

KINETICS AND CATALYTIC MECHANISM OF THE OXIDATION OF L-ASCORBIC ACID BY Ce(IV) IN AN ACIDIC MEDIUM**Umendra Kumar**

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Abstract:

The kinetics of the oxidation of L-ascorbic acid by cerium (IV) in an acidic medium have been investigated spectrophotometrically at a constant ionic strength and temperature. The reaction showed first-order dependence with respect to each Ce(IV) and ascorbic acid, and the overall reaction is second-order. The final oxidation product of ascorbic acid was identified by spectral analysis as dehydroascorbic acid. The effect of Cu⁺² ions as catalyst on the oxidation of ascorbic acid has also been studied, which affects the reaction to a considerable extent, and the kinetic results suggest that the reaction rate is increased by an increase in Cu⁺² ion concentration. A plausible mechanistic scheme for catalysed oxidation was proposed.

Keywords: Ascorbic, Oxidation, Cerium(IV), Kinetics, Mechanism, spectrophotometric.

Introduction:

Ascorbic acid (AsCH₂, vitamin C) is a water-soluble ketolactone with two ionizable hydroxyl groups. It has two pK_a's, pK₁ is 4.2 and pK₂ is 11.6; thus, the ascorbate monoanion, AscH⁻, is the dominant form at physiological pH. Ascorbate is an excellent reducing agent and readily undergoes two consecutive, one-electron oxidations to form ascorbate radical (Asc•⁻) and dehydroascorbic acid (DHA). The ascorbate radical is relatively unreactive due to resonance stabilisation of the unpaired electron; it readily dismutates to ascorbate and DHA ($k_{obs}=2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, pH 7.0) [1]. In the presence of catalytic metals, this oxidation is accelerated [2,3]. Ascorbate can also have pro-oxidant effects. In fact, the combination of iron and ascorbate has long been used as an oxidising system; the combination of these two reagents is referred to as the Udenfriend system and is used for the hydroxylation of alkanes, aromatics, and other oxidations. [4,5] L-ascorbic acid's redox reaction is of important interest in chemistry, biochemistry, pharmacology, and a number of medical specialties. In chemical and biological systems, it functions as a reducing agent with one or two electron reductants [6-8] Ascorbic acid has been known to have a wide range of applications. It is used extensively in medicine, (cure and prevention of scurvy), in agriculture, in the food industry, in the flour industry, in metallurgy, and also by chemists, but little is known about the kinetics and mechanisms of many of its important reactions [9,10]. Cerium (IV) is a significant single electron oxidant in acid media [11-13]. The oxidizing potentialities of cerium (IV) in sulfuric acid medium were conclusively established [14,15]. In the present study, we have investigated the oxidation of L-ascorbic acid by cerium (IV) in an acidic medium, and based on the experimental results, a suitable mechanism is proposed.

Experimental:

All the reagents used in this study were pure for analysis. and their solutions were prepared by dissolving the required amounts of the samples in doubly distilled water. Ceric ammonium sulphate (Merck) was employed as a source of cerium (IV). The standardized solution of cerium (IV) content was prepared as per I.P. 1996. The solution of cerium (IV) was stored in a dark glass bottle and used after 24 hours [16]. The HCl GPR grade of Merck was used after testing for its purity. The absorbance was measured on a Pyeunicam UV-Vis spectrophotometer. IR spectrum of final product was recorded on Phillips P.U.-9706 i.r. spectrophotometer.

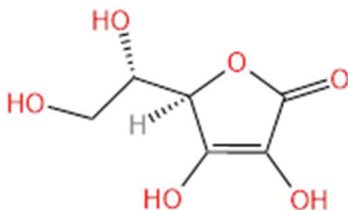


Figure 1., Structure of L-ascorbic acid

Molecular formula of Ascorbic acid (vitamin C) is $C_6H_8O_6$ and molecular weight is 176.12 g/mol

Kinetic measurements:

The kinetics of ascorbic acid (vitamin C) were carried out spectrophotometrically. After trying a number of solvents like methanol, ethanol, acetic acid, dioxane, and DMF, vitamin C remained soluble for a considerable period of time, depending upon the reaction conditions. The kinetics of the ascorbic acid were carried out by using 0.01N HCl as solvent, it does not absorb radiation in the UV region. Since the redox reactions using $Ce(IV)$ ions are highly sensitive to traces of impurities, Therefore, double distilled water has been used for preparing and making solutions throughout this investigation. The reaction was carried out in the dark in a borosilicate glass flask of 250 ml capacity to avoid the possibility of any photochemical change in the reaction mixture. The reaction was started by running a known volume of ceric ammonium sulphate into the reaction vessel containing the other reactant, which was immersed in a thermostatic water bath maintained at the desired temperature. The reaction mixture vessel was stoppered and shaken to make the reaction mixture homogenous. The kinetics of the reaction were observed spectrophotometrically and conc. Of the reactants was kept such that the conc. The product formed may be within the range of applicability of Beer & Lambert's Law. An adequate quantity of samples was taken from time to time with the help of a pipette with a broad tip for quick transfer to the cuvette. The absorption maximum of the solution was found at 244 nm. The whole process of pipetting out, transferring, and measuring the absorbance of the reaction took only 18–20 seconds, depending on the value of the absorbance recorded at different time intervals.

Results and discussion:

At the very outset, preliminary observations were made in order to find suitable conc. of reactants. Ascorbic acid is very sensitive to oxygen and heat, so these factors have been avoided, and the

reaction of vitamin C and cerium (IV) in HCl was carried out in an inert atmosphere of nitrogen and found to have λ_{\max} at 244 nm. The oxidation in inert medium is very slow compared to air. The reaction was repeated several times at different concentrations. The results were fairly reproducible and fell within the range of experimental error.

Overall order of the reaction

The order of the reaction of ascorbic acid and Ce(IV) was determined by the integration method using the equimolar concentrations of the two reactants. The rate of kinetics is reported in Table 1. The overall order of the reaction comes out to be two, when $\log 1/(a-x)$ is plotted against time and a linear curve was obtained. A graphical representation has been shown in Figure 2, indicating the order of the reaction is two [17, 18] From the values of the rate constant, it is clear that the rate constant increased with an increase in the concentration of the reactant.

Table 1., Kinetic runs at the temperature of 30°C

SET -I [Ce(IV) = 5.0×10^{-4} M] [Ascorbic acid = 5.0×10^{-4} M] [Hydrochloric acid = 0.01 N]		SET-II [Ce(IV) = 7.5×10^{-4} M] [Ascorbic acid = 7.5×10^{-4} M] [Hydrochloric acid = 0.01 N]	
Time (Min.)	Absorbance	Time (Min.)	Absorbance
00	0.9788	00	0.9366
03	0.8078	03	0.7698
06	0.2718	06	0.3013
09	0.1976	09	0.1938
12	0.1134	12	0.1136
15	0.0945	15	0.1078
18	0.0784	18	0.0888
21	0.0658	21	0.0756
24	0.0588	24	0.0656

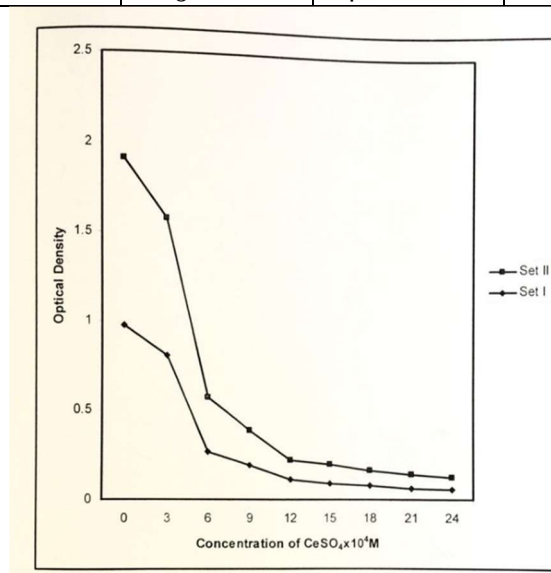


Figure 2. Order of the reaction

Order of the reaction with respect to ceric ammonium sulphate:

The order of the reaction w.r.t. to $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ was calculated by the integration method, and it came out to be unity [19]. The kinetic data are tabulated in Table 2. The concentration of ascorbic acid was kept constant, and that of ceric ammonium sulphate was varied. The experimental results analysis suggested that the rate constant decreased with an increase in the concentration of ceric ammonium sulphate, and a graphical representation has been shown in Figure 3, which clearly indicates that the rate constant was dependent on the concentration of ceric ammonium sulphate.

Table 2. Kinetic runs at the temperature. of 30°C

SET -I [Ce(IV) = 2.0×10^{-3} M] [Ascorbic acid = 1.0×10^{-4} M] [Hydrochloric acid = 0.01 N]		SET -II [Ce(IV) = 4.0×10^{-3} M] [Ascorbic acid = 1.0×10^{-4} M] [Hydrochloric acid = 0.01 N]		SET -III [Ce(IV) = 6.0×10^{-3} M] [Ascorbic acid = 1.0×10^{-4} M] [Hydrochloric acid = 0.01 N]		SET -IV [Ce(IV) = 8.0×10^{-3} M] [Ascorbic acid = 1.0×10^{-4} M] [Hydrochloric acid = 0.01 N]	
Time (Min.)	Absorbance	Time (Min.)	Absorbance	Time (Min.)	Absorbance	Time (Min.)	Absorbance
00	1.3012	00	1.972	00	0.8098	00	0.6881
03	0.7961	03	0.7328	03	0.6023	03	0.5608
06	0.4949	06	0.5017	06	0.4438	06	0.4556
00	0.3012	09	0.3233	09	0.3327	09	0.317
12	0.1807	12	0.2112	12	0.2515	12	0.3046
15	0.1105	15	0.1396	15	0.1905	15	0.2478
18	0.0708	18	0.1106	18	0.1426	18	0.2000
21	0.0434	21	0.0708	21	0.0927	21	0.1645
24	0.0247	24	0.0508	24	0.0807	24	0.1378

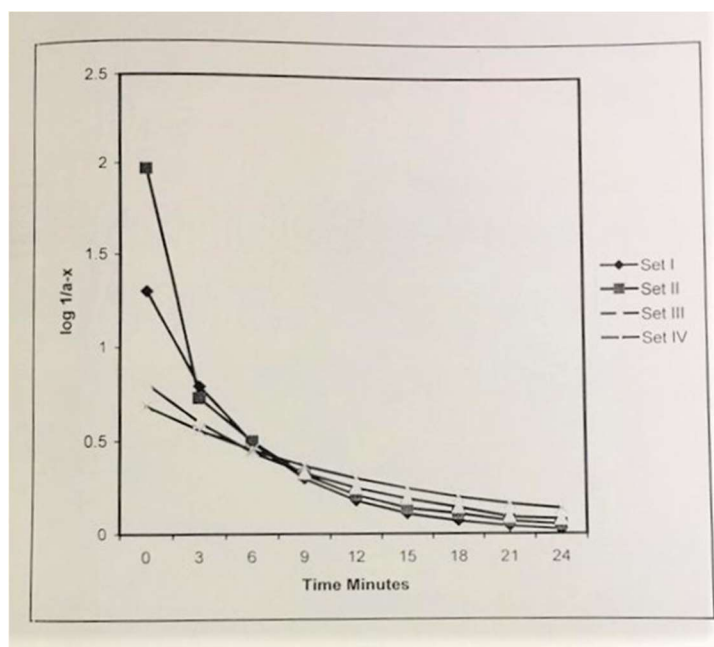


Figure 3. Order of the reaction w.r.t. to Ceric ammonium sulphate

Order of the reaction with respect to L-Ascorbic acid;

The integration approach was used to determine the order of the reaction with respect to l-ascorbic acid, and the result was unity [20,21]. Table 3 lists the kinetic information. Ascorbic acid concentration was adjusted while the concentration of ceric ammonium sulphate was maintained constant. The analysis and experimental results indicated that the rate constant reduced as the concentration of L-ascorbic acid increased, indicating unequivocally that the rate constant (Figure4), was a function of L-ascorbic acid concentration

Table 3. Kinetic runs at the temperature. of 30°C

SET -I [Ce(IV) = 2.0 x 10 ⁻⁴ M] [Ascorbic acid = 2.0 x 10 ⁻³ M] [Hydrochloric acid = 0.01 N]		SET -II [Ce(IV) = 2.0 x 10 ⁻⁴ M] [Ascorbic acid = 4.0 x 10 ⁻³ M] [Hydrochloric acid = 0.01 N]		SET -III [Ce(IV) = 2.0 x 10 ⁻⁴ M] [Ascorbic acid = 6.0 x 10 ⁻³ M] [Hydrochloric acid = 0.01 N]		SET -IV [Ce(IV) = 2.0 x 10 ⁻⁴ M] [Ascorbic acid = 8.0 x 10 ⁻³ M] [Hydrochloric acid = 0.01 N]	
Time (Min.)	Absorbance	Time (Min.)	Absorbance	Time (Min.)	Absorbance	Time (Min.)	Absorbance
00	1.224	00	0.9588	00	0.9033	00	0.6778
03	0.7447	03	0.6578	03	0.6778	03	0.5688
06	0.3798	06	0.4439	06	0.5017	06	0.4767
09	0.2799	09	0.2145	09	0.3927	09	0.3977
12	0.1707	12	0.2009	12	0.2924	12	0.3374
15	0.0998	15	0.1614	15	0.2113	15	0.2836
18	0.0605	18	0.1107	18	0.1707	18	0.1972
21	0.0412	21	0.0509	21	0.1308	21	0.1673
24	0.0248	24	0.0411	24	0.0980	24	0.1176

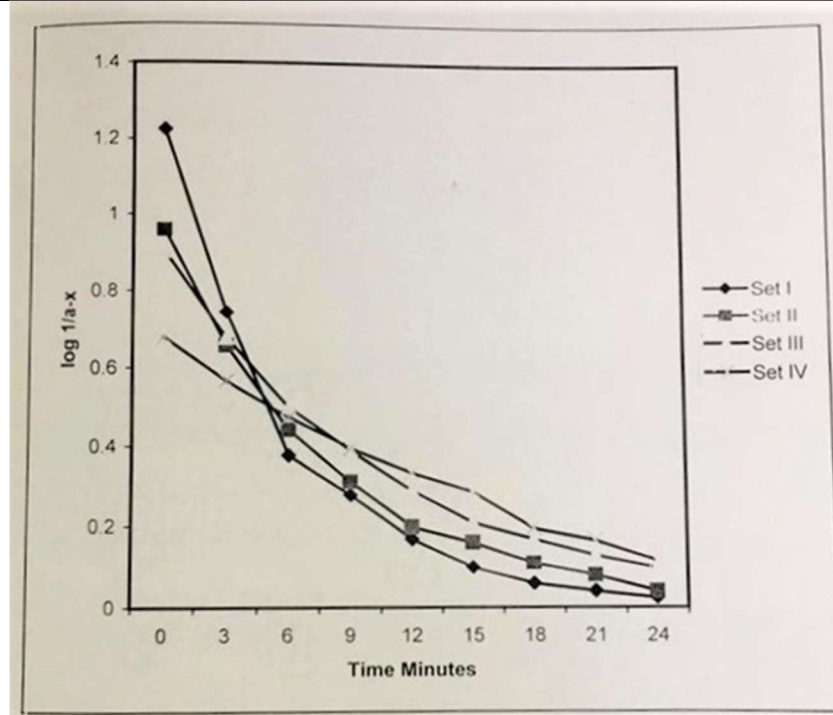


Figure 4. Order of the reaction w.r.t. to L-Ascorbic acid

Effect of catalyst on reaction rate:

The effect of catalyst on the reaction rate was determined spectrophotometrically by using a Pyeunicam UV-Vis spectrophotometer. In order to know the role of the Cu^{+2} ion as catalyst in the kinetics of this reaction, the reaction was carried out using different concentrations of CuSO_4 . It has been concluded that the Cu^{+2} ion greatly affects the oxidation of ascorbic acid. The kinetic data was tabulated in Table 4, and a graphical representation has been shown in Figure 5. These results clearly indicate that the reaction rate is increased by an increase in Cu^{+2} ion concentration. Moreover, it was found that the specific rate, like other Cu^{+2} -catalyzed reactions, was linear, which was evident from the linearity of the plot of $\log K$ versus conc. of Cu^{+2} ions. The linearity was being governed by the relation $K = K_0 + m\text{CCu}^{+2}$, where K_0 is the constant for the uncatalyzed reaction, is $10 \times 10^{-2} \text{ min}^{-1}$, and was found to be almost the same as found experimentally for the uncatalyzed reaction under similar conditions

Table4. Kinetic runs at temperature 30°C

[Ce(IV) = $2.0 \times 10^{-4} \text{ M}$]			[Ascorbic acid = $8.0 \times 10^{-3} \text{ M}$]		
[Hydrochloric acid = 0.01 N]			Temperature 30 °C		
$\text{CuSO}_4 \times 10^3$					
Time (Min.)	Conc. 0.0 M	Conc. 1.0 M	Conc. 2.0 M	Conc. 3.0 M	Conc. 4.0 M
	Absorbance	Absorbance	Absorbance	Absorbance	Absorbance
00	0.9033	0.9976	1.0972	1.1551	1.2210
03	0.6678	0.7102	0.7445	0.7448	0.7571
06	0.4947	0.4947	0.5086	0.4888	0.4686
09	0.3615	0.3566	0.3421	0.3183	0.2924
12	0.2834	0.2556	0.2337	0.2075	0.1806
15	0.1971	0.1807	0.1581	0.1308	0.1134
18	0.1455	0.1222	0.1108	0.0860	0.0682
21	0.1077	0.0888	0.0731	0.0984	0.0435
24	0.0783	0.0632	0.0506	0.0361	0.0268

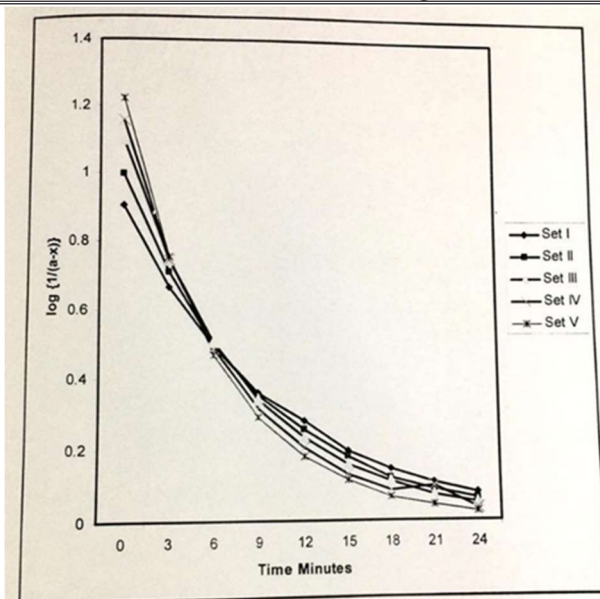


Figure 5. Effect of catalyst CUSO4

Reaction products:

It was noticed that the colour of the reaction mixture in standby changed over time. As a result, the solution goes from being somewhat yellow to dark brown. This resulted in the conclusion that ascorbic acid undergoes multiple stages of oxidation, and the formation of the final product, dehydroascorbic acid (Figure 6), was verified with the help of i.r. spectroscopy (Figure 7).

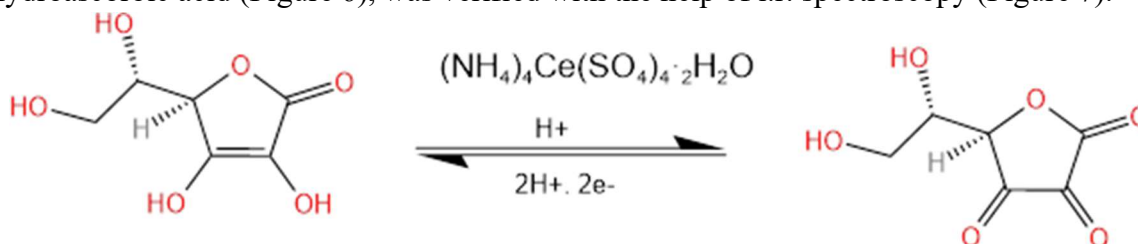


Figure 6., Redox reaction of oxidation of L-Ascorbic acid to L-Dehydroascorbic acid.

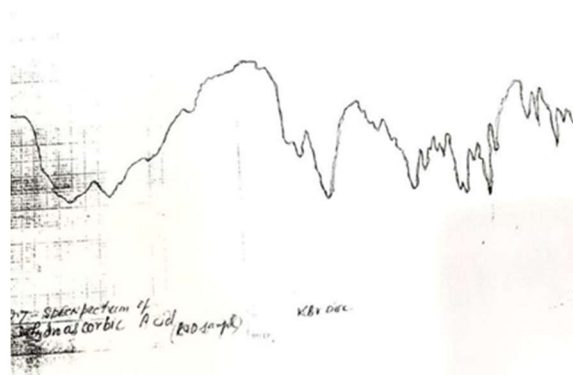


Figure 7. IR spectrum of dehydroascorbic acid.

Conclusion:

The reaction was found to be first order with respect to Ce(IV) and ascorbic acid. The overall order of reaction was found to be two, and the reaction was appreciably catalyzed by Cu²⁺ ions. The specific rate was linearly related to the concentration of Cu²⁺ and is governed by the equation $K = K_0 + mCCu^{2+}$. The final product is identified as dehydroascorbic acid.

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