Transition Met Chem (2014) 39:41–45
DOI 10.1007/s11243-013-9770-0

Kinetics and mechanism of oxidation of L-ascorbic acid by platinum(IV) in aqueous acid medium

N. K. Soni · Riya Sailani · C. L. Khandelwal · P. D. Sharma

Received: 11 August 2013 / Accepted: 7 October 2013 / Published online: 31 October 2013

Abstract The oxidation of l-ascorbic acid (H_2A) by platinum(IV) in aqueous acid medium exhibits overall second-order kinetics, being first order with respect to each reactant. Increasing both hydrogen and chloride ion concentrations inhibits the rate. The stoichiometry involves reaction of one platinum(IV) ion with H_2A to give dehydroascorbic acid. A reaction mechanism consistent with all the experimental observations is proposed.

Introduction

Platinum(IV) complexes find applications in cancer chemotherapy and treatment of various other diseases and as gel components for several types of medical implants (breast implants, joint replacement prosthetics, artificial lumbar disks, vascular access ports, etc.). Ascorbic acid (vitamin C), being an important biochemical compound, is also suspected to play some role in the treatment of various tumors. Hence, the interactions of platinum(IV) with ascorbic acid appear to be worthy of investigation. L-ascorbic acid in recent years has been extensively studied as a reductant both for free metal ions and for metal complexes [1–12]. These reactions are categorized into three main groups, namely outer-sphere, inner-sphere, and mixed outer-and-inner-sphere electron-transfer reactions.

N. K. Soni · R. Sailani (✉) · C. L. Khandelwal · P. D. Sharma
Department of Chemistry, University of Rajasthan, Jaipur 302055, India
e-mail: l.p_riya@yahoo.co.in

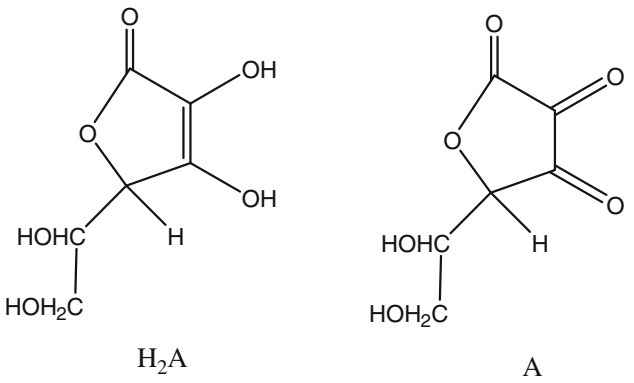
Trace metal ion catalysis in the oxidation of ascorbic acid, for example by peroxodiphosphate [13] in acetate buffers and peroxo-bound chromium(V) [14] in acid medium, is another important category of the reactions of ascorbic acid. The title reaction has been studied previously [15], but the proposed reaction mechanism is not complete as it lacks the effect of chloride ion concentration on the rate. This has prompted us to undertake a study of the kinetics of oxidation of ascorbic acid by platinum(IV) in aqueous acid medium, so that a comprehensive mechanism accounting for the effect of chloride ion can be delineated.

L-ascorbic acid can exhibit one-equivalent or two-equivalent nature in oxidations. Further, characteristic hydrogen ion dependence is reported in a large number of oxidations of ascorbic acid by metal ion oxidants. We were interested to see if such hydrogen ion dependence would also be observed in the present system.

Experimental

Materials and methods

L-ascorbic acid (Merck) (AnalaR grade) was used as received, and its aqueous solution was standardized iodimetrically [16]. A stock solution of platinum(IV) was prepared by dissolving the requisite quantity of hexachloroplatinic acid (Acros) in 0.3 mol dm^3 HCl and standardized iodometrically. Both solutions were kept in bottles painted black from the outside to suppress photodecomposition. Other reagents were either of AnalaR or guaranteed reagent grade and were employed as supplied. Triply distilled water was used to prepare the solutions; the second and third distillations were from alkaline permanganate and edta, respectively, in an all-glass still.



Scheme 1 Structural representation of Ascorbic acid and De-hydro ascorbic acid

Kinetic procedure

The reactions were conducted in glass-stoppered Erlenmeyer flasks immersed in a water-bath thermostated at ±0.1 °C unless stated otherwise. The reactions were initiated by adding Pt(IV) solution to temperature pre-equilibrated reaction mixtures containing all the other reagents. The time of initiation was recorded when the solution of platinum(IV) from the pipette was half-released into the reaction mixture. Aliquots (5 cm^3) of the reaction mixture were withdrawn at different time intervals and then discharged into ice-chilled cerium(IV) sulfate solution of known concentration. The excess cerium(IV) was estimated by titrating against iron(II) sulfate solution employing ferroin as an indicator. Further experiments showed no difference whether the reaction was initiated by adding Pt(IV) or ascorbic acid. Initial rates (k_i, mol dm^{-3} s^{-1}) were computed [17] by employing the plane mirror method. Second-order plots were made for comparable concentrations of the reactants. Triplicate rate measurements were reproducible to within ±5 %.

Stoichiometry

The stoichiometry of the reaction was determined by conducting a set of reactions with an excess concentration of Pt(IV) over that of ascorbic acid, or vice versa, in a thermostated water-bath maintained at (30.0 ± 0.1) °C for ca. 6 h. The excess ascorbic acid was estimated iodimetrically in ice-cold solution. The results corresponded to the stoichiometry of the reaction shown in Eq. (1);

$$Pt(IV) + H_2A \rightarrow Pt(II) + 2H^+ + A \quad (1)$$

where H_2A and A represent ascorbic acid and dehydroascorbic acid, respectively (Scheme 1); the latter was also detected qualitatively [18]. Dehydroascorbic acid being of triketo structure has also been reported [19, 20] in other oxidation reactions of ascorbic acid.

Table 1 Initial rates (k_i, mol dm^{-3} s^{-1}) and second-order rate constants (k, dm^3 mol^{-1} s^{-1}) in the reaction of Pt(IV) and ascorbic acid in aqueous acid medium ($[H^+]$ = 0.5 mol dm^{-3}; 30 °C)

10^4[Pt(IV)] mol dm^{-3}	10^3[H_2A] mol dm^{-3}	10^7 (k_i) mol dm^{-3} s^{-1}	(k) mol^{-1} dm^3 s^{-1}
2.0	0.5	0.46	0.46 (0.45)
4.0	0.5	0.90	0.45 (0.48)
5.0	0.5	1.10	0.44 (–)
7.0	0.5	1.50	0.44 (0.48)
8.0	0.5	1.80	0.45 (0.49)
10.0	0.5	2.00	0.40 (0.46)
5.0	1.0	1.90	0.40 (0.46)
5.0	2.0	4.17	0.42 (0.40)
5.0	3.0	6.46	0.43 (–)
5.0	4.0	8.75	0.44 (–)
5.0	5.0	10.42	0.42 (–)
5.0	0.5	1.10	– (0.43)*
10.0	1.0	2.50	– (0.47)*
15.0	1.5	5.20	– (0.42)*
20.0	2.0	6.60	– (0.42)*

Second-order rate constants in parenthesis are from second-order plots

*Marked asterisk second-order rate constants are from stoichiometric plots

The stoichiometry of the reaction was further confirmed by studying the kinetics of a few reactions using stoichiometric concentrations of the reactants under identical experimental conditions. Second-order plots of $1/[H_2A]_t$– versus time were made, and the second-order rate constants calculated from the gradients of the resulting straight lines were in agreement with the rate constants calculated from initial rates and second-order plots made for comparable concentrations of the reactants (Table 1).

Results

The order with respect to the oxidant was determined by varying the concentration of Pt(IV) at fixed concentrations of other reactants at (30.0 ± 0.1) °C. Initial rates (k_i, mol dm^{-3} s^{-1}) were computed by employing the plane mirror method [17]. A plot of initial rate versus concentration of Pt(IV) yielded a straight line passing through the origin, conforming that the reaction is first order with respect to the oxidant. Similarly, initial rates for varying concentrations of ascorbic acid at constant concentrations of other reactants were calculated. The plot of initial rate against the concentration of ascorbic acid also yielded a straight line passing through the origin, conforming to first-order dependence with respect to the substrate. Second-order rate

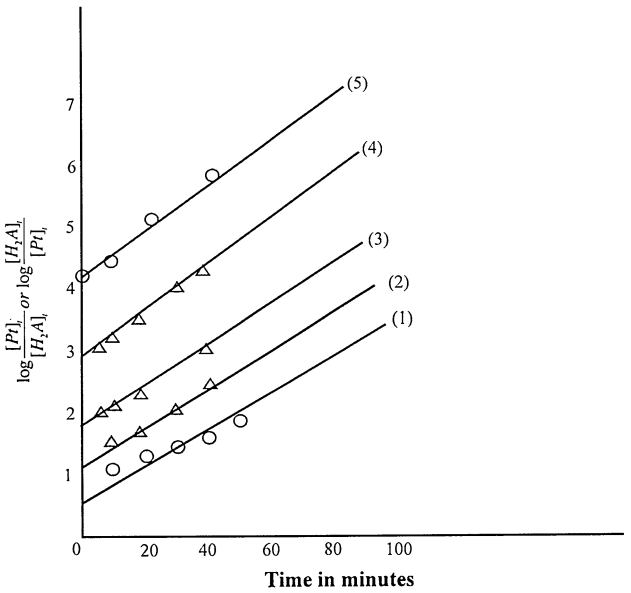


Fig. 1 Second-order plots in the reaction of Pt(IV) and ascorbic acid (H_2A). [Pt(IV) = (1) 4.0×10^{-4} (2) 7.0×10^{-4} (3) 8.0×10^{-4} (4) 1.0×10^{-3} (5) 2.0×10^{-4} mol dm^{-3}]; [H_2A] = 5.0×10^{-4} mol dm^{-3}; 30 °C

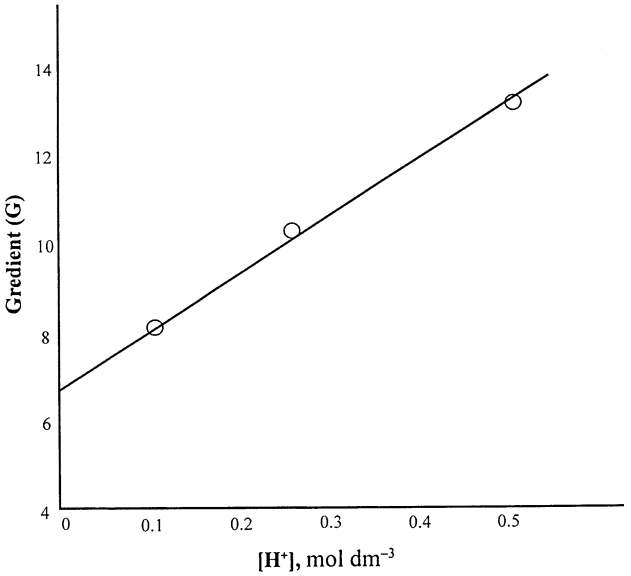


Fig. 2 A plot of slope versus [H^+]. I = 1.0 mol dm^{-3}; 30 °C

constants were evaluated from second-order plots of $\log[Pt(IV)]_t$ versus $[H_2A]_t$ or $\log[H_2A]_t$ versus $[Pt(IV)]_t$ (Fig. 1) for comparable concentrations of the reactants, and found to be in close agreement with those calculated from initial rates and stoichiometric plots (Table 1).

The concentration of sodium chloride was varied in the range of (0.05–0.5) mol dm^{-3}, keeping fixed concentrations of other reactants. Initial rates were found to decrease with increasing concentration of chloride ion. Hydrogen ion concentration was varied from 0.1 to 0.5 mol dm^{-3} at fixed concentrations of other reactants at I = 1.0 mol dm^{-3} (Ionic strength (I) was kept constant by employing lithium perchlorate). The rate decreased with increasing hydrogen ion concentration.

The effect of ionic strength was studied by employing lithium perchlorate; the rate increased with increasing ionic strength, consistent with an interaction between like-charged species of the reactants (Fig. 2). The effect of temperature on the rate of the reaction was studied at constant concentrations of all reactants. The energy and entropy of activation were calculated as (48.24 ± 0.49) kJ mol^{-1} and (−92.31 ± 1.65) JK^{-1} mol^{-1}, respectively, by employing Eyring's equation [21].

Discussion

If one takes into account the percentage distribution of ascorbic acid species, namely H_2A, HA^-, and A^{2-} considering the following equilibria (2) and (3), HA^- appears to be the predominant species of ascorbic acid under the experimental conditions used in this study.

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \quad (2)$$

$$HA^- \overset{K_2}{\rightleftharpoons} A^{2-} + H^+ \quad (3)$$

where the values of pK_1 and pK_2 for steps (2) and (3) are 4.03 and 11.3, respectively.

In view of the decelerating effect of chloride ion, the speciation of platinum(IV) appears to be governed by equilibrium (4). This effect of chloride ion also has been observed previously [15].

The effect of ionic strength on the rate has been studied by employing lithium perchlorate; contrary to the effect of chloride ion, the rate increases with increasing ionic strength under these conditions. This pattern of reactivity can be explained by considering a mechanism consisting of step (2) above and steps (4–6). It is worth mentioning that the effect of chloride ion was assumed to be equivalent to the effect of ionic strength in an earlier study [15], whereas the present study shows that this is an oversimplification, due to the observed rate increase when using lithium perchlorate to increase the ionic strength. Such an effect requires an interaction of like-charged species of reactants. Therefore, step (6) in the proposed mechanism is predominant. This revised mechanism is more reasonable; in that, it accounts for the effects of both chloride ion and ionic strength on the rate.

$$PtCl_6^{2-} \overset{K_2}{\rightleftharpoons} PtCl_5^- + Cl^- \quad (4)$$

$$PtCl_5^- + H_2A \xrightarrow{k} \text{Products} \quad (5)$$

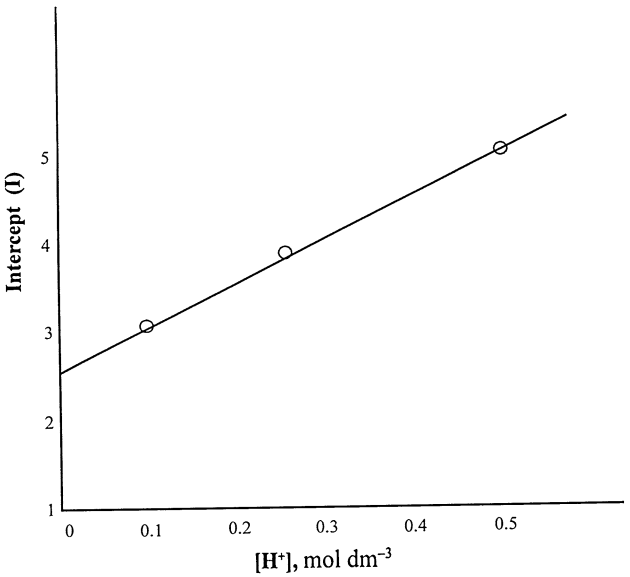


Fig. 3 A plot of intercept versus $[H^+]$. $I = 1.0$ mol dm^{-3}; 30 °C

$$PtCl_5^- + H_2A \xrightarrow{k'} \text{Products} \quad (6)$$

Thus, the interaction between $PtCl_5^-$ and HA^- in step (6) can be considered to be the rate limiting step, leading to the rate law (7)

$$\frac{-d[H_2A]}{dt} = \frac{k'K_1K_2[H_2A][Pt(IV)]}{(K_2 + [Cl^-])(K_1 + [H^+])} \quad (7)$$

where $[H_2A]$ and [Pt(IV)] are the gross analytical concentrations of ascorbic acid and platinum(IV), respectively. Rearrangement of Eq. (7) gives Eq. (8);

$$k = \frac{k'K_1K_2}{(K_2 + [Cl^-])(K_1 + [H^+])} \quad (8)$$

where k is the observed second-order rate constant (Table 1).

Since the variation of chloride ion concentration was made at constant hydrogen ion concentration, Eq. (8) can be simplified to Eq. (9),

$$k = \frac{k'K_1K_2(A)}{(K_2 + [Cl^-])} \quad (9)$$

where $(A) = \frac{1}{(K_1 + [H^+])}$ is a constant that co-relates to hydrogen ion concentration.

Taking double reciprocals of Eq. (9) and rearranging, Eq. (10) is obtained.

$$1/k = \frac{[Cl^-]}{kK_1K_2(A)} + \frac{1}{kK_1(A)} \quad (10)$$

A plot of $1/k$ versus $[Cl^-]$ was made according to Eq. (10), giving a straight line with nonzero intercept. The gradient (G) and intercept (I) of such a plot are given by Eqs. (11) and (12), respectively.

$$G = \frac{1}{k'K_1K_2(A)} \quad (11)$$

and

$$I = \frac{1}{k'K_1(A)} \quad (12)$$

the value of K_2 was calculated from the ratio of intercept and gradient as (0.37 ± 0.10) mol dm^{-3}.

Equations (11) and (12) in terms of hydrogen ion concentration can be rewritten and rearranged as Eqs. (13) and (14), respectively, as follows:

$$G = \frac{1}{k'K_2} + \frac{[H^+]}{kK_1K_2} \quad (13)$$

and

$$I = \frac{1}{k'} + \frac{[H^+]}{k'K_1} \quad (14)$$

Further plots according to Eq. (13) between gradient (G) and $[H^+]$ (Fig. 2) and (I) versus $[H^+]$ from Eq. (14) (Fig. 3) also yielded straight lines with nonzero intercepts. The values of $k'K_2$ and $k'K_1K_2$ were calculated from the intercept and slope of Figs. 2 and 3, and the ratio of these two yielded K_1 as (0.51 ± 0.10) mol dm^{-3}. Similarly, k' was calculated from the intercept as (0.38 ± 0.10) mol dm^{-3}.

Conclusion

The previous kinetic analysis of this system was deficient; in that, the effect of chloride ion concentration on the rate of the reaction was not treated properly. In fact, the ionic strength has a pronounced effect on the rate, whereas chloride ion inhibits the rate. The revised mechanism proposed in this paper accounts separately for the effects of both ionic strength and chloride ion. The reaction appears to occur via an outer-sphere mechanism.

References

1. Kimura M, Yamamoto M, Yamabe S (1982) Kinetics and mechanism of the oxidation of L-ascorbic acid by tris(oxalato) cobaltate(III) and tris(1,10-phenanthroline)iron(III) complexes in aqueous solution. J Chem Soc, Dalton Trans 2:423–427
2. Martinez P, Zuluaga J, Kraft J, Van Eldik R (1988) Kinetics and mechanism of the oxidation of L-ascorbic acid by trisoxalatocobaltate(III) in basic aqueous solution. Inorg Chim Acta 146:9–12
3. Tsukahara K, Izumitani T, Yamamoto Y (1982) The reduction of cobalt(III) complexes by ascorbic acid. II. The kinetics and mechanism of the reactions of diaqua and aquqhydraxo macrocyclic N_4 complexes. Bull Chem Soc Jpn 55:130–135

4. Tsukahara K, Yamamoto Y (1981) A kinetic study of reactions of several cobalt(III) complexes with ascorbic acid. Bull Chem Soc Jpn 54:2642–2645
5. Williams NH, Yandell JK (1982) Outer-sphere electron transfer reactions of ascorbate anions. Aust J Chem 35:1133–1144
6. Abe Y, Okada S, Horii H, Taniguchi S, Yamabe S (1987) A theoretical study on the mechanism of oxidation of L-ascorbic acid. J Chem Soc Perkin Trans 2:715–720
7. Macartney DH, Sutin N (1983) The oxidation of ascorbic acid by tris(2,2′-bipyridine) complexes of osmium(III), ruthenium(III) and nickel(III) in aqueous media: applications of the Marcus cross-relation. Inorg Chim Acta 74:221–228
8. Pelizzetti E, Mentasti E, Pramauro E (1978) Kinetics and mechanism of oxidation of ascorbic acid by manganese(III) in aqueous acidic perchlorate media. J Chem Soc Dalton Trans 1:61–63
9. Taqui Khan MM, Shukla RS (1988) Inner sphere oxidation of L-ascorbic acid by Ru(III) ion and its complexes in aqueous acidic medium. Inorg Chim Acta 149:89–94
10. Dixon DA, Sadler NP, Dasgupta TP (1995) Mechanism of the oxidation of L-ascorbic acid by the pentaammineaquacobalt(III) ion in aqueous solution. Trans Met Chem 20:295–299
11. Yatsimirskii KB, Strizhak PE (1995) Effect of radionuclides cesium-137 and strontium-90 on oxidation of ascorbic acid by methylene blue in the presence of copper(III) ions. Theor Exptl Chem 31:86–90
12. Agrawal A, Rao I, Sharma PD (1993) Trace metal-ion catalysis: kinetics and mechanism of oxidation of l-ascorbic acid by chromium (VI) in phosphate buffers. Trans Met Chem 18:191–196
13. Mishra DK, Dhas TPA, Sharma PD, Bhargava AP, Gupta YK (1990) Role of trace metal ions. Kinetics and mechanism of the copper(II)-catalyzed oxidation of ascorbic acid with per oxodiphosphate in acetate buffers. J Chem Soc Daltan Trans 4:1265–1270
14. Ghosh SK, Gould ES (1989) Electron transfer. 98. Copper (II) and vanadium (IV) catalysis of the reduction of peroxide-bound chromium (IV) with ascorbic acid. Inorg Chem 28:1948–1951
15. Mehrotra US, Agrawal MC, Mushran SP (1970) Reduction of hexachloroplatinate by ascorbic acid. J Inorg Nucl Chem 32:2325–2329
16. Kolthoff IM, Belcher R, Stenger R, Matsayan G (1957) Volumetric analysis. Interscience 3:212
17. Latshaw M (1925) A simple tangent meter. J Am Chem Soc 47:793–794
18. Feigl F (1966) Spot tests in organic analysis. Elsevier, Amsterdam
19. Hvoslef J (1972) Structure of the crystalline dimer of dehydro-L-ascorbic acid. Acta Cryst B28:916–923
20. Dellien I, Hall FM, Hepler LG (1976) Chromium, molybdenum and tungsten: thermodynamic properties, chemical equilibrium and standard potentials. Chem Rev 76: 283–310 and references cited therein
21. Lente G, Fabian I, Poe AJ (2005) A common misconception about the Eyring equation. New J Chem 29:759–760