

Kinetics and Mechanism of Oxidation of L-ascorbic Acid by Silver (I) in Acid Perchlorate Medium



Chemistry

KEYWORDS : Kinetics; Mechanism; Oxidation; Silver (I); L-Ascorbic acid.

Narendra Kumar Soni Department of Chemistry, University of Rajasthan, Jaipur 302004(India)

Riya Sailani Department of Chemistry, University of Rajasthan, Jaipur 302004(India)

Prem Dutt Sharma Department of Chemistry, University of Rajasthan, Jaipur 302004(India)

ABSTRACT

The kinetics of oxidation of l-ascorbic acid (H₂A) by silver (I) has been studied in acid nitrate medium potentiometrically. The reaction is second order – first order with respect to oxidant and substrate respectively. The stoichiometry of the reaction is represented by eqn(1). $2Ag(I) + H_2A \rightarrow 2Ag(O) + 2H^+ + A(1)$ where 'A' is dehydro ascorbic acid. The kinetic rate law (2) corresponds to the proposed mechanism. $-\frac{1}{2} \frac{d[Ag(I)]}{dt} = (k_1 + \frac{k_2 K}{[H^+]}) [Ag(I)]^{1/2} [H_2A]$ (2) Energy and entropy of activation have also been evaluated.

Introduction

The most vital role of l-ascorbic acid known to be vitamin C is, no doubt, considered to be a water soluble vitamin in human body in forming blood vessel walls apart from assimilating iron and amino acids.¹ It is l-enantiomer of ascorbic acid. Vitamin C as not only refers to l-ascorbic acid but also for its first oxidation product 'dehydroascorbic acid' too. Plants and some animals make² their vitamin C but human body fails to do. It is this reason that it is sought in human body from other sources.

Despite being a simple sugar molecule, its biochemistry is little understood owing to its complex redox chemistry that makes the molecule an interesting and complex reducing agent in inorganic chemistry.³ A large number of solution studies of oxidation of ascorbic acid by metal-ions have been reported.⁴⁻¹⁶ Martell *et al*¹⁷⁻¹⁸ established the role of metal-ions as catalysts in the oxidation of vitamin C.

Metal-ascorbate may be considered a biomimetic models for enzyme catalyzed processes¹⁹ besides redox chemistry. Iron ascorbate and copper ascorbate can be suggested²⁰ for reductase and ascorbate oxidase respectively. Vanadium diasorbates represent endogeneous quabain like factors in human urine. Polynuclear chromium ascorbate complexes can be regarded as models for the insulin stimulating forms of chromium.

The oxidation of l-ascorbic acid by a wide range of metal ions and metal complexes has been accomplished with sufficient kinetic details. Also, a review published recently has highlighted such studies.¹⁸

In general, a characteristic pH dependence of the rate of oxidation of ascorbic acid has been reported. However, there are reactions wherein hydrogen ion dependence is related either to the dissociation constants of the acid and/or

hydrolytic equilibria of the oxidant or both.

Our interest in this study generated mainly because of a complex analytical method employed for monitoring the kinetics of this reaction.¹⁹ The electro-analytical method as employed in this study is simple in its handling and more accurate in periodical assaying of its concentration. Since the undissociated ascorbic acid, ascorbic acid anion and ascorbate dianion can all in principle be kinetically important in ascorbic acid reactions,²⁰ complications in these reactions are so widespread that no general pattern of the acid dependence has clearly emerged out of such studies.

Experimental

Material and Method

L-ascorbic acid (H₂A) (E. Merck) was employed as supplied. The solution of the acid was standardized iodimetrically.²¹ Since l-ascorbic acid deteriorates even at ambient temperature owing to atmospheric oxygen, the solution was always kept in bottles painted black from the out-side or brown colored glass bottles which were properly glass stoppered at refrigerated temperature (~5°C).

All other chemicals employed in this study were of either AnalaR or guaranteed reagents grade and were used as received.

Doubly distilled water was employed throughout kinetics studies and also analytical work, second distillation was from alkaline potassium permanganate solution in an all glass assembly. Since the air oxidation of ascorbic acid is reportedly catalyzed by trace metal-ions, such a possibility was, however, eliminated by employing triply distilled water in which no such trace metal-ion catalysis was observed. The third distillation was made after adding edta in doubly distilled water.

calculated by dividing this term by the concentration of ascorbic acid.

Results and Discussion

The reactions were carried out under pseudo first order conditions $[H_2A] \gg [Ag(I)]$. Since $E \propto \log [Ag(I)]_t$, the plot of E versus time were linear to two half-lives of the reaction. Suggesting order with respect to silver (I) is unity. Also pseudo first order rate constants calculated from the slope as given in Table-1 are independent of gross analytical concentration of silver (I) confirming first order dependence with respect to the oxidant. The rate increases with increasing concentration of l-ascorbic acid at constant hydrogen ion concentration. The second order rate constants (k, $dm^3 mol^{-1} s^{-1}$) were also evaluated as mentioned in Table-1.

Table-1

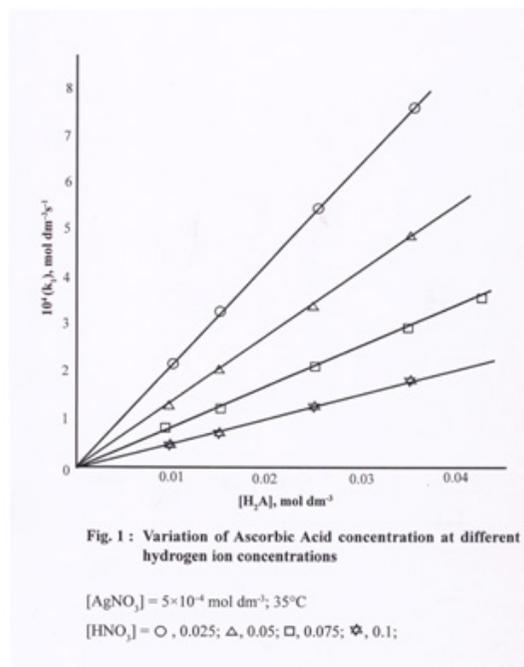
First order (k_1, s^{-1}) and second order rate constants (k, $dm^3 mol^{-1} s^{-1}$) in the reaction of Ag (I) and ascorbic acid in aqueous acid medium.

T = 35°C

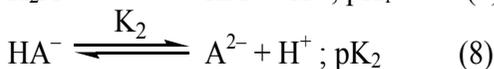
$10^4 [H_2A]$ $mol\ dm^{-3}$	$10^4 [Ag^I]$ $mol\ dm^{-3}$	$[H^+]$ $mol\ dm^{-3}$	10^4 (k_1) s^{-1}	(k) $mol^{-1} dm^3 s^{-1}$
1.0	5.0	0.025	2.20	0.85
1.5	5.0	0.025	3.33	0.86
2.5	5.0	0.025	5.56	0.86
3.5	5.0	0.025	7.71	0.85
1.0	5.0	0.05	1.31	0.52
1.5	5.0	0.05	2.08	0.54
2.5	5.0	0.05	3.30	0.51
3.5	5.0	0.05	4.79	0.53
1.0	5.0	0.075	0.80	0.31
1.5	5.0	0.075	1.20	0.31
2.5	5.0	0.075	2.08	0.32
3.5	5.0	0.075	2.90	0.32
1.0	5.0	0.10	0.58	0.22
1.5	5.0	0.10	0.83	0.21
2.5	5.0	0.10	1.30	0.20
3.5	5.0	0.10	1.92	0.21

1.5	2.0	0.10	0.10	-
1.5	4.0	0.10	0.60	0.20
1.5	6.0	0.10	0.80	0.21
1.5	8.0	0.10	0.80	0.21
1.5	10.0	0.10	1.00	0.25

Since overall order of the reaction is two and the rate decreases with increasing hydrogen ion concentration (0.025 - 0.1) $mol\ dm^{-3}$ as in (Fig. 1), the mechanistic proposals as envisaged account for such experimental observations.



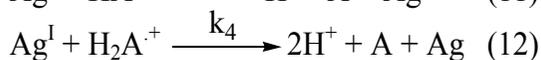
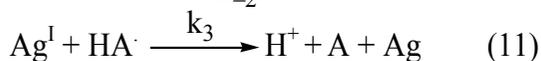
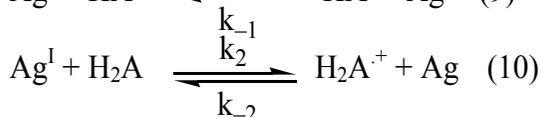
Ascorbic acid²² being a dibasic acid dissociates, as in eqn (7) and (8) pK_1 and pK_2 are reported to be ~ 4.03 and 11.3 respectively at $25^\circ C$.



Both the species of ascorbic acid H_2A and HA^- might be reactive with HA^- species being predominantly reactive in view of rate dependence on hydrogen ion concentration employed in the reaction. Since hydrogen ion concentration

dependence cannot be co-related to the oxidant is only comes from ascorbic acid.

In reactions of ascorbic acid HA^- has also found to be the reactive form of the acid. If molecular and anion forms of ascorbic acid are taken into account as the reactive species, the following reaction mechanism can be envisaged to account for the reaction events as observed experimentally,



Applying steady-state treatment to the species $H_2A^{+\cdot}$ and $HA\cdot$, the rate eqn(14) is obtained with the valid inequalities as follows

$$k_3[Ag^I] > k_{-1}[Ag] \text{ or } k_{-1} \quad \text{and} \\ k_4[Ag^I] > k_{-2}[Ag] \text{ or } k_{-2} \quad (13)$$

$$-\frac{1}{2} \frac{d[Ag(I)]}{dt} = \left\{ k_2 + (k_1 - k_2) K_a / ([H^+] + K_a) \right\} [Ag^I] [H_2A] \quad (14)$$

Where $[H_2A]$ and $[Ag^I]$ are the gross analytical concentrations of ascorbic acid and silver (I) respectively.

Since $[H^+] \gg K_a$, and $k_1 \gg k_2$, eqn (14) is further reduced to eqn (15) or (16).

$$-\frac{1}{2} \frac{d[Ag(I)]}{dt} = \{ k_2 + (k_1 [H^+]^{-1}) K_a \} [Ag(I)] [H_2A] \quad (15)$$

or

$$k = k_2 + k_1 K_a / [H^+] \quad (16)$$

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

A plot of k versus $[H^+]^{-1}$ was made from eqn (16) that yielded a straight line passing through the origin with insignificant intercept (Fig. 2) showing that the step (10) does not contribute or

contributes least as compared to step (11) in the reaction mechanism.

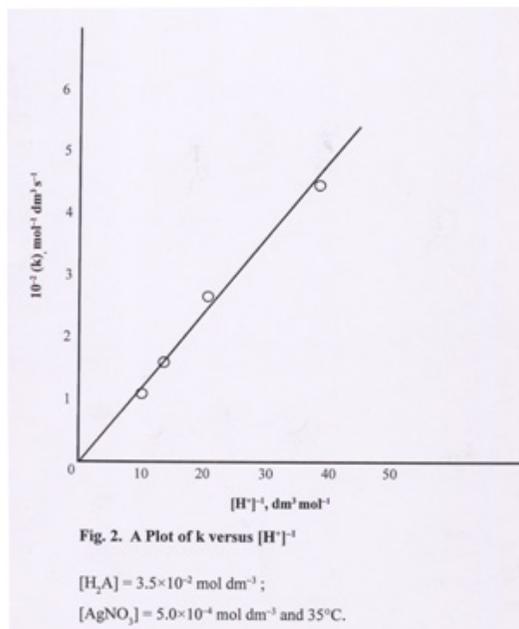


Fig. 2. A Plot of k versus $[H^+]^{-1}$

$[H_2A] = 3.5 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[AgNO_3] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ and 35°C .

However, such a rate law is similar to one observed for reactions of $HgCl_2$, $[CO_2(O_2)(NH_3)_{10}]^{3+}$, $Cr^{IV}(\text{dien})(O_2)_2$ (dien-diethylenetriamine) and ruthenium(III) complexes with ascorbic acid.

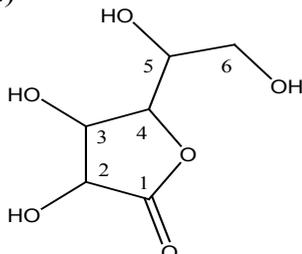
If one employs ' K_a ' to be 1.12×10^{-4} at 25°C and $I = 1.0 \text{ mol dm}^{-3}$, k_1 can be estimated to be $1.07 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This further shows that k_2 must be much less than k_1 as observed in all related reactions.¹⁰ Such an observation further confirms that HA^- species of l-ascorbic acid is more reactive than its molecular form H_2A .

The lower reactivity of H_2A than HA^- can also be assigned to intrinsic thermodynamic factors if one takes into account the rate constants²³ for the self-exchange reactions of $H_2A^{+\cdot} / H_2A$ and HA/HA^- to be $10^{-5} - 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ and $2.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively and the reduction potentials¹⁰ for the $H_2A^{+\cdot} / H_2A$ and $HA\cdot / HA^-$ redox couples to be 1.17 and 0.71V respectively. The existence of ascorbate free radicals as postulated in the reaction mechanism has been established

and is now well matured observation in redox reactions of ascorbic acid.

Conclusion

Metal complex formation of ascorbic acid is a possibility as the organic acid has several donor atoms, however, HA^- with metals interacts monodentately through O(3) atom or by chelate formation *via* O(3) and O(2)



The formation constants of 1:1 complexes are in the range $< 10^3$ which are significantly small in view of the low (-)ve charge ruling out the possibility of formation of silver(I)-ascorbic acid complex. First, if such a complex is considered, it will not be stable owing to its fast hydrolytic reaction.

Secondly, if the possibility of formation of intermediate complex is considered, a variable kinetic order with respect to ascorbic acid should have been observed. Experimentally observations are contrary to it despite the fact that electron transfer from substrate to the oxidant is energetically more feasible. It is, therefore, the direct encounter between silver (I) and anionic ascorbic acid species as has been envisaged in the mechanism. It can now be concluded that the oxidation of l-ascorbic acid by silver (I) is redox controlled and not substitution controlled reaction.

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