



Comparative Study of Uncatalysed Oxidation of Valine and Arginine by Cerium (IV) in Aqueous Sulphuric Acid Medium

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Abstract

The comparative study of oxidation of valine and arginine by cerium (IV) has been studied spectrophotometrically in the presence of aqueous sulphuric acid medium. The reaction was studied under pseudo first order conditions with respect to cerium (IV). The reaction show first order kinetics with respect to Ce (IV) and fractional order with respect to valine and arginine. It is found that pseudo first order rate constant, k_{obs} decreases with increase of $[HSO_4^-]$ and increases with the increase of $[H^+]$. The stoichiometry of the reaction was found to be 1:2. The main oxidation product of oxidation of valine were identified as 2-methylpropanal while 1-(4-oxobutyl) guanidine was identified as oxidation product of oxidation of arginine. Ce (III), ammonia and carbon dioxide were identified as the by product. Added products do not have any significant effect on the reaction rate.

Keywords Kinetics, Valine, Arginine, Oxidation, Cerium (IV), Sulphuric acid.

Introduction

Amino acids are the building blocks in protein synthesis. In metabolism, amino acids are subjected to many reactions, and can supply precursors for various endogenous substances, as for example, hemoglobin in blood. Amino acids undergo various kinds of reaction, depending on whether the particular amino acids contain non-polar groups, polar substituent, acidic or basic substituent. The study of amino acids is one of the most exciting fields of organic chemistry. They play a significant role in a number of metabolic reactions like biosynthesis of polypeptide, protein and nucleotides. Thus, the mechanism of analogous non enzymatic chemical processes in the oxidation of amino acids is a potential area for intensive investigation¹ in order to understand some aspects of enzyme kinetics.

L-Valine is an essential, non-polar, aliphatic amino acid used to hold proteins together. It is needed for muscle metabolism and coordination, tissue repair and for the maintenance of proper nitrogen balance in the body. The oxidation of biologically important amino acid arginine is very significant because it may reveal the mechanism of amino acid metabolism.

Cerium (IV) is a powerful oxidizing agent in acidic medium with the reduction potential in $HClO_4$ as 1.75 volts². The oxidizing potential of cerium (IV) in H_2SO_4 medium have conclusively been established and oxidant is

reported to exist in the form of sulphato species. The oxidation of organic compounds by cerium (IV) usually proceeds via an intermediate complex³⁻⁵. In all cases, evidence of a free radical was observed and reduction of Ce (IV) to Ce (III) by one electron transfer was postulated. In these studies, it has been pointed out that oxidation by cerium (IV) is complicated by complexation steps and reaction intermediates and postulation of a detailed mechanism has seldom been possible. In perchloric acid media, hydrolytic equilibria lead to at least three cerium (IV) species, where as in sulphuric acid medium, several sulphate complex species of the metal ion could also be produced⁶⁻⁷.

Methodology

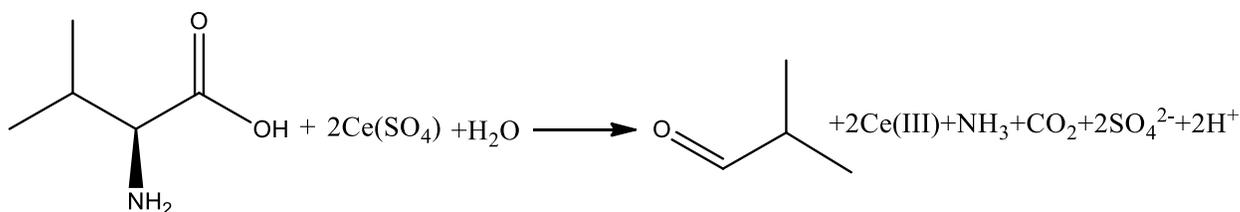
In the present work, double distilled water was used throughout the study. A stock solution of L-Valine and Arginine (E. Merck) was prepared by dissolving it in water. The cerium (IV) stock solution was obtained by dissolving cerium (IV) ammonium sulphate (E. Merck) in 1.0 mol dm⁻³ sulphuric acid and standardized with iron (II) ammonium sulphate solution. Other chemicals and reagents such as sodium sulphate, sulphuric acid, acetonitrile used were of analytical grade.

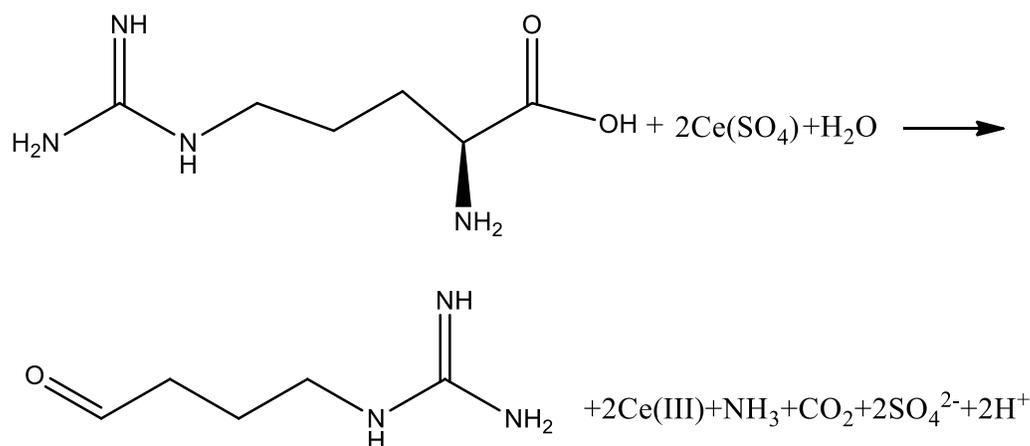
Kinetics of oxidation of valine and arginine have been investigated at 40°C. The reaction was initiated by mixing reactant solution thermally equilibrated at the desired temperature. Kinetic studies were carried out in sulphuric acid medium under pseudo first order conditions with a large excess over Ce (IV). The reaction was followed by measuring the absorbance of unreacted Ce (IV) at 360 nm in a 1 cm cell placed in the thermostated compartment of a systronics (166) UV-Visible spectrophotometer. The observed rate constants were reproducible within the experimental error $\pm 5\%$.

Results and Discussion

Stoichiometry and product analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce (IV)] was in excess over [Valine] and [Arginine] at constant ionic strength, acid concentration were kept for 24 hours at 40°C. The unreacted Ce (IV) was measured by absorbance at 360 nm. The main reaction products are Ce (III), 2-methylpropanal, 1-(4-oxobutyl) guanidine, ammonia and CO₂. 2-methylpropanal and 1-(4-oxobutyl) guanidine was confirmed by the IR spectrum of the corresponding hydrazone. The reaction mixture was treated with acidified 2,4-dinitrophenyl hydrazine solution, which yielded a hydrazone. Further, aldehyde group was confirmed with qualitative test such as Tollen's reagent⁸ and Schiff's reagent. Nitrile test was negative, the product usually reported in the oxidation of amino acids. Ammonia was confirmed with Nessler's test. Therefore, the stoichiometry of the oxidation reactions with positive test of aldehyde represented by the following equations





Effect of cerium (IV)

The reaction rate was measured with various $[Ce(IV)] = 5 \times 10^{-5}$ to 5×10^{-4} mol dm⁻³ at fixed $[Val]$ and $[Arg] = 5 \times 10^{-3}$ mol dm⁻³, $[H^+] = 1.0$ mol dm⁻³, $[Na_2SO_4] = 0.5$ mol dm⁻³, and temp. = 40°C. The plot of log absorbance versus time was linear indicating that the reaction is first order with respect to $[Ce(IV)]$. The pseudo first order rate constant k_{obs} are independent of the $[Ce(IV)]$.

Effect of amino acids

The kinetic runs were carried out with various concentrations (1×10^{-3} to 1×10^{-2} mol dm⁻³) of valine and arginine at fixed $[Ce(IV)] = 5 \times 10^{-4}$ mol dm⁻³, $[H^+] = 1.0$ mol dm⁻³, $[Na_2SO_4] = 0.5$ mol dm⁻³, and temp. = 40°C, k_{obs} increases with the increase of $[Val]$ and $[Arg]$. The Observed reaction order of valine and arginine is less than unity.

Table 1. Effect of cerium (IV), valine, arginine and $[H^+]$ on oxidation of valine and arginine by cerium (IV) in aqueous sulphuric acid medium at 40°C

10^4 [Ce(IV)] mol dm ⁻³	10^3 [Val] mol dm ⁻³	10^3 [Arg] mol dm ⁻³	$[H^+]$ mol dm ⁻³	$10^4 k_{obs} \text{ sec}^{-1}$	
				Valine	Arginine
0.5	5.0	5.0	1.0	3.34	2.86
1.0	5.0	5.0	1.0	3.32	2.83
2.0	5.0	5.0	1.0	3.22	2.82
3.0	5.0	5.0	1.0	3.35	2.86
4.0	5.0	5.0	1.0	3.33	2.82
5.0	5.0	5.0	1.0	3.32	2.85
5.0	1.0	1.0	1.0	1.22	0.92
5.0	2.0	2.0	1.0	2.28	1.81
5.0	3.0	3.0	1.0	2.95	2.51
5.0	4.0	4.0	1.0	3.67	3.02
5.0	5.0	5.0	1.0	3.91	3.46

5.0	6.0	6.0	1.0	4.29	3.98
5.0	7.0	7.0	1.0	4.48	4.22
5.0	8.0	8.0	1.0	4.68	4.31
5.0	9.0	9.0	1.0	4.87	4.40
5.0	10.0	10.0	1.0	4.96	4.43
5.0	5.0	5.0	0.20	1.32	1.02
5.0	5.0	5.0	0.40	2.28	1.91
5.0	5.0	5.0	0.60	2.76	2.62
5.0	5.0	5.0	0.80	3.33	3.23
5.0	5.0	5.0	1.0	3.91	3.46

Effect of $[H^+]$

The reaction rate were measured with various $[H^+] = 0.2$ to 1.0 mol dm^{-3} at fixed $[HSO_4^-]$, $[Val]$ and $[Arg] = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $[Ce(IV)] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 1.50 \text{ mol dm}^{-3}$, The rate of reaction increases with increase of $[H^+]$, the reaction was observed positive fractional order with respect to $[H^+]$.

Effect of $[HSO_4^-]$

$[HSO_4^-]$ was varied in the range of 0.2 to 1.0 mol dm^{-3} at fixed $[H^+] = 0.2 \text{ mol dm}^{-3}$, $[Ce(IV)]$, $[Val]$, $[Arg]$ and temperature. Here $HSO_4^- \approx [NaHSO_4] + [H_2SO_4]$, ignoring the dissociation of $[HSO_4^-]$ in strongly acidic medium. k_{obs} decreases with increase of $[HSO_4^-]$. Therefore HSO_4^- shows a rate retarding effect.

Effect of ionic strength

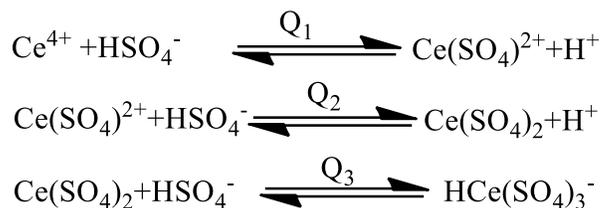
At fixed concentration of $[Ce(IV)]$, $[Val]$, $[Arg]$, $[H_2SO_4]$ and temperature, the ionic strength was varied from 1.2 to 2.0 mol dm^{-3} , it is found that ionic strength has slightly affected the rate of reaction.

Effect of added product

The effect of cerium (III) on the rate was also studied and was found to be independent of cerium (III) concentration, ruling out any possibility of the rate limiting step preceded by the reversible equilibrium involving cerium (III).

Reactive Species of Ce (IV)

Under the experimental conditions in aqueous sulphuric acid medium, the important Ce(IV) sulphato complexes are $Ce(SO_4)^{2+}$, $Ce(SO_4)^2$ and $HCe(SO_4)_3^-$ and relevant equilibria are⁹



The value of equilibrium constants are $Q_1 = 3.5 \times 10^3$ (25°C), $Q_2 = 2 \times 10^2$ (25°C) and $Q_3 = 0.6$ (at 20°C). Insignificant amount of unhydrolyzed species of cerium (IV) would also exist along with these sulphato complexes. In the light of above equilibrium, inverse bisulphate dependence can be explained by assuming $\text{Ce}(\text{SO}_4)_2$ as the reactive species. Furthermore the rate of reaction slightly affected by ionic strength, indicate that there must be a neutral molecule in the rate determining step, which confirms $\text{Ce}(\text{SO}_4)_2$ as the kinetically active species in present study. A negative value of ΔS^\ddagger suggests that the two ionic species combine in rate determining step to give a single intermediate complex which is more ordered than the reactants. The low value of rate constant for slow step of the mechanism confirms that the oxidation apparently occurs through an inner-sphere mechanism.

Conclusion

The oxidation of valine and arginine by cerium (IV) in acidic medium follows fractional order kinetics with respect to amino acids and first order kinetics with respect to oxidant. The reactive species for the oxidation of cerium (IV) in acidic medium was $\text{Ce}(\text{SO}_4)_2$, although other species might be active to a much lesser extent.

Acknowledgment

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