Kinetics and Mechanism of Oxidation of L-Ascorbic Acid by Peroxomonophosphate in Aqueous Acid Medium

NARENDRA K. SONI, RIYA SAILANI, C. L. KHANDELWAL, P. D. SHARMA

Department of Chemistry, University of Rajasthan, Jaipur 302 055, India

Received 16 July 2011; revised 18 November 2011, 2 February 2012; accepted 25 March 2012

DOI 10.1002/kin.20741
Published online 20 November 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The kinetics of oxidation of L-ascorbic acid (H_2A) by peroxomonophosphate in acid aqueous medium has been studied. The stoichiometry of the reaction corresponds to the reaction as represented by the equation

$$H_3PO_5 + H_2A \rightarrow H_3PO_4 + H_2O + A \quad (1)$$

where A is dehydroascorbic acid. The reaction is second order versus first order with respect to each reactant. The rate is retarded by hydrogen ion concentration. A plausible reaction mechanism has been suggested. The derived rate law (2) from such a mechanism accounts for all experimental observations:

$$\frac{d[H_2A]}{dt} = \frac{(k_1k_2[H^+] + K_2K_1K_2)}{(K_1 + [H^+])(K_2 + [H^+])}[H_3PO_5][H_2A] \quad (2)$$

Such pH dependence is somewhat different from that observed in the case of metal ion oxidants. © 2012 Wiley Periodicals, Inc. Int J Chem Kinet 45: 41–46, 2013

INTRODUCTION

The oxidation studies of ascorbic acid (H_2A) are important both biochemically [1–17] and biomedically [18–21]. The kinetic studies of such reactions have further generated an interest to understand its oxidation reactions by metal ions, nonmetal ions, and metal ion complexes as oxidants [22–26] in acid aqueous medium. Also, L-ascorbic acid is considered to be an important biological compound of immense significance as a water-soluble vitamin C [27]. Its application in photoconversion is of an added importance.

Peroxomonophosphate (PMP) is a hydrolytic product of peroxodiphosphate and is considered to be a more potential oxidant than its parent analogue [28–33]. The title study is taken from the following viewpoints:

First, the L-ascorbic acid (H_2A) is a dibasic acid. The ascorbate (HA^-) is considered to be a reactive species in most of its reactions. However, free radical ($A^\bullet$) is

Correspondence to: Riya Sailani; e-mail: l.p_riya@yahoo.co.in.

unreactive and decays to ascorbic acid (H_2A), ascorbate (HA^-), and dehydroascorbic acid (A). Whether or not the same trend of reactivity pattern, L-ascorbic acid is observed in lower pH of the title reaction. It will be interesting to further probe whether or not the hydrogen ion dependence exhibits a similar trend as reported in other reactions of ascorbic acid.

Second, whether or not there is any possibility of complexation between the oxidant and substrate in view of the complexation reported in the case of metal-complex ion oxidants with the substrate.

Third, ascorbic acid species in acid medium exhibits the following sequence of reactivity toward the oxidants of varied nature:

$$A^{2-} > HA^- > H_2A$$

Whether or not the species H_2A is kinetically reactive at lower pH, H_2A species has been least reactive as reported in a large number of reactions of ascorbic acid.

EXPERIMENTAL

Materials and Method

Materials. L-Ascorbic acid (E. Merck) was employed as supplied. PMP is the hydrolytic product of peroxodiphosphate (a gift from FMC Corp., Philadelphia, PA). It was prepared by hydrolyzing [34–36] peroxodiphosphate (0.05 mol dm^{-3}) in perchloric acid (0.5 mol dm^{-3}) at 45°C in a thermostated water bath for 1.5 h. The solution was standardized iodometrically [37]. H_2O_2 as a minor hydrolytic product was negated by the tests with either cerium(IV) or permanganate. The concentrations of the H_2O_2 ($\sim 0.1 \times 10^{-6}$) can be tested qualitatively by $KMnO_4$ in acid solutions. However, Maruthamuthu and Neta [38] detected H_2O_2 only to the extent of $\sim 1 \times 10^{-6}$ mol dm^{-3} in hydrolysis of peroxodiphosphate conductometrically. Perxomonophosphate and ascorbic acid solutions were kept in bottles painted black from the outside to check decomposition by diffused light. Such solutions are quite stable, if kept, at refrigerated temperature (~5°C). Afresh solutions of the oxidant and substrate, respectively, were, however, always employed in kinetics studies.

All other chemicals were of the reagent grade, and these were used as received.

Triply distilled water was employed throughout the study; it was obtained by redistilling doubly distilled water in the presence of EDTA, which eliminated traces of metal ions such as Cu(II) or iron(II).

Kinetic Procedure. The reactions were allowed to occur in glass-stoppered Erlenmeyer flasks, which were painted black from the outside. These flasks were immersed in a thermostated water bath at ±0.1°C unless stated otherwise. The reaction mixtures containing all other ingredients except H_2A were allowed to attain the temperature of water bath. The temperature preequilibrated solution of PMP of required concentration was added to the reaction mixture. The time of initiation of the reaction was recorded when half of the contents from the pipette was released into the reaction mixture.

An aliquot (5 cm^3) of the reaction mixture was withdrawn at different time intervals and then discharged into ice-cold water to assay the remaining ascorbic acid iodimetrically. PMP, however, did not interfere with the pH of the titrating mixture.

Initial rates (k_i, mol dm^{-3} s^{-1}) were computed employing a plane mirror method. Since most of the reactions were conducted taking comparable concentrations of the reactants, viz. [PMP] = 2.0×10^{-3} mol dm^{-3}, [H_2A] = 2.0×10^{-3} mol dm^{-3}, pH 1.7 at 25°C, second-order plots of $[H_2A]_t/[PMP]_t$ or $[PMP]_t/[H_2A]_t$ versus time were made (Fig. 1). However, an interesting observation was of an initial fast reaction to the extent of 10%–30% on mixing of the reagents. This is an ample evidence of trace metal ion catalysis of the reaction in doubly distilled water.

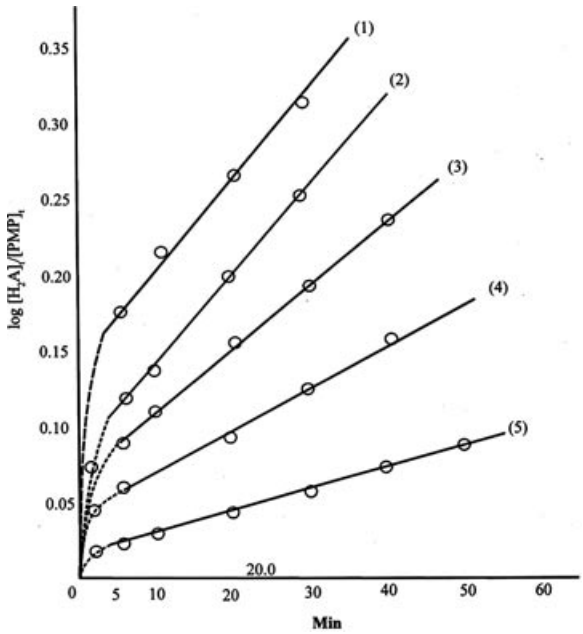
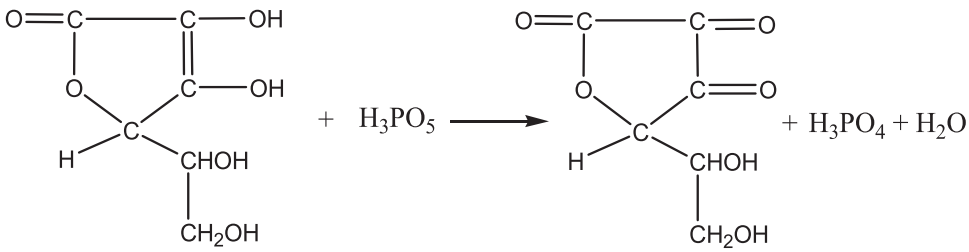


Figure 1 Second-order plots in the reaction of ascorbic acid and PMP. [PMP] = 2.0×10^{-3} mol dm^{-3}; pH 1.65, 25°C. [H_2A] = (1) 8.0×10^{-4}; (2) 1.2×10^{-3}; (3) 1.4×10^{-3}; (4) 1.6×10^{-3}; (5) 1.8×10^{-3} mol dm^{-3}.

Rates in triplicate were reproducible to within ±6% when peroxodiphosphate of the same batch was employed for preparation of PMP.

Stoichiometry. The reaction mixtures with an excess concentration of ascorbic acid (H_2A) over that of PMP under kinetic conditions were allowed to react in a thermostated water bath for ca. 5 h; the excess ascorbic acid was estimated iodimetrically. However, when [PMP] was taken in excess over [H_2A], the excess concentration of PMP was estimated ceremetrically. The stoichiometric results under both these conditions represent that 1 mol of ascorbic acid reacts with 1 mol of per acid corresponding to the stoichiometry as represented by Eq. (1):



(1)

RESULTS

The concentration of PMP was varied at fixed concentrations of other reaction ingredients at 25°C, Second-order plots were made between log $[PMP]_t/[H_2A]_t$ or log $[H_2A]_t/[PMP]_t$ versus time (Fig. 1) because of comparable concentrations of the reactants to evaluate second-order rate constants.

The concentration of L-ascorbic acid was similarly varied keeping constant concentrations of other reaction ingredients at 25°C. Second-order rate constants calculated in such a variation are in agreement with the rate constants obtained in variation of [PMP]. Such an agreement confirms that the reaction is second order versus first order with respect to oxidant and substrate, respectively. Thus an empirical rate law as given by Eq. (2) conforms to the second-order nature of the reaction:

$$\frac{-\mathrm{d}\,[H_2A]}{\mathrm{d}t} = \mathrm{B}\,[H_2A]\,[H_3PO_5] \qquad (2)$$

where B is an empirical rate constant.

The pH variation was made by employing perchloric acid at fixed concentrations of other reaction ingredients at ionic strength (I) = 0.5 mol dm^{-3} (I was adjusted by employing lithium perchlorate) and 25°C. The rate decreases with increasing hydrogenion concentration conforming to empirical rate law (3):

$$\frac{\mathrm{d}\,[H_2A]}{\mathrm{d}t} = \frac{\mathrm{B}\,[H_3PO_5]\,[H_2A]}{\mathrm{C} + [H^+]} \qquad (3)$$

where C is another empirical constant.

The concentration of copper(II) was varied by employing copper sulfate at fixed concentrations of other reaction ingredients and pH 1.7 at 25°C. The rate increases with increasing concentration of copper(II) (Fig. 2). It is also clear from such a plot that an intercept accounts for catalysis by traces of metal ions present in the reaction mixture in doubly distilled water.

The kinetics of the reaction was also studied at 15, 20, and 25°C, respectively, at fixed concentrations of reaction ingredients. The energy of

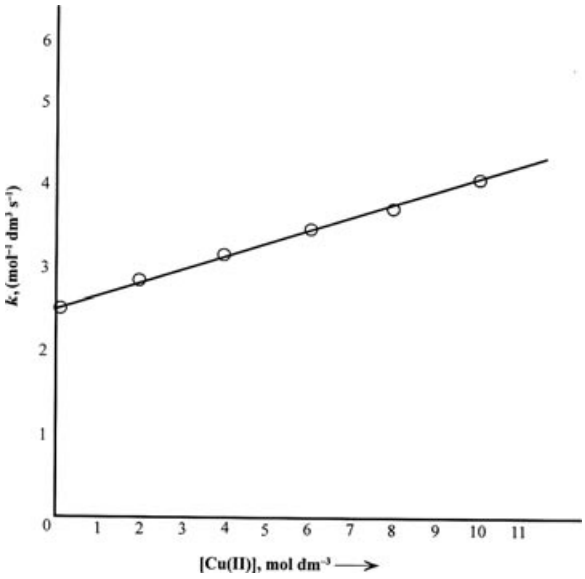
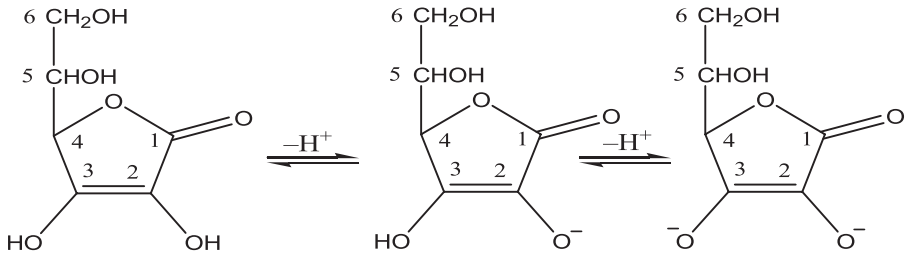


Figure 2 Copper(II) concentration variation in the reaction of ascorbic acid and PMP. [H_2A] = 2.0 × 10^{-3} mol dm^{-3}; [PMP] = 2.0 × 10^{-3} mol dm^{-3}; pH 1.7 and 25°C.

activation to be 49 ± 2 kJ $mol^{-1}$and entropy of activation to be –65 ± 0.4 J K^{-1} mol^{-1} were calculated in a conventional manner. The energy of activation is of the same order as usually obtained for second-order reactions.

DISCUSSION

Ascorbic acid (H_2A) is a dibasic acid and dissociates into monoanion (HA^-) and dianion (A^{2-}) species represented as follows:



(H_2A) (HA^-) (A^{2-})

pK_1 exhibits a hydroxyl group at C-3 of the enol group of H_2A and pK_2 for the hydroxyl group at C-2 of the enol group of HA^-.

There is a significant difference in the oxidizing properties of L-ascorbic acid [H_2A] and its conjugate base species such as HA^- and A^{2-}. Since the acid [39] is diabasic with pK_1 and pK_2 being 4.04 and 11.3, respectively, at I = 1.0 mol dm^{-3}, the oxidation reactions of ascorbic acid, therefore, should exhibit a characteristic pH dependence at which the oxidizing trend of such species is exclusively delineated provided that hydrolytic equilibria governing oxidant species are not significant. Thus, if pH of the medium is any guide, H_2A species in strongly acid medium (0 < pH < 1), HA^- species in dilute acid medium (2.5 < pH < 5.5), and A^{2-}species toward higher pH > 6, respectively, are the reactive species of ascorbic acid.

Similarly, peroxomonophosphoric acid species being hydrogen ion dependent are governed by equilibria (4)–(6)

$$H_3PO_5 \rightleftharpoons H_2PO_5^- + H^+ \quad (4)$$

$$H_2PO_5^- \rightleftharpoons HPO_5^{2-} + H^+ \quad (5)$$

$$HPO_5^{2-} \rightleftharpoons PO_5^{3-} + H^+ \quad (6)$$

The dissociation constants K_1, K_2, and K_3 of peracid reported by Edwards et al. [36] are 8.0×10^{-2}, 4.2×10^{-6}, and 1.6×10^{-13} mol dm^{-3}, respectively.

$H_2PO_5^-$ and not HPO_5^{2-} or PO_5^{3-} appears to be the reactive form of peracid in view of the pH of the medium. On similar arguments, HA^- species of ascorbic acid is more reactive than H_2A. Therefore, considering $H_2PO_5^-$ to be the reactive form of peracid, H_2A and HA^- to be the reactive species of ascorbic acid, the following reaction mechanism consisting of steps (4) and (7)–(9) can be envisaged to account for the kinetic observations:

$$H_3PO_5 \overset{k_2}{\rightleftharpoons} H_2PO_5^- + H^+ \quad (4)$$

$$H_2A \overset{k_1}{\rightleftharpoons} HA^- + H^+ \quad (7)$$

$$H_2PO_5^- + H_2A \xrightarrow{k_1} \text{Products} \quad (8)$$

$$H_2PO_5^- + HA^- \xrightarrow{k_2} \text{Products} \quad (9)$$

The loss of ascorbic acid leads to the rate law (10) or (11)

$$\frac{d[H_2A]}{dt} = \frac{(k_1K_2[H^+] + k_2K_1K_2)}{(K_1 + [H^+])(K_2 + [H^+])}[H_3PO_5][H_2A] \quad (10)$$

where $[H_3PO_5]$ and $[H_2A]$ are the gross analytical concentrations of peracid and L-ascorbic acid, respectively.

$$k = \frac{k_1K_2[H^+] + k_2K_1K_2}{(K_1 + [H^+])\,(K_2 + [H^+])} \quad (11)$$

where k is an observed second-order rate constant. Equation (12) is obtained on rearranging Eq. (11)

$$k(K_1 + [H^+])(K_2 + [H^+]) = k_1K_2[H^+] + k_2K_1K_2 \quad (12)$$

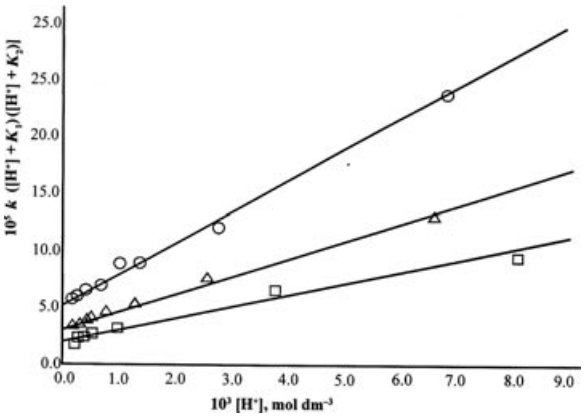


Figure 3 A plot of $k'([H^+] + K_1)$ $(K_2 + [H^+])$ versus $[H^+]$. $[H_2A] = 2.0 \times 10^{-3}$ mol dm^{-3}; [PMP] $= 2.0 \times 10^{-3}$ mol dm^{-3}; $I = 0.5$ mol dm^{-3}; and □ 15°C, Δ 20°C, ○ 25°C.

A plot of the left-hand side of Eq. (12) versus $[H^+]$ yielded a straight line with nonzero intercept (Fig. 3). k_1K_2 from the slope and $k_2K_1K_2$ from the intercept were 2.7×10^{-2} s^{-1} and 5.0×10^{-5} mol dm^{-3} s^{-1}, respectively, at 25°C.

It is well established [40] that copper(II) forms complexes with various species of ascorbic acid. A qualitative portrait of the reaction events in copper(II)-catalyzed oxidation of ascorbic acid by peroxomonophosphoric acid can be envisaged as follows:

$$H_2A \rightleftharpoons HA^- + H^+ \tag{7}$$

$$Cu^{2+} + H_2A \rightleftharpoons \left[Cu^{II} - H_2A\right]^{2+} \tag{13}$$

$$Cu^{2+} + HA^- \rightleftharpoons \left[Cu^{II} - HA\right]^{+} \tag{14}$$

$$\left[Cu^{II} - H_2A\right]^{2+} + PMP \rightarrow \text{Products} \tag{15}$$

$$\left[Cu^{II} - HA\right]^{+} + PMP \rightarrow \text{Products} \tag{16}$$

The peroxo-coordinated adducts [41] are readily formed, and the reduction of such adducts proceeds through a transient species with properties similar to that of a peroxobridged precursor complex. Such a mechanism, however, indicates first-order dependence with respect to peracid.

Therefore, copper(II)-catalyzd oxidation of ascorbic acid occurs in a similar manner as was observed in copper(II)-catalyzed oxidation of ascorbic acid by peroxodiphosphate in acetate buffers [40]. Thus the mechanism should consist of steps (17)–(19) as follows:

$$\left[Cu^{II} - H_2A\right]^{2+} \rightarrow Cu^{I} + \text{Other products} \tag{17}$$

$$\left[Cu^{II} - HA^-\right]^{+} \rightarrow Cu^{I} + \text{Other products} \tag{18}$$

$$Cu^{I} + PMP \xrightarrow{\text{Fast}} \text{Products} \tag{19}$$

Such a mechanism accounts for the rate to be independent of peroxomonophosphoric acid. This allows operation of Cu^{II}/Cu^{I} catalyst redox cycle. A complete kinetic study of such a catalyzed reaction will be undertaken separately to establish such a tentative mechanism.

CONCLUSIONS

The kinetics of oxidation of L-ascorbic acid by PMP in aqueous acid medium has been studied. The stoichiometry of the reaction corresponds to a reaction of 1 mol of peracid with 1 mol of ascorbic acid. The reaction is second order versus first order with respect to the oxidant and substrate, respectively.

The reaction kinetics exhibits complex hydrogen ion dependence. The rate law and proposed mechanism correspond reasonably well to the experimental observations. The reaction is also catalyzed by copper(II) ions, and a tentative mechanism for copper(II)-catalyzed oxidation of L-ascorbic acid with PMP has been suggested.

BIBLIOGRAPHY

1. Kustin, K.; Toppen, D. L. Inorg Chem 1973, 12, 1404–1407.
2. Mushran, S. P.; Agrawal, M. C.; Mehrotra, R. M.; Sanehi, R. J Chem Soc, Dalton Trans 1974, 1460–1462.
3. Mehrotra, U. S.; Agarwal, M. C.; Mushran, S. P. J Inorg Nucl Chem 1970, 32, 2325–2329.
4. Hoddenbagh, J. M. A.; Macartney, D. H. J Chem Soc, Dalton Trans 1990, 615–620.
5. Khan, M. M. T.; Martell, A. E. J Am Chem Soc 1967, 89, 4176–4185; (b) Khan, M. M. T.; Martell, A. E. J Am Chem Soc 1968, 90, 6011–6017; (c) Khan, M. M. T.; Martell, A. E. J Am Chem Soc 1969, 91, 4668–4672.
6. Rickman, R. A.; Sorensen, R. L.; Watkins, K. O.; Davies, G. Inorg Chem 1977, 16, 1570–1572.
7. Harris, F. L.; Toppen, D. L. Inorg Chem 1978, 17, 74–77.
8. Hayakawa, K.; Minami, S.; Nakamura, S. Bull Chem Soc Jpn 1973, 46, 2788–2791.
9. Tondreau, G. A.; Wilkins, R. G. Inorg Chem 1986, 25, 2745–2750.
10. Macartney, D. H.; Sutin, N. Inorg Chim Acta 1983, 74, 221–228.

11. Macartney, D. H.; McAuley, A. Can J Chem 1981, 59, 132–137.
12. McAuley, A.; Spencer, L.; West, P. R. Can J Chem 1985, 63, 1198–1203.
13. Davies, M. B. Inorg Chim Acta 1984, 92, 141–146.
14. Pelizzetti, E.; Mentasti, E.; Pramauro, E. Inorg Chem 1976, 15, 2898 –2900.
15. Pelizzetti, E.; Mentasti, E.; Pramauro, E. J Chem Soc, Dalton Trans 1978, 61–63.
16. Greenwood, C.; Palmer, G. J Biol Chem 1965, 240, 3660–3663.
17. Bielski, B. H. J.; Allen, A. O.; Schwarz, H. A. J Am Chem Soc 1981, 103, 3516–3518.
18. Lunee, J.; Blake, D. R. Free Radical Res Commun I 1986, 31.
19. Hollis, L. S.; Amundsen, A. R.; Stern, E. W. J Am Chem Soc 1985, 107, 274–276.
20. Wang, S. M.; Lai, L. J.; Li, N. C. Inorg Chim Acta 1987, 138, 11–12.
21. Jacobs, A.; Worwood, M. Iron in Biochemistry and Medicine; Academic Press: London, 1980; p. 3.
22. Stolyarov, K. P.; Amantova, I. A. Talanta 1967, 14, 1237–1244.
23. Abe, Y.; Okada, S.; Horii, H.; Taniguchi, S.; Yamabe, S. J Chem Soc, Perkin Trans 2 1987, 715–720.
24. Martinez, P.; Uribe, D.; Zuluaga, J.; Van Eldik, R. Inorg Chim Acta 1987, 136, 11–16.
25. Martinez, P.; Zuluaga, J.; Kraft, J.; Van Eldik, R. Inorg Chim Acta 1988, 146, 9–12.
26. Scurlock, R. D.; Gilbert, D. D.; Dekorte, J. M. Inorg Chem 1985, 24, 2393–2397.
27. (a) Michaelis, L. J Biol Chem 1932, 96, 703–715; (b) Holder, A. A.; Brown, R. F. G.; Marshall, S. C.; Payne, V. C. R.; Cozier, M. D.; Allcyne, W. A.; Bovell, C. O. Trans Met Chem 2000, 25, 605–611.
28. Vijai, N.; Mala, D.; Khandelwal, C. L.; Sharma, P. D. J Ind Chem A 2008, 47, 859–862.
29. Singh, G.; Khandelwal, C. L.; Sharma, P. D. J Ind Chem Soc 2008, 85(6), 615–621.
30. Thenraja, D.; Subramaniam, P.; Srinivasan, C. Tetrahedron 2002, 58(21), 4283–4290.
31. Suthakaran, R.; Rajagopal, S.; Srinivasan, C. Tetrahedron 2001, 57(7), 1369–1374.
32. Ghanem, R.; Carmona, C.; Munoz, M. A.; Guardado, P.; Balon, M. J Chem Soc, Perkin Trans 2 1996,30, 2197–2202.
33. Srisailam, V.; Rao, M. A. Acta Cienc Indica 1995, 25(1), 21–28.
34. Fortnum, D. H.; Battaglia, C. J.; Cohen, S. R.; Edwards, J. O. J Am Chem Soc 1960, 82, 778–782.
35. Secco, F.; Venturini, M. J Chem Soc, Dalton Trans 1976, 1410–1414.
36. Battaglia, C. J.; Edwards, J. O. Inorg Chem 1965, 4, 552–558.
37. Secco, F.; Celsi, S. J Chem Soc A 1971, 1092–1096.
38. Maruthamuthu, P.; Neta, P. J Phys Chem 1977, 81(10), 937–940.
39. Holder, A. A.; Im, S. C.; Dasgupta, T. P. Trans Met Chem 1997, 22, 135–140.
40. Mishra, D. K.; Dhas, T. P. A.; Sharma, P. D.; Bhargava, A. P.; Gupta, Y. K. J Chem Soc, Dalton Trans 1990, 1265–1270 and references cited therein.
41. Tylklar, A.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. J Am Chem Soc 1989, 111, 388-389.