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A Kinetic and Mechanistic Study on Degradation of Acid Orange – IV using HCF(III) ions in Aqueous Alkaline Medium

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ABSTRACT: The degradation of acid orange–IV, a monoazo dye, in aqueous alkaline medium was investigated by using hexacyanoferrate(III) ions abbreviated as HCF(III). Kinetics of the reaction has been studied spectrophotometrically at 440 nm, λ_{max} of the dye. The influence of experimental parameters such as concentration of dye, oxidant and solution pH on the reaction rate has been studied on the rate of degradation of orange–IV dye. The results reveal that the reaction follows first order kinetics with respect to [HCF(III)] and [Dye] at an optimum pH of 8.0. Thermodynamic parameters have been calculated by studying the reaction rate at four different temperatures; 40°C to 55°C. The low value of energy of activation suggest high rate of degradation. A reaction mechanism, which assumes the formation of a transient complex between anionic form of dye and HCF(III) has been suggested. Degradation of dye into more simpler and less hazardous products has been confirmed by UV-vis and LC-MS methods of analysis.

Keywords: Kinetics, degradation, Acid orange–IV, HCF(III), thermodynamic parameters

I. INTRODUCTION

Synthetic dyes are the organic compounds which are very hazardous to environment. Dyes are normally used for coloration of various substrates like leather, textile, papers etc. Sometimes dyes are fused with heavy metals on the structural interface and are considered to have relatively bad effect on the environment due to their toxic and inhibitory nature [1]. Azo dyes constitute the largest and diverse class of synthetic or natural azo compounds (N=N) which are resistant to the chemical and biological degradation processes, due to low reactivity of azo linkage [2].

For the removal of dyes physico-chemical methods such as electrochemical decolorization, floatation, membrane separations, nanofiltration, photocatalysis, advanced oxidation processes have been reported. Usually complete demineralization is expensive with physico-chemical methods and these methods only transport dyes from one medium to another, rather than degrading them [3]. Hexacyanoferrate (III) anion is the most important iron(III) cyanide complex. It has Fe^{3+} centre bound in the octahedral geometry to six cyanide ligands. Being a mild oxidant it attacks the compound at a particular stage. It abstracts only one electron from the substrate yielding a simple step in any reaction mechanism: and being a one electron oxidant with a redox potential of +0.45 V of $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ couple in alkaline medium, the oxidant exhibits appreciable stability in solution and yields a stable reduction product hexacyanoferrate(II)[4-5]. The present study is in continuation to our previously reported work on the degradation of methyl orange[6]; acid red 14 and acid red 26[7] dyes by HCF(III) in aqueous alkaline medium. Here, we have attempted to degrade acid orange–IV, abbreviated as O-IV, (Fig. 1) using the mild oxidant hexacyanoferrate(III) and presented the kinetic and thermodynamic data of its oxidation.

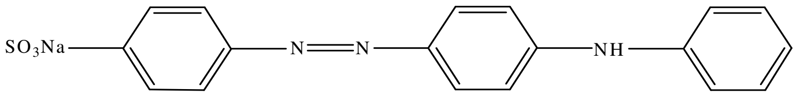


Fig.1. Structure of Acid orange-IV.

II. EXPERIMENTAL

All the chemicals and reagents used in the study were of AR grade. pH of the reaction mixture was adjusted by using KH_2PO_4 and NaOH as buffer. The kinetic experiments were carried out as reported earlier by mixing the required quantity of HCF(III), buffer and water in an iodine flask kept at the same temperature and stirred a little with help of the pipette [8]. The reaction mixture and stock solution of dye was then clamped separately in a thermostat at 40 ± 0.1 ºC. After about half an hour, a required amount of dye solution was added to the mixture and stirred to start the reaction. Progress of the reaction was measured spectrophotometrically. Aliquots were withdrawn from the reaction mixture after repeated intervals of 5 min and the absorbance were recorded. The absorbance vs time plots were made for all the sets. The initial rate method was used to decide the kinetic behavior of the reaction. Initial rates $(da/dt)_i$ were evaluated after 5 min from the start of the reaction by using plane mirror method from the plot of absorbance (a) vs time (t). The best fitting curve were obtained by the method of least square. The first order rate constant was calculated by the plot of log $(a–x)$ vs time with slope equal to $–k_1/2.303$.

The products were extracted by ethyl acetate and identified by LCMS. The mobile phase for extracted product of O-IV consisted of water: acetonitrile (70: 30).

III. RESULTS AND DISCUSSION

In order to investigate the mechanism of oxidation, the kinetic behavior of O-IV has been studied at constant pH and temperature at different concentrations of one reactant keeping the concentration of others constant.

Effect of pH : pH is one of the most important operating parameters that affect the degradation of organic compounds. The effect of pH was studied by varying it from 7–12 for O-IV. Figure 2 shows that the rate of degradation was found to be maximum at optimum pH of 8.

Effect of HCF(III) : The kinetic results represented in Fig. 3 show that oxidation of O-IV follows first order kinetics with respect to [HCF(III)]. The concentration of HCF(III) was varied from 1×10^{-6} to 9×10^{-6} mol dm^{-3}.

Effect of [substrate] : The effect of substrate concentration on reaction rate was studied by varying its concentration from 1×10^{-5} to 9×10^{-5} mol dm^{-3}. The graph presented in Fig. 4 shows the linear increase in reaction rate with the increase in substrate concentration. It is observed that the O-IV is easier and faster to degrade than AR-14 and AR-26 but difficult to be degraded than methyl orange. This difference is due to different molecular structures of the dyes. AR-14 and AR-26 dyes have two sulphonic groups which form sulphate ions that leads to reduction in the rate of degradation [3]. While, O-IV consist of a stable phenyl group attached to amine which is difficult to degrade and methyl orange bear a dimethyl group which show higher reactivity in comparison to phenyl group [9].

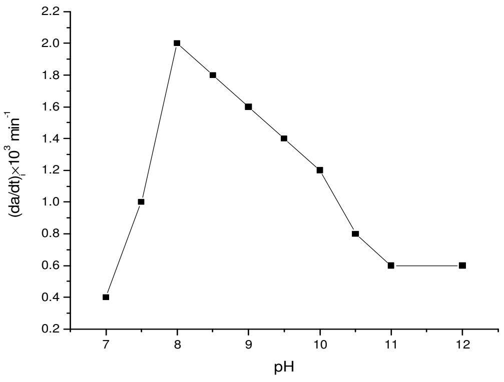


Fig. 2. Effect of pH on initial degradation rate of O-IV. by [HCF(III)]. Experimental conditions: $[O\text{-}IV]=3.0 \times 10^{-5}$ mol dm^{-3}; $[HCF(III)] = 3.0 \times 10^{-6}$ mol dm^{-3}; temperature = 40 ± 0.1°C.

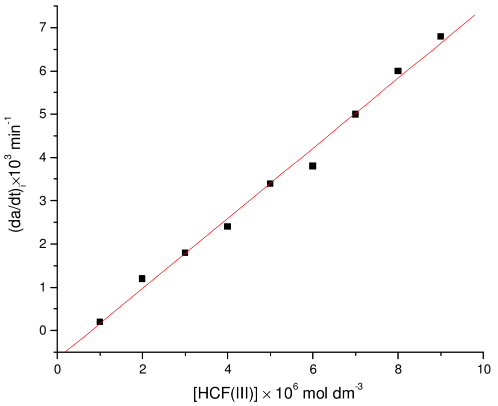


Fig. 3. Effect of [HCF(III)] on initial degradation rate of O-IV by [HCF(III)]. Experimental conditions: $[O\text{-}IV] = 3.0 \times 10^{-5}$ mol dm^{-3}; pH 8.0; temperature = 40 ± 0.1°C.

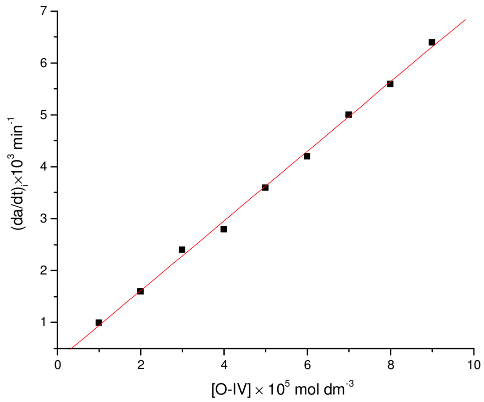


Fig. 4. Effect of [O-IV] on initial degradation rate of O-IV by [HCF(III)]. Experimental conditions: [HCF(III)] = 3.0 × 10^{-6} mol dm^{-3}; pH 8.0; temperature = 40 ± 0.1°C.

Thermodynamic parameters : The thermodynamic parameters for oxidation of O-IV (shown in Table 2) have been evaluated by studying the reaction at four different temperatures in the range of 40 to 55 ºC. The degradation rate of O-IV depending on temperature follows Arrhenius equation (Fig. 5):

$$k = Ae^{-Ea/RT}$$

Where; k is the rate constant, T is the absolute temperature, A is Arrhenius factor, Ea is activation energy, R is universal gas constant. Activation parameter, Ea and (A) were evaluated from Arrhenius plot. The high value of activation energy (E_a) and negative entropy of activation ($\Delta S^\#$) reveals low rate of degradation and formation of polar species during the reaction. The energy of formation for O-IV and the three dyes discussed earlier; AR-14 (79.0kJ/mol) and AR-26 (76.14 kJ/mol^{-1}) are similar this suggests that, they follow similar mechanism of reaction.

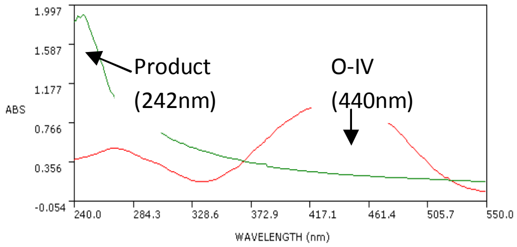


Fig. 6. UV-vis spectra of O-IV and product.

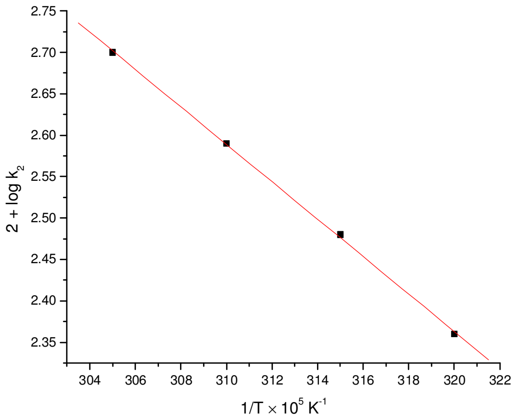


Fig. 5. Arrhenius plot for initial degradation of O-IV by [HCF(III)]. Experimental conditions: [O-IV]=3.0×10^{-5} mol dm^{-3}; [HCF(III)]=3.0×10^{-6}; pH=8.

Identification of degradation products : Degradation of the azo dye was monitored by UV-vis spectroscopy (Fig. 6). The spectra show that O-IV is characterized by maximum absorption at 440 nm attributed to the chromophore containing azo linkage of the dye molecule in the solution [9]. The disappearance of this band and formation of new bands at 242 nm supports the degradation [10]. In order to provide supported evidences for degradation, identification of degradation products was carried out by HPLC-MS shown in Fig 7. The HPLC-MS analysis shows formation of two major products with retention time of 19.63 and 21.62 min. The MS (given in figure 8) of both the retention times is almost similar suggesting formation of expected products 1,4-dibutanoic acid, 4-amino benzene sulphonic acid, 4-hydroxy phenol as major and aniline, sulphonic acid and 2-amino ethanoic acid as minor products (listed in Table 1).

Table 1: Thermodynamic Parameters. Experimental conditions: [O-IV] = 3.0 × 10^{-5} mol dm^{-3}; [HCF(III)] = 3.0 × 10^{-6} mol dm^{-3}; pH = 8.0; max=440nm Temperature = 40 ± 0.1°C to 55± 0.1°C.

PARAMETER	VALUES [O-IV]
Ea (kJ mol-1)	41.84
$\Delta H^\#$ (kJ mol^{-1})	44.01
$\Delta S^\#$ (e.u.)	-24.64
$\Delta F^\#$ (kJ mol^{-1})	77.05
A (l mol^{-1} sec^{-1})	8.41× 10^{-7}

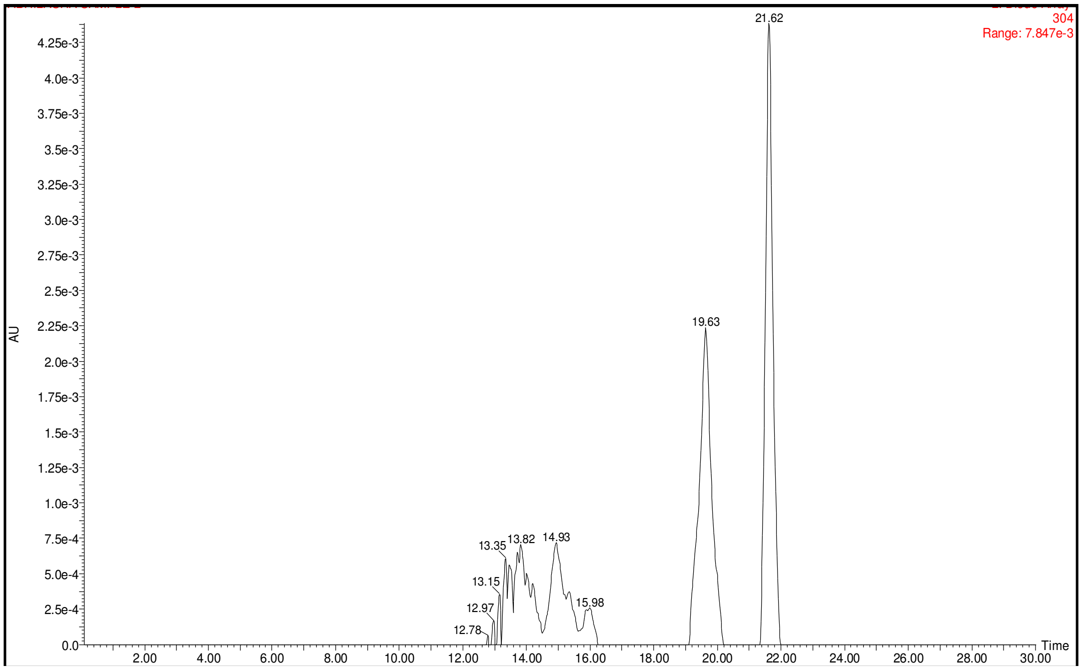


Fig. 7. HPLC-MS of O-IV product.

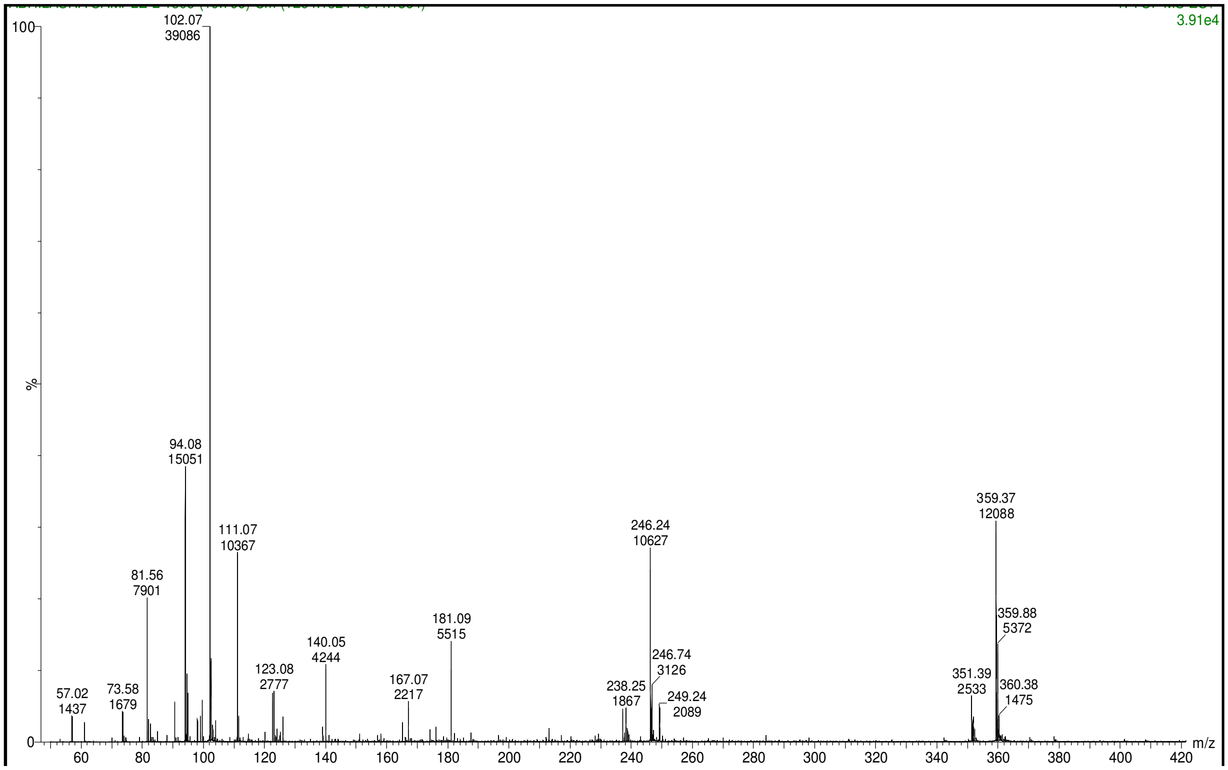
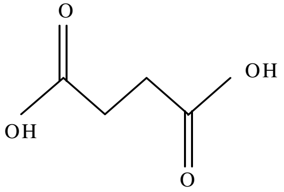
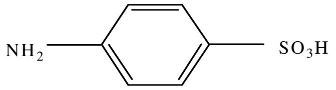
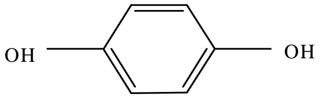
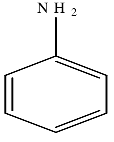
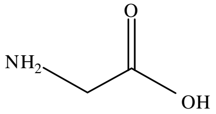


Fig. 8. LC-MS spectra of degraded products of O-IV.

Table 2: Proposed chemical structures of degradation products.

Molecular Weight	Proposed Structure
102	 1,4-dibutanoic acid
167	 4-amino benzene sulphonic acid
111	 4-hydroxy phenol
94	 Amino benzene
81	SO_3H Sulphonic acid
73	 2-amino ethanoic acid

Mechanism: Based on the above kinetic study, thermodynamic data, LC-MS analysis and previously reported work [6,7] the following reaction mechanism for the oxidation of dyes can be proposed:-

$$D^- + [Fe(CN)_6^{3-}] \overset{K}{\rightleftharpoons} \text{Complex (C)}$$

$$\text{Complex (C)} \xrightarrow[\text{Slow}]{k_1} \text{Product} + [Fe(CN)_6^{4-}]$$

According to the above mechanism, it is assumed that dye (D) molecule exist as an anion (D^-) in the alkaline medium which forms complex with HCF(III)[11]. This complex dissociates through a slow step into product and $Fe(CN)_6^{4-}$. The intermediate product is further oxidized to final product, mainly carboxylic acids, through fast steps.

Derived rate law: Based on the above mechanism and experimental facts, the following rate law has been derived:

$$r = k_1K\,[D^-][HCF(III)]$$

which is similar to experimental rate law

$$R_{obs} = k[D^-][HCF(III)] \text{ where, } k = k_1K$$

IV. CONCLUSION

Degradation of azo dye, O-IV was investigated spectrophotometrically by HCF(III) which proved its ability as potential oxidant for the removal of dyes. The oxidative degradation kinetics of O-IV by HCF(III) follow first order kinetic model with respect to [HCF(III)] and [Dye]. The pH of reaction mixture played a significant role in the degradation of the azo dye. The rate of degradation of O-IV is higher than AR-14 and AR-26 but lower than methyl orange due to different structures of dyes. A plausible mechanism has been proposed and thermodynamic parameters have been evaluated which supports the derived rate law. Some compounds have also been identified as the major degradation products by LC-MS which are less hazardous than azo dyes.

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