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Effect of metal ions on acetone dicarboxylic acid catalyzed peroxomonosulphate reactions

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ABSTRACT

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.

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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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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).

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

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).

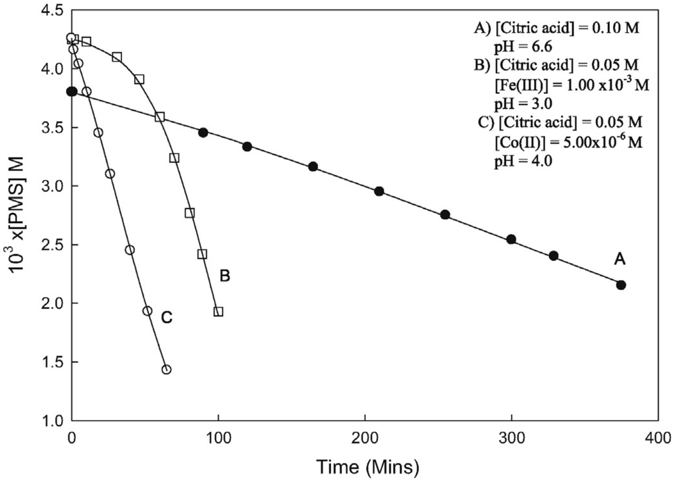

Fig. 1. Plot of [PMS] vs. time at 31.0 °C.

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

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).

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

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

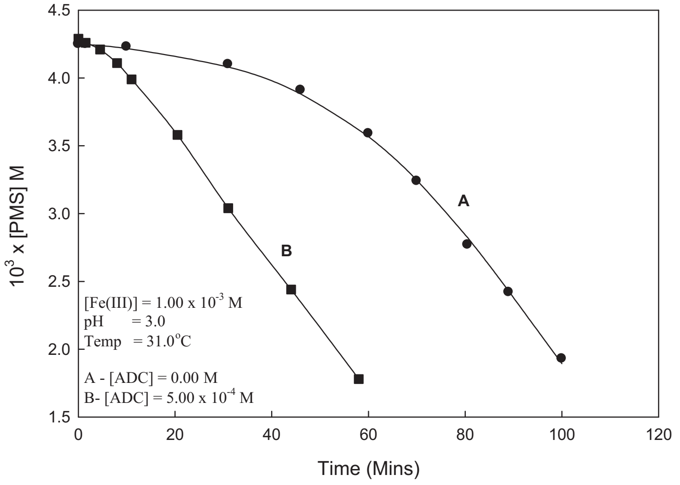

Fig. 2. PMS–time profile for Fe(III) ion catalyzed reaction.

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