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Oxidation and Kinetics Study of Polar and Non-Polar Amino Acids by Using Green Oxidants Potassium and Sodium Ferrate

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KEYWORDS Potassium Ferrates (VI), Sodium Ferrate (VI) amino acids, Kinetics, oxidation	ABSTRAC This researce application of potentials for is revealed. techniques (oxidant for oxidant does was found t Reaction was spectrophoto	F: ch paper presents a comprel of potassium and sodium ferra r organic and inorganic substar The first part of the paper p FTIR, UV-Visible, SEM, XI the oxidation of polar and r not have a negative impact fa hat ferrate Fe (VI) strong oxi as examined at acidic to stro- meter data are used to determine	nensive overview ate as oxidizing a aces, impurities ar provide synthesis RD) and In the non polar amino actor for human sp dizing agent and rong alkaline me ne the Kinetics of	 in preparation, gents. Due to spend also in water tra- and characteriza second part focus acids at different becies and environ it oxidized amino- edium for both or reaction. 	characterization and cific strong oxidizing eatment their literature tion by using various on the application of PH scales. Ferrate as mental remediation. It o acids in short time. oxidants. Further the

1. Introduction

Ferrates (VI) were powerful oxidizing agents for amino acids; the specific purpose of this work is to (a) the determination of reactivity of Polar and non polar amino acids towards ferrates (VI) (b) Evaluate the impact of P^{H} the on reaction rate, effect of temperature on the reaction, and concentration change of oxidant. The p^{H} of the reaction medium in the experiment is taken as the range of p^{H} 5- $p^{H}10$ due to ferrates specification ^[1]. Preparation of ferrate can be done by three methods (A) dry oxidation method (B) electrochemical method (C) Wet of oxidation method ^{[2].} The oxidation of different amino acids is done at 35° C temperature. The main purpose of this study is to reduce the preparation cost of oxidant potassium ferret and investigation of oxidation and Kinetics of Different polar and non polar amino acids at different P^H and concentration. The data provided in this paper would be important to predict the potassium and sodium ferrate performance to amino acid oxidation^[3]

Chemical name	Crystal structure	Molecular weight	Density	Physical state &Colour	Solubility	Decomposition temperature
Potassium ferrate	2K ⁺ ^{Fe} ^{Fe} ^{Fe} ^{Fe} ^O ^C	198 g/mol	2.825 g/cm ³	Brown red colour crystals	Soluble 1 M KOH solution	198·C
Sodium ferrate	2Na ⁺ 0Fe 0	135.84g/mol	4.05g/cm ³	Radish Purple crystals	Soluble 1M KOH solution	285*C

Table: 1 Physical and chemical properties of potassium and sodium ferrate ^[4], solubility, ^[5] structure) ^[6,7] colour^[8],

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2. Characterization of oxidant By Spectroscopic Technique

2.1. FT-IR

The ferrate (VI) infrared spectrum was shown in Figure 1, 2, 3 and 4. The stretching of water, which may be absorbed, was attributed to the peak at 3166.55 cm^{-1} in case of potassium ferrate and 3362.1 cm^{-1} in sodium

ferrate. Four equivalent, symmetric Fe-O bonds have stretching vibrations at 570 cm⁻¹,585cm⁻¹, 864.84 cm⁻¹. The oxygen atoms surrounding the iron centre to be distributed in an equivalent, symmetrical, and tetrahedral manner based on the interpretation of stretching frequencies^{[8],[9]}



Figure: 1 FT-IR spectrum of potassium ferrate (100-650cm⁻¹) in finger print region



Figure: 2 FT-IR spectrum of potassium ferrate (650-4000cm⁻¹) in functional group region

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Figure: 4. FT-IR spectrum of Sodium ferrate (650-4000cm⁻¹) in functional group region

2.2. SCANING ELECTRON MICROSCOPY [SEM]

The morphology of the synthesized ferrate crystals was visualized with SEM images in Figure 5 and 6, which

indicated the powders were crystalline having polyhedral morphology. These crystals are smaller than those described by Licht et al^{.[10]} and range in size from 25 to 200 μ m in length and 1 to10 μ m in breadth.

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Figure 5 SEM Analysis of Potassium Ferrate



Figure 6 SEM Analysis of sodium Ferrate

2.3. Uv-VISIBLE SPECRTOSCOPY

The Uv-visible absorption spectra of oxidants show two peaks at 503 and 804 nm correspond to the red-violet

colour of an aqueous solution of ferrate ions (Figure 7 and 8). Other studies supported the potassium and sodium ferrates absorption spectra during their own experiments at 505 and 802 nm $^{[11], [8]}$



Figure: 7 and 8 UV Visible Spectrum of Potassium and sodium ferrate

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2.4. XRD INTERPRETATION

The X-Ray Diffraction patterns of potassium and sodium ferrates are shown in Figure 9. The XRD patterns were analyzed by XRDML at $2\theta \square$ range from starting position 5.015°.to end position 89.97°. Crystals of potassium and sodium ferrate show sharp peak at 2 theta value are 32.40°, 33.29°, 37.54°, 39.36°, 44.51° and 47.30. (K₂FeO₄) and 29.27°, 41.35° and 51.35° 59.6° 67.81° (Na₂FeO₄).Data's of XRD resembles with reported method and ferrate had orthorhombic crystalline shape ^[8].



Figure 9: XRD pattern of (a) Potassium ferrate and (b) Sodium Ferrate

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3. Result and Discussion

EXPERIENTAL

3.1 Synthesis of ferrates:

The synthesis of ferrates by wet oxidation is good as compared to dry oxidation and electrochemical method, because it gives high purity minimum side product and Chemicals wastage and reaction condition is easily available^{[12,13].} Ferrates were prepared by using alkaline hypochlorite oxidant and Solid ferric chloride, sodium hypochlorite, sodium hydroxide and potassium hydroxide. All the solutions are prepared with distilled water and glacial acetic acid solvent ^[14]. The preparation of ferrate by wet oxidation method, the iron firstly oxidized under strong alkaline medium sodium hypochlorite in the presence of sodium hydroxide by the addition of potassium Hydroxide the potassium ferrate solution of obtain^[15]. Potassium ferrate could be made as high purity 96.5% but yield was low about 10-15% but this limitation was taking away by Schreyer at el and Williams and rilev [16]

In this study potassium and sodium ferrate were prepared according to the following scheme

 $\begin{array}{ccc} Fe^{+3} + 3OH^{-} & & & Fe (OH)_{3} \\ 2Fe & & & (OH)_{3} + 3NaCHO + 4NaOH \\ 2Na_{2}FeO_{4} + 3NaCl + 5H2O \\ Na_{2}FeO_{4} + 2KOH & & & & K_{2}FeO_{4} + 2NaOH \end{array}$

3.2Stoichiometry

The pH was a determinant factor in dissociation of amino acids in the medium. Amino acids can exist as a dipolar ion or zwitter ion in an alkaline or acidic medium ^[17]. The reactions in the experiment were performed in basic medium, so the zwitter ions would be changed into the reactive species, the anion species was taking part in the reaction.



Cation Anion Zwitterions

The stoichiometry of the reaction was determined during the experiment at 310 K, under the condition of [Oxidant] [Substrate], containing acetic Acid–water [70% (v/v). The overall reaction showing two-electron transfer, and can be represented as:

 $\hat{R}CH(NH_2)COOH + 2Fe^{VI} \longrightarrow RCN + CO_2$ + $2Fe^{IV} + 4H^+$

The above equation is in consistence with the earlier observations with PFC and QFC expected the stoichiometry to be in agreement ^[18]

3.3 Determination of rate constant

The solvent is prepared by 30% glacial acetic acid and 1 M solutions of different amino acids are prepared by using the same solution. The wavelength of oxidant is 508 nm is set in the spectrophotometer and reaction is carried out.10 ml solution was taken which contains 1 ml oxidant 1 ml substrate and 8 ml solvent. Temperature of reaction medium is maintained by thermostat. The concentration of substrate is decrease with increasing time and is determined in the terms of optical density. The reaction was completed fastly, rate constant was determined by the plotting a graph in between change in concentration (optical density) with time by using data analyzer. The reaction was followed by monitoring the decrease in the absorbance at 508 nm by thermostatted compartment of UV/Vis EQ 820A Spectrophotometer. The kinetic runs examined up to more than 75% of the substrate consumed.

Amino acids	Coefficient of correlation	Rate constant in (dm ⁻³ mol ⁻ s ⁻) (K ₂ FeO ₄)	Coefficient of correlation	Rate constant in (dm ⁻³ mol ⁻ s ⁻) (Na ₂ FeO ₄)
Glycine	0.994012	4.8123	0.986741	4.3306
Alanine	0.995241	4.2314	0.986420	3.92131
Leucine	0.989214	4.2104	0.9927317	3.42614
Phenyl alanine	0.992148	3.1734	0.989624	3.15267
Valine	0.998734	4.7341	0.995061	4.00473

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Methionine	0.998241	3.16416	0.994247	3.46242
Iminodiacetic acid	0.987694	2.34941	0.992826	4.73261
Glutamic Acid	0.99824	5.2734	0.987241	4.07676

Table 2: Rate constant for the oxidation of amino acids by potassium and sodium ferrate

3.4. Influence of p^H on the oxidation reaction

Amino acids P ^H	Coefficient of correlation	Rate constant in (dm ³ mol ⁻ s ⁻¹)	Coefficient of correlation	Rate constant in (dm ³ mol ⁻ s ⁻¹)
		[K ₂ FeO ₄]		[Na ₂ FeO ₄]
4.5	0.9973218	2.20156	0.983827	1.37241
5.5	0.9940184	2.27386	0.988273	1.29914
6.5	0.9954890	3.17057	0.992832	2.34736
7.5	0.9923416	3.72901	0.998273	3.46621
8.5	0.9907841	3.89623	0.996431	4.73732
9.5	0.9943871	4.84340	0.979281	3.92483
10.5	0.9895429	4.73924	0.984867	4.82436
11.5	0.9928654	4.58041	0.972834	4.78342
12.5	0.9868352	4.39672	0.998641	5.00346
13.5	0.98965320	3.81275	0.993624	4.36798

Table 3: Effect of P^H on rate constant of Reaction

The results of experiment are specified that stability of ferrate is highly depends on P^H the reaction medium. The reaction medium is taken highly basic for better results. (Table 3).It is observed that p^H is taken 9.5-10.5 then the

reaction is completed within few minutes and rate constant is considerable higher as compared to pH 6.5- $7.5^{\left[19\right]}$

3.5 Temperature effect on rate constant

Temperature (K)	Rate constant in (dm ³ mol ⁻ s ⁻¹) [K ₂ FeO ₄]	Rate constant in (dm ³ mol ⁻ s ⁻¹) [Na ₂ FeO ₄]
305	1.182047	0.982761
315	2.641662	1.27342
325	4.79731	5.28691
335	7.86641	5.37691

Table 4: effect of temperature on the rate of reaction

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Figure 9: Effect of Temperature on Oxidation Reaction

On Observations, it was found that in case of low temperature reaction did not started instantly after mixing reactants, but take some time. This duration of time was called induction period. On increasing temperature induction period decrease and reaction proceed slow to fast and attain a maximum rate at a certain time and then becomes slow down.

4. Conclusions:

The powered form of potassium and sodium ferrate (VI) were use as oxidizing reagent, synthesized by the wet oxidation method. This paper elucidates the oxidative nature of ferrates in aqueous mediums which are useful in amino acid oxidation. Temperature, concentration of substrate and pH are important factors that influence the oxidation reaction. Ferrate (VI) was a powerful, non toxic and green oxidizing agent and its oxidizing power was comparatively more from Cr and Mn. In this paper the spectroscopic properties (Uv-Visible SEM,FT-IR,XRD) and kinetics of Fe (VI) oxidant were studies for the Fe (VI) oxidation of amino acids.

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