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- (c) oxidation reactions in the presence of homogeneous, heterogeneous, immobilised and enzymic catalytic systems, combustion, fires, explosions;
- (d) regulators of selective oxidation synthesis of valuable oxygen-containing compounds; highly enantioselective oxidation; stereoselective synthesis;
- (e) biological and biochemical oxidation processes; medical image processing; neural networks and fuzzy logic techniques;
- (f) photochemical oxy-reduction interactions;
- (g) methods for prognosis and evaluation of performance terms or/and storage terms of the materials, as mentioned above in (b);
- (h) tribochemical interactions on metal and other surfaces in the presence of molecular oxygen or its activated species;
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Compiled by S. K. Ivanov, Zh. D. Kalitchin, M. I. Boneva, J. P. Ivanova, N. Evtimova and V. Shishkova. Volume 45 (2022) will be published in four separate books, issued at 31.03.2022, 30.06.2022, 30.09.2022 and 31.12.2022. The editorial board can publish special issues in case of over-accumulation of manuscripts submitted for publication. Regular subscription rate: EUR 800/Europe and US\$ 942/rest, 10% agency discount, plus extra postage charges: for Europe EUR 30 without priority mail and EUR 60 with priority mail; for all other countries US\$ 50 without priority mail and US\$ 90 with priority mail, including packing, handling and postage. Bank charges are shared according to the banks requirements. Prices are subject to change without notice, in accordance with market fluctuations. Advertising and announcements are accepted and published in the Journal at US\$ 3 per 1 cm<sup>2</sup>.

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## **KINETIC, MECHANISTIC AND THERMODYNAMIC STUDY OF Ir(III) CATALYSED OXIDATION OF LEUCINE BY HEXACYANOFERRATE(III) IN AQUEOUS ALKALINE MEDIUM**

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249 196 Uttarkashi, India*

### **ABSTRACT**

Kinetics of oxidation of leucine by hexacyanoferrate(III) abbreviated as HCF(III) in presence of Ir(III) in aqueous alkaline medium has been investigated spectrophotometrically at  $35 \pm 0.1^\circ\text{C}$  and constant ionic strength of  $0.50 \text{ mol dm}^{-3}$  in order to elucidate the mechanism of the reaction. Experimental results reveal that the rate of oxidation increases with increase in the concentration of oxidant, HCF(III) and catalyst, Ir(III), and shows first order dependence while the order of the reaction was found to be one at the lower substrate concentration tending towards zero at its higher concentration. The reaction shows positive salt effect with KCl. The stoichiometry between  $[\text{HCF}]:[\text{leucine}]$  is 2:1. To evaluate the activation parameters, the reaction has been studied at four different temperatures, i.e. 35, 40, 45 and  $50^\circ\text{C}$ . A mechanism involving the complex formation between catalyst, substrate and oxidant has been proposed.  $\alpha$ -Keto isocaproic acid has been identified as the ultimate product of the reaction. Based on the experimental results, reaction stoichiometry and product analysis, a suitable mechanism consistent with the observed kinetics has been proposed and rate law has been derived.

*Keywords:* HCF(III), leucine, Ir(III),  $\alpha$ -keto isocaproic acid, kinetics, mechanism.

### **AIMS AND BACKGROUND**

Amino acids, derived largely from protein in the diet or from the degradation of intercellular proteins, are the ultimate class of biomolecules whose oxidation makes

---

\* For correspondence.

ORIGINAL RESEARCH PAPER

## Polyvinylpyrrolidone and Brij-35 Stabilized IrO<sub>2</sub> Nanoclusters As Highly Effective Catalyst In The Degradation Of Acid Orange 10: A Comparative Study

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### ABSTRACT

In this study, the degradation of azo-dye acid orange 10 (AO 10) has been investigated using Polyvinylpyrrolidone (PVP) and Polyoxyethylene Lauryl Ether (Brij-35) stabilized Iridium oxide (IrO<sub>2</sub>) nanoclusters as catalysts. A simple chemical reduction method was used to synthesize the above-mentioned nanoclusters. The characteristics of the nanocatalysts were determined by UV-visible spectrophotometer, TEM, and XRD. The kinetic study has been carried out at  $\lambda_{max}$  of the reaction mixture i.e. 479 nm spectrophotometrically. The degradation follows first-order kinetics concerning oxidant and catalyst concentration while an order is one at lower substrate concentration tending towards zero at higher concentration. The degradation kinetics has been supported by the derived rate law. The results showed that PVP-stabilized IrO<sub>2</sub> nanoclusters outperformed Brij-35 stabilized IrO<sub>2</sub> nanoclusters, exhibiting the fastest degradation rate. The progress of the degradation process was monitored by UV-vis spectroscopy. Using PVP-stabilized IrO<sub>2</sub> nanoclusters as a catalyst is a very promising approach for the remediation of acid orange 10 due to the fast degradation rate and high degradation efficiency. In addition, PVP-stabilized IrO<sub>2</sub> nanoclusters can be easily recovered and recycled for three consecutive cycles. It can be inferred from this study that catalytic oxidation methods are active and environment-friendly for the remediation of dyes.

**Keywords:** Degradation, Kinetics, PVP, Brij-35, Rate law, Acid orange10

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### INTRODUCTION

Synthetic dyes have been widely used in various fields, especially in the textile and printing industries. Azo dyes which constitute a significant proportion of synthetic dyes pose a significant threat to the environment and eco-biology because of their non-biodegradability and potential genotoxic and carcinogenic nature [1,2]. Dye removal or degradation from wastewater has been extensively studied to reduce its impact on the environment [3,4]. Several physicochemical and

biological methods, such as adsorption, ozonation, photocatalysis, Fenton, reductive and oxidative degradation, and two or more combination methods have been successfully applied to the treatment of various dyes [5-7].

Among these methods, oxidative degradation is a fast, simple, and low-cost method, which is easy to implement in industries for the degradation of dyes [8]. Conventional chemical oxidation of dyes typically involves the use of oxidizing agents such as chlorine in the form of sodium hypochlorite, ozone (O<sub>3</sub>), hydrogen peroxide, and permanganate

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## **DETERMINATION OF Ir(III) IN THE OXIDATION OF VALINE BY HCF(III) IN AQUEOUS ALKALINE MEDIUM BY KINETIC SPECTROPHOTOMETRIC METHOD**

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### **ABSTRACT**

The present paper deals with a novel method for the determination of iridium based on the Ir(III) catalysed oxidation of valine by hexacyanoferrate(III) in an aqueous alkaline medium by kinetic spectroscopic method. By this method, the Beer's law is obeyed in the range of 1.99–19.98  $\mu\text{g ml}^{-1}$  of Ir(III). The Sandell's sensitivity and molar sensitivity are found to be 0.216 to 0.213  $\mu\text{g cm}^{-2}$  and  $0.9 \times 10^3$  to  $1.2 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ , respectively. The value of the correlation coefficient lies between (–0.9993 to 0.9978) which indicates the high precision involved in the determination and almost perfect correlation of the data. The effect of a few interfering ions has also been worked out for developing the calibration curves in terms of absorbance or initial rate or pseudo-first-order rate constant versus Ir(III) at  $\lambda_{\text{max}}$  of 420 nm. The results show the method is simpler, more sensitive, selective and inexpensive than the reported method. This method avoids the use of hazardous solvents as the reaction occurs in aqueous medium.

*Keywords:* microgram determination, oxidation, hexacyanoferrate, Valine, Ir(III).

### **AIMS AND BACKGROUND**

Oxidation reactions of amino acids are among the most interesting and useful chemical processes. Basically amino acids are used in parental and enteral nutrition, medicine, feed, food, cosmetics and raw materials for the chemical industry. Poly (amino acids) as biodegradable polymers have attracted attention in connection with environmental protection<sup>1</sup>. Thus due to their biological significance and selectivity towards the oxi-

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