with and without the added ADC. The kinetic constants for the Fe(III)–citric acid–PMS system with no ADC at the start (Fig. 2A) calculated with Eq. (8) are: $k_{1\,obs} = 1.01 \pm 0.07 \times 10^{-5}\ s^{-1}(3.77 \pm 1.08 \times 10^{-5}\ s^{-1})$ and $k_{2\,obs} = 17.56 \pm 0.45 \times 10^{-2}\ M^{-1}\ s^{-1}$ $(13.22 \pm 0.94 \times 10^{-2}\ M^{-1}\ s^{-1})$. The values in the parenthesis correspond with ADC (Fig. 2B) at the start. Similar values to the Co(II) ion catalyzed reaction (Fig. 3A and B) are: $k_{1\,obs} = 14.26 \pm 0.17 \times 10^{-5}\ s^{-1}$ $(14.55 \pm 1.37 \times 10^{-5}\ s^{-1})$ and $k_{2\,obs} = 9.66 \pm 0.02 \times 10^{-2}\ M^{-1}\ s^{-1}(9.07 \pm 0.73 \times 10^{-2}\ M^{-1}\ s^{-1})$. The close agreement between the kinetic constant values from the reactions in the absence and in the presence of ADC suggests that the kinetic scheme proposed for the oxidation of metal citrate may explain the experimental results.

The kinetic constants $k_{1\,obs}$, $k_{2\,obs}$ and k_{obs} were calculated at different experimental conditions. The results show that sulphate ion has no effect on the rate. However, all the kinetics studies were carried out only in the presence of 0.05 M sulphate ion. The kinetic constants $k_{1\,obs}$, $k_{2\,obs}$ and k_{obs} were found to be independent of citric acid concentration in all the reactions.

The $k_{1\,obs}$ values were found to increase with Co(II) and Ni(II) ion concentration and the plots $k_{1\,obs}$ vs. [M(II)] were in straight lines passing through the origin (Fig. 7). Therefore the correlation between $k_{1\,obs}$ and [M(II)] can be represented as in Eq. (10). The k_1 values calculated at different pH values are shown in Tables 2 and 3).

$$k_{1\,obs} = k_1 \cdot [\mathrm{M(II)}] \qquad (10)$$

The initial oxidation of Fe(III)–citric acid by PMS is very slow and this may be the reason why the initial part of [PMS]–time profile is almost parallel to time axis(Fig. 2A). Therefore $k_{1\,obs}$ values of Fe(III)–citrate may be associated with high uncertainty. Moreover the $k_{1\,obs}$ values differ from $k_{2\,obs}$ by a factor of ~10^{-4}. The kinetic studies were usually carried out with $[\mathrm{PMS}]_0 \approx 4.0 \times 10^{-3}$ M and hence $k_{1\,obs} \ll k_{2\,obs}[PMS]_0$. The $k_{1\,obs}$ values for Fe(III)–citric acid system calculated by non-linear regression may have large fluctuation and this may be the reason that the correlation between $k_{1\,obs}$ and [Fe(III)] could not be obtained.

At constant pH and citric acid, $k_{2\,obs}$ values were independent of Co(II) and Ni(II) concentration whereas in ferric citrate oxidation $k_{2\,obs}$ showed a linear correlation with [Fe(III)]. The plots $k_{2\,obs}$ vs. [Fe(III)] were straight lines passing through (approximately) the origin. The kinetic constant values were also calculated in the presence of aliphatic alcohols such as ethanol and tert. butyl alcohol so as to ascertain the formation of radical intermediates such as sulphate ion radical and or hydroxyl radical [12,13,48,49]. The concentration of alcohols used were ~100:1 molar ratio of the alcohol vs. the oxidant PMS. The alcohols did not affect the rate or rate constants and this suggests that the possibility of the reaction mechanism involving radical intermediates such as $SO_4^{-\bullet}$ and $OH^\bullet$ radicals can be neglected.

Peroxomonosulphate dissociates to give the dinegative anion as in Eq. (11).

$$HSO_5^- \overset{K_d}{\rightleftarrows} SO_5^{2-} + H^+ \qquad (11)$$

The pK_a value of PMS is 9.4 at 25 °C [50] and at the experimental pH values (3.0–6.0) the equilibrium will be shifted towards left, that is all the PMS will exist as HSO_5^-.i. *The acetone dicarboxylic acid catalyzed decomposition of PMS*

Acetone dicarboxylic acid is a weak acid with pK_a [51] values 3.23 and 4.27 at 25 °C (Eqs. (12) and (13)). The experimental results (Eq. (2)) in the absence of metal

$$\mathrm{HOOC\ CH_2COCH_2COOH} \overset{K_{a1}}{\rightleftharpoons} \mathrm{HOOC\ CH_2COCH_2COO^-} + H^+ \qquad (12)$$

$$\mathrm{HOOC\ CH_2COCH_2COO^-} \overset{K_{a2}}{\rightleftharpoons} \mathrm{{}^-OOC\ CH_2COCH_2COO^-} + H^+ \qquad (13)$$

ions suggest that the loss of PMS can be due to the ADC catalyzed decomposition of PMS. The results are similar to the ketone catalyzed decomposition of caroate [34,35]. By analogy, some reactive intermediate such as oxirane may be responsible for the ADC catalyzed decomposition of PMS also. The detailed mechanistic scheme is shown in Fig. 8.

Based on the experimental observations the following kinetic scheme for the ADC catalyzed decomposition of PMS can be proposed.

$$\mathrm{HOOC\ CH_2COCH_2COOH} + HSO_5^- \xrightarrow{K_1^{ADS}} \mathrm{Products} + O_2 \uparrow \qquad (14)$$

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Table 2
Kinetic constants for the Co(II)–citrate oxidation.

Temp. (°C)	k_1 (M^{-1} s^{-1})			
	pH			
	3.0	4.0	4.8	6.0
25.0	2.28 (±0.04)	17.23 (±1.15)	59.27 (±3.09)	289.83 (±20.95)
31.0	4.89 (±0.15)	28.58 (±1.95)	95.31 (±4.45)	471.52 (±40.44)

Table 3
Kinetic constants for the Ni(II)–citrate oxidation.

Temp. (°C)	$10^3 \times k_1$ (M^{-1} s^{-1})			
	pH			
	3.0	4.0	4.8	6.0
25.0	1.10 (±0.15)	11.76 (±0.09)	75.24 (±1.06)	362.1 (±7.20)
31.0	3.06 (±0.12)	27.0 (±5.1)	101.0 (±1.0)	548.0 (±44.0)

$$\mathrm{HOOC\ CH_2COCH_2COO^-} + \mathrm{HSO_5^-} \xrightarrow{K_2^{ADS}} \mathrm{Products} + \mathrm{O_2}\uparrow \tag{15}$$

$$\mathrm{^-OOC\ CH_2COCH_2COO^-} + \mathrm{HSO_5^-} \xrightarrow{K_3^{ADS}} \mathrm{Products} + \mathrm{O_2}\uparrow \tag{16}$$

The k^{ADC} values calculated from Eq. (9) can be written as $k^{ADC} = \alpha_{H_2A} \cdot k_1^{ADC} + \alpha_{HA} \cdot k_2^{ADC} + \alpha_A \cdot k_3^{ADC}$ where α represents the fraction of the total acid present as corresponding ionized form. At pH 6.0, ADC exists exclusively (>98%) as the doubly ionized form so that $k^{ADC} = k_3^{ADC}$. Similarly from the values of k^{ADC} (Table 1) and α values at different pH values the k values are calculated as $k_1^{ADC} = 0.02\,M^{-1}\,S^{-1}$, $k_2^{ADC} = 0.07\,M^{-1}\,S^{-1}$ and $k_3^{ADC} = 0.15\,M^{-1}\,S^{-1}$ at 31 °C. The observed difference can be explained via intra molecular hydrogen bonding in ADC proposed by earlier researchers [51].

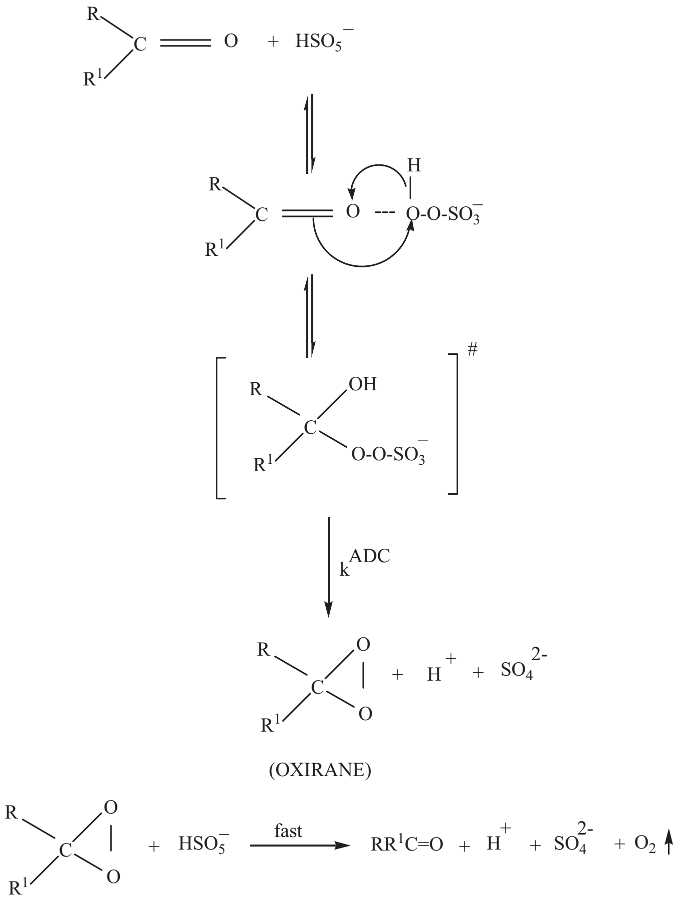
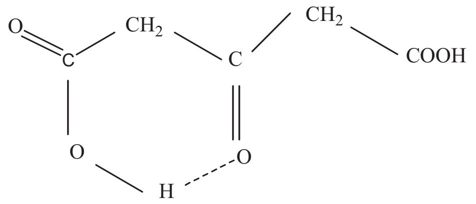


Fig. 8. Mechanism for acetone dicarboxylic acid catalyzed decomposition of PMS.



The studies on the self decomposition of PMS [50] showed that the peroxide oxygen in SO_5^{2-} is a nucleophile while HSO_5^- is an electrophile. Therefore, the first step in the interaction between ADC and HSO_5^- is the electrophilic interaction of PMS with the carbonyl oxygen (Fig. 8). The hydrogen bonding with the carbonyl group would inhibit this reaction. Therefore, one would expect that the reaction is more favorable in doubly ionized acetone dicarboxylic acid and less in unionized ADC. Hence the expected order of rate constant values would be $k_3^{ADC} > k_2^{ADC} > k_1^{ADC}$ and the calculated values are in accordance with this expectation.

ii. *The metal ion catalyzed oxidation of citric acid*:

Citric acid (H_3Cit) is an alpha hydroxy aliphatic acid and has four removable hydrogen atoms (as protons), three from carboxyl groups and one from the hydroxyl group. Therefore, citrate ion can act as a multidentate ligand towards transition metals. The metal ion–citrate complex equilibria in solution have been investigated extensively and the various complexes can be represented by the following equations.

$$\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + \mathrm{H_2Cit^-} \rightleftharpoons [\mathrm{M\ H_2Cit}] \tag{17}$$

$$\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + \mathrm{HCit^{2-}} \rightleftharpoons [\mathrm{M\,HCit}] \tag{18}$$

$$\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + \mathrm{Cit^{3-}} \rightleftharpoons [\mathrm{MCit}] \tag{19}$$

$$\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + 2\mathrm{Cit^{3-}} \rightleftharpoons [\mathrm{M(Cit)_2}] \tag{20}$$

$$\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + 2\mathrm{Cit^{3-}} + \mathrm{H^+} \rightleftharpoons [\mathrm{M(Cit)(HCit)}] \tag{21}$$

$$\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + \mathrm{Cit^{3-}} \rightleftharpoons [\mathrm{M(H_{-1}Cit)}] + \mathrm{H^2} \tag{22}$$

$$2\mathrm{M}\left(\begin{matrix}\mathrm{II}\\\mathrm{III}\end{matrix}\right) + 2\mathrm{Cit^{3-}} \rightleftharpoons [\mathrm{M_2(H_{-1}Cit)_2} + 2\mathrm{H^+}] \tag{23}$$

The complexation of citric acid with Ni(II) and Co(II) ions involves the bonding with carboxylate groups but no interaction

Table 4
Kinetic constants for the Fe(III)–citrate oxidation.

Temp. (°C)	k_3 (M^{-1} s^{-1})			
	pH			
	3.0	4.0	4.8	6.0
25.0	71.22 (±8.34)	70.59 (±8.70)	53.69 (±4.64)	56.64 (±3.35)
31.0	102.78 (±12.65)	123.33 (±4.15)	85.17 (±7.01)	95.63 (±12.34)

with the hydroxyl group. The complexes given in Eqs. (17)–(21) are observed in Ni(II)–citric acid system [52,53] and Co(II)–citrate [53] complexes can be represented as in Eqs. (17)–(19). A simple calculation using the reported equilibrium constant values [52,53] shows that ~20–30% of $[M(II)]_T$ exists as (un complexed) free ion at pH 3.0 which decreases to an insignificant level (~1–3%) as the pH is increased to 4.0. The nature of the complex depends upon the pH of the reaction mixture. At pH 3.0 Ni(II)–citrate exists as NiHCit (~50%) and NiH_2Cit^+ (~26%). At a higher pH (≥4), the Ni(II) ion exists mainly as $Ni(Cit)(HCit)^{3-}$ and as $Ni(Cit)_2^{4-}$. When the pH is increased, the concentration of $Ni(Cit)(HCit)^{3-}$ decreases while that of $Ni(Cit)_2^{4-}$ increases. Similarly, Co(II)–citrate exists as CoH_2Cit^+ (~15%) and CoHCit (~50%) at a pH 3.0; and above this pH, it is a mixture of CoHCit and $CoCit^-$. Fe(III)–citrate complexes involve the interaction with deprotonated hydroxyl group of citric acid represented by $H_{-1}Cit$. Perusal of literature [54,55] shows that the complex equilibria between Fe(III) and citric acid/citrate can be represented as in Eqs. (19), (22) and (23). Ferric citrate exists mainly (~92%) as complexes of deprotonated hydroxyl group ($[Fe(H_{-1}Cit)]^-$, 19% and $[Fe_2(H_{-1}Cit)_2]^{2-}$, 73%) even at pH 3.0 and only a minor fraction as [FeCit]. When the pH ≥4.0 $[Fe_2(H_{-1}Cit)_2]^{2-}$ increases to ~80%, $[Fe(H_{-1}Cit)]^-$ remains at the same level and [FeCit] can be neglected. Therefore, it can be inferred from the above discussion that almost all the metal ions exist in the complexed state even at the lowest pH (3.0) used in this study.

The quenching studies with aliphatic alcohols such as ethanol and tert-butanol show that the formation of radical intermediates such as $OH^{\bullet}$ and $SO_4^{-\bullet}$ [12,13,48,49] in the present investigation can be excluded. Therefore, the oxidation of metal–citrate by PMS proceeds through two electron processes, probably by oxygen atom transfer, and the product is ADC. The catalyst ((C) in Eq. (2)) ADC enhances the rate of oxidation through an intermediate with PMS. The detailed kinetic scheme for the oxidation of metal citrate by PMS can be written as in the following equations:

$$M\left(\begin{matrix} II \\ III \end{matrix}\right) - \text{Citrate} + HSO_5^- \xrightarrow{k_1} \underset{\text{(ADC)}}{\text{Acetone dicarboxylic acid}} + CO_2\uparrow + \text{products} \tag{24}$$

$$\text{ADC} + HSO_5^- \xrightarrow{k_2} \text{Intermediate} + \text{products} \tag{25}$$

$$\text{Intermediate} + M\left(\begin{matrix} II \\ III \end{matrix}\right) - \text{Citrate} \xrightarrow{k_3} 2\,\text{ADC} + \text{products} \tag{26}$$

The experimental results suggest that Eq. (25) is the rate limiting step for the oxidation of Ni(II) and Co(II) citrates and Eq. (26) is in Fe(III)–citrate. The rate equation for Co(II) and Ni(II) can be written as in Eq. (27).

$$\frac{-d[\text{PMS}]}{dt} = k_1.[\text{M} - \text{Citrate}][\text{PMS}] + k_2[\text{ADC}][\text{PMS}] \tag{27}$$

If there is no side reaction, the concentration of the catalyst ADC can be approximated to the [PMS] reacted. Eq. (27) is identical with Eq. (7) if $k_{1\,obs}$ is replaced by $k_1[M - \text{Citrate}]$ and $k_{2\,obs}$ by k_2. Under the experimental conditions, all the metal ions will exist as metal–citrate, and hence, the term [M − Citrate] in Eq. (27) can be replaced by the metal ion concentration as [M(II)] itself. Therefore, Eq. (27) explains all the experimental observations, namely the linear correlation between $k_{1\,obs}$ vs. [M(II)] and independent of $k_{2\,obs}$ with respect to [M(II)]. Moreover, if intermediate formation is the rate limiting step, then Eq. (25) is identical to the reactions as represented in Eqs. (14)–(16). The k_2 values should be equal to k^{ADC} calculated from Eq. (9). The k_2 values (in the parentheses) along with k^{ADC} at various pHs are displayed in Table 1. Perusal of the results shows that they are in close agreement with each other and justifies this expectation.

In the case ferric citrate oxidation, Eq. (26) may be the rate limiting step. The concentration of M(III)–citrate is constant (equal to [M(III)]), and hence Eqs. (25) and (26) can be considered as the consecutive reactions with the second step as the slowest step. Therefore, the second term in Eq. (27) is replaced by $k_3 \cdot [\text{ADC}] \cdot [\text{PMS}] \cdot [\text{Fe(III)}]$ and this will explain why $k_{2\,obs}$ shows a linear correlation with [Fe(III)]. The kinetic constants calculated are shown in Table 4.

Perusal of the k_1 values shows that the rate of oxidation of M(II) or M(III)–citrate by PMS is Co(II) ≫ Ni(II) ≫ Fe(III). The complexation with transition metal ions enhances the ionization of citrate hydroxyl group [56,57], thereby leading to a metal-oxide bonding. The hydroxyl group is completely ionized and the tetra ionized citrate complex predominates in Fe(III) citrate as in Eqs. (22) and (23). Ni(II)–citrate also exhibits an appreciable degree of polarization/ionization, and bonding by the hydroxyl group is reported [57]. The oxidation of citrate to acetone dicarboxylic acid involves the hydroxyl group and the carboxylate group (as carbon dioxide) attached to the same carbon atom. Therefore, the ease of oxidation may inversely depend upon the polarization of hydroxyl group, and this will explain the observed order of oxidation.

4. Conclusion

The oxidation of citric acid by peroxomonosulphate in the pH range 3.0–6.0 (citric acid buffer) occurs only in the presence of a metal ion. The Fe(III), Co(II) and Ni(II) citrates follow auto catalyzed mechanism. Acetone dicarboxylic acid is the product which catalyzes the oxidation of metal citrate. In the absence of metal ions, acetone dicarboxylic acid catalyzes the decomposition of PMS at pH 3.0–6.0 as in ketone catalyzed one at neutral or weak alkaline pH. However, the complexation with metal ion changes the mechanism to the acetone dicarboxylic acid catalyzed oxidation of metal–citrate by PMS.

Acknowledgements

The financial assistances from MKU, Madurai (USRF to Ragukumar) and UGC, New Delhi (Meritorious fellowships to Andal and Lavanya, RGNF to Murugavelu) are gratefully acknowledged.

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Please cite this article in press as: G. Ragukumar, et al., J. Mol. Catal. A: Chem. (2014), http://dx.doi.org/10.1016/j.molcata.2014.02.023

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