

# Kinetics and oxidation of thiocarbohydrazide by hexacyanoferrate(III) in aqueous perchloric acid medium

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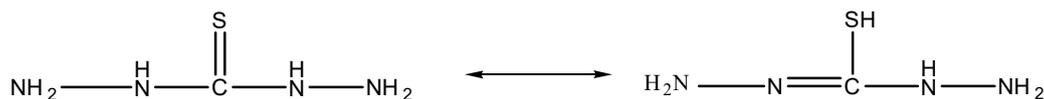
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**ABSTRACT:** Hexacyanoferrate(III) [HCF(III)] was used to oxidize thiocarbohydrazide (TCH) in an aqueous perchloric acid (HClO<sub>4</sub>) medium, and the reaction kinetics were studied spectrophotometrically at 420 nm while keeping a constant ionic strength of 1.0 mol dm<sup>-3</sup> and modulating the temperature between 298K and 318K. The stoichiometry of the reaction among TCH and HCF in the HClO<sub>4</sub> medium is 1:2. The reaction has a lower than unit order in both TCH and HClO<sub>4</sub> and is of the first order in HCF. The impact of varying the ionic strength and dielectric constant of the medium on the rate has been investigated. The effect of temperature on the reaction rate was studied, and different activation parameters of reaction E<sub>a</sub>, ΔH<sup>#</sup>, ΔS<sup>#</sup>, ΔG<sup>#</sup>, and log<sub>10</sub> A were calculated. The products of oxidation were analyzed by simple qualitative analysis. On the basis of the collected data, the rate law has been derived, and a probable mechanism has been proposed.

**KEYWORDS:** thiocarbohydrazide; hexacyanoferrate; oxidation; kinetics; mechanism

## 1. Introduction

TCH and their derivatives possess high biological activities and extensive synthetic as well as analytical applications. TCH is amphoteric and soluble in both diluted bases and acids. Both basic and acidic functionalities in its structure are as shown in **Scheme 1**. TCH acts as a peroxide decomposer, enzyme inhibitor, electron donor, radical scavenger, metal chelating agent, hydrogen donor, synergist, and singlet oxygen quencher. TCH is widely used in the determination of metal ions and structural determinations of tissues and cells<sup>[1]</sup>.



**Scheme 1.** Structure of the thione and thiol forms of thiocarbohydrazide.

TCH decomposes at its melting point<sup>[2]</sup>, with the loss of hydrogen sulfide and ammonia<sup>[3]</sup>, and they have a tendency to react with some ions, including Bi<sup>3+</sup>, Ni<sup>2+</sup>, Mo<sup>IV</sup>, U<sup>VI</sup>, and Cu<sup>2+</sup>, which results in typical precipitation for which thermogravimetric curves have been created<sup>[4,5]</sup>. TCH functions as an aldehyde-blocking agent, and it inhibits galactose oxidase-mediated transformation of human peripheral

lymphocytes<sup>[6,7]</sup>. In the presence of 2,2'-bipyridine (bpy), TCH undergoes Cu<sup>2+</sup>-mediated oxidation in DMF to create cis-[Cu(bpy)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>]<sup>[8]</sup>. The oxidation of TCH can be observed when it reacts with sodium hypochlorite in a neutral or alkaline environment. This reaction is characterized by its rapid nature, accompanied by the release of gas<sup>[9]</sup> and the generation of unpleasant odors. Additionally, TCH can also undergo oxidation when exposed to ammoniacal silver nitrate under cold conditions, as well as when reacting with ferric chloride or iodine, resulting in the liberation of nitrogen. The more significant iron(III) cyanide complex is the HCF(III) anion, [Fe(CN)<sub>6</sub>]<sup>3-</sup>, a mild oxidant with the Fe<sup>3+</sup> center bound to 6 (six) cyanide ligands in octahedral geometry. The small reduction potential of the couple ([Fe(CN)<sub>6</sub>]<sup>3-</sup>)/[Fe(CN)<sub>6</sub>]<sup>4-</sup>: 0.356V hinders<sup>[10]</sup> studies employing HCF(III) as an oxidant in acidic media. In acidic media, HCF(III) forms different species<sup>[11]</sup>. Iodometric techniques have been utilized to investigate the kinetics and mechanism of TCH oxidation in its free state and in its metal complex by Chloramin-T, Dichloramin-T, N-Bromo Succinimide, and N-Bromo acetamide<sup>[12]</sup>. Spectrophotometric analysis at 420 nm was used to investigate the oxidative pathway of TCH with HCF(III) in a perchloric acid medium. The main objective of the present work is to study the effect of oxidants, TCH, and acidic media on the rate of oxidation of TCH and reactive species of hexacyanoferrate in an acidic medium and to compute the various activation parameters affecting the rate of reaction. The study also focuses on predicting the mechanism, pathway of reaction, and rate law derivation based on experimental results.

## 2. Experimental section

### 2.1. Chemicals used

All chemicals, HCF, KNO<sub>3</sub>, HClO<sub>4</sub>, CH<sub>3</sub>OH, and acrylonitrile, that were utilized were of a grade suitable for analytical use, and their solutions were made with double-distilled (DD) water that was free of carbon dioxide and dissolved oxygen. The CH<sub>3</sub>OH and acrylonitrile that were utilized were of a grade suitable for analytical use.

### 2.2. Synthesis of TCH

In the synthesis of TCH, drop by drop, carbon disulfide was added to a vigorously stirred 95% hydrazine hydrate solution in water. The reaction's temperature was kept below 60 °C. Following a 30-min reflux, the obtained reaction mixture was ice-cooled, the precipitated TCH was filtered out, and then thoroughly washed with ethanol and ether and dried. Recrystallization was done with the minimum amount of water and acidification with a few drops of concentrated HCl, yielding colorless needle-shaped crystals of TCH, and the reaction is shown in **Scheme 2**. Its melting point and yield were found to be 169 °C–170 °C and 60%, respectively.



**Scheme 2.** Synthesis of thiocarbonylhydrazide.

The TCH solution was made by dissolving the necessary amount of sample in HClO<sub>4</sub> [0.1 M]. The TCH solution concentration was determined using the iodometric technique<sup>[13]</sup> under neutral pH conditions, which were maintained by a phosphate buffer<sup>[14]</sup>.

### 2.3. Kinetic measurements

The oxidation of TCH by HCF was studied in conditions of pseudo-first order, in which TCH was found at higher concentrations than HCF. The reaction was started by combining HCF and TCH with

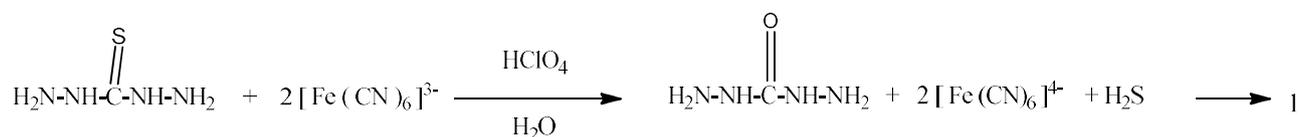
the necessary amounts of  $\text{KNO}_3$  and  $\text{HClO}_4$  to maintain the appropriate levels of acidity and ionic strength, respectively. The reaction was maintained spectrophotometrically at 420 nm by maintaining the lower absorbance owing to HCF with the molar absorptivity index, ' $\epsilon$ ' which was found to be  $\epsilon = 1060 \pm 1.5\% \text{ M}^{-1}\text{cm}^{-1}$ . The reaction was followed to over 90% completion, and  $\log(\text{absorbance})$  against time plots yielded a first-order rate constant ' $k$ ', and up to 80% of the reaction's completion, the plots were found to be linear, and rate constants were reproducible to within  $\pm 4\%$ . The slopes of  $\log k$  versus the corresponding species concentration were used to determine the orders for different species.

## 2.4. Instruments used

The dual-beam smart UV-vis spectrophotometer was performed on model 2203 (SYSTRONICS Instruments) and was used for absorption studies. The 1 cm quartz cell was placed in the thermostated cell compartment of the spectrophotometer (Systronics). The glassware utilized was Borosil. All investigations were conducted at room temperature (RT).

## 2.5. Stoichiometry and product analysis

The stoichiometry of the reaction was determined by achieving equilibrium in the reaction mixture, which consisted of an excess of HCF over TCH. The mixture also contained certain amounts of potassium nitrate and  $\text{HClO}_4$ . The equilibration process was carried out for a duration of 24 h at RT. The unreacted oxidant HCF was estimated by the iodometric method. Based on the calculated amount of unreacted HCF, Equation (1) reveals that two moles of HCF are used up for every mole of TCH. However, it was obtained that, when the reaction solution was finally examined soon afterward, the reaction ended, or directly after the reaction for experiments with higher initial HCF(III) and TCH concentrations, carbohydrazide ( $\text{H}_2\text{NNHCONHNH}_2$ ) was formed. Thus, the initial products formed by the reaction between TCH and HCF(III) ions appear to be carbohydrazide and  $\text{Fe}(\text{CN})_6^{4-}$  (Equation (1)).



## 3. Results and discussion

### 3.1. Reaction order

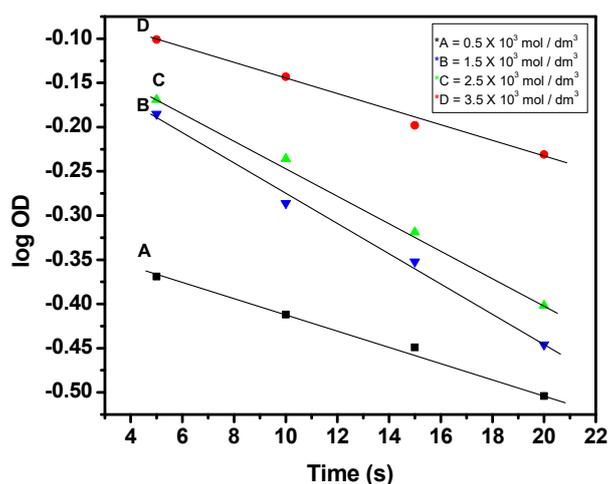
The log of the rate constant vs. the log of the concentration was plotted to identify the orders with regard to HCF, TCH, and  $\text{HClO}_4$ . These orders were found by changing the concentrations of HCF, TCH, and  $\text{HClO}_4$  while holding the other concentrations constant.

### 3.2 Effect of HCF(III) concentration

The HCF concentration was changed within a specific range of  $0.5 \times 10^3$  to  $4.5 \times 10^3 \text{ mol dm}^{-3}$  at room temperature by keeping the concentrations of TCH ( $1.5 \times 10^2 \text{ mol dm}^{-3}$ ),  $\text{HClO}_4$  ( $1.0 \times 10^2 \text{ mol dm}^{-3}$ ) and  $\text{KNO}_3$  ( $1 \times 10^2 \text{ mol dm}^{-3}$ ) constant (**Table 1**). The lack of change in the pseudo-first-order rate constants ( $k$ ) at different HCF concentrations implies that the order in HCF is unity<sup>[15]</sup>. The log OD (absorbance) against time plots was linear up to 80% of completion of the reaction, confirming unit-order behavior (**Figure 1**)<sup>[16,17]</sup>.

**Table 1.** Effect of variation of HCF, TCH, HClO<sub>4</sub>, and KNO<sub>3</sub> on oxidation of TCH by HCF(III) in aqueous HClO<sub>4</sub> medium at 25 °C and I = 1.0/mol dm<sup>-3</sup>.

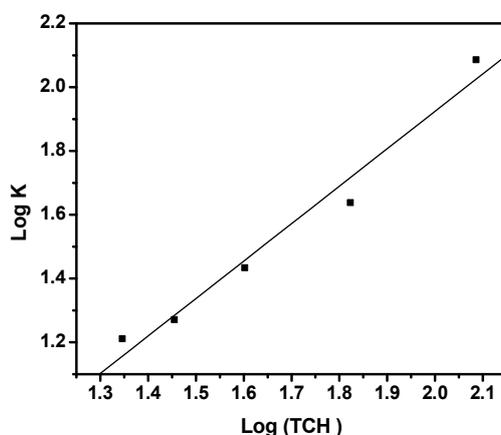
[HCF] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[TCH] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[HClO <sub>4</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[KNO <sub>3</sub> ] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	k <sub>obs</sub> × 10 <sup>2</sup> (s <sup>-1</sup> ) experimental	k <sub>obs</sub> × 10 <sup>2</sup> (s <sup>-1</sup> ) calculated
0.5	1.5	1.0	1.0	3.68	3.66
1.5	1.5	1.0	1.0	3.72	3.68
2.5	1.5	1.0	1.0	3.80	3.82
3.5	1.5	1.0	1.0	3.85	3.88
4.5	1.5	1.0	1.0	3.90	3.93
1.5	0.5	1.0	1.0	2.79	2.81
1.5	1.5	1.0	1.0	3.32	3.34
1.5	2.5	1.0	1.0	3.78	3.80
1.5	3.5	1.0	1.0	4.02	4.06
1.5	4.5	1.0	1.0	4.26	4.28
1.5	1.5	0.25	1.0	3.02	3.04
1.5	1.5	0.50	1.0	4.60	4.62
1.5	1.5	1.0	1.0	4.86	4.89
1.5	1.5	2.0	1.0	5.12	5.15
1.5	1.5	3.0	1.0	5.38	5.41
1.5	1.5	1.0	0.5	2.79	2.81
1.5	1.5	1.0	1.0	2.79	2.81
1.5	1.5	1.0	2.5	2.79	2.81
1.5	1.5	1.0	3.5	2.79	2.81
1.5	1.5	1.0	4.5	2.79	2.81

**Figure 1.** A graph of log OD against time in seconds shows first-order dependence at 25 °C with HCF(III).

### 3.3. Effect of TCH concentration

The TCH concentration was changed within the specific range of  $0.5 \times 10^2$  to  $4.5 \times 10^2$  mol dm<sup>-3</sup> by keeping HCF ( $1.5 \times 10^3$  mol dm<sup>-3</sup>), HClO<sub>4</sub> ( $1.0 \times 10^2$  mol dm<sup>-3</sup>) and KNO<sub>3</sub> ( $1 \times 10^2$  mol dm<sup>-3</sup>) reactant concentrations constant (**Table 1**). It has been noticed that the pseudo-first-order rate constant increases as substrate concentration increases. The plot of log K<sub>obs</sub> versus log [TCH] for various initial TCH

concentrations is linear, with a fractional slope of 0.93. **Figure 2** demonstrates a clear indication of the fractional order dependence on the reaction rate.



**Figure 2.** A graph of log [TCH] against log  $K_{\text{obs}}$  shows fractional order with respect to TCH.

### 3.4. Effect of $\text{HClO}_4$ concentration

At 298 K, the influence of  $\text{HClO}_4$  on the reaction rate was investigated by varying its concentration from  $0.25 \times 10^2$  to  $3 \times 10^2 \text{ mol dm}^{-3}$  at a constant concentration of TCH ( $1.5 \times 10^2 \text{ mol dm}^{-3}$ ), HCF ( $1.5 \times 10^3 \text{ mol dm}^{-3}$ ), and  $\text{KNO}_3$  ( $1 \times 10^2 \text{ mol dm}^{-3}$ ). The rate of the reaction rises as the concentration of perchloric acid increases. The slope of the  $\log_{10} k$  versus  $\log_{10}$  concentration (0.25) showed an obvious dependence, which is less than the unit order in the concentration of the  $\text{HClO}_4$ . The impact of acid on the rate of a reaction is to increase the rate of the reaction while maintaining a constant concentration of reactants and ionic strength.

### 3.5. Effect of ionic strength and dielectric constant of the medium

We examined the effect of ionic strength by changing the  $\text{KNO}_3$  concentration from  $0.5 \times 10^2$  to  $4.5 \times 10^2 \text{ mol dm}^{-3}$ , while keeping all other concentrations of the reactant constant. As per the observation, with an increase in the concentration of  $\text{KNO}_3$ , the rate constant also increases. This implies that the mechanistic step involves the participation of both an anion and a neutral molecule. The study investigated the impact of the dielectric constant (D) of the medium on the oxidation rate of TCH. This was achieved by introducing varying amounts of ethanol into the reaction mixture while maintaining the other reactants' concentrations constant. The obtained data clearly indicates that as reaction mixtures dielectric constant decreases, the rate of oxidation of TCH decreases.

### 3.6. Polymerization study

The oxidation reaction of TCH by HCF(III) was maintained by adding acrylonitrile (monomer) and allowing it to react for a duration of 2 h by storing it under inert conditions. After that, the reaction mixtures were subjected to dilution using methanol, and the formation of no precipitation in the reaction mixtures represents the nonexistence of free-radical species, hence leading to the conclusion that the reaction proceeds by an ionic mechanism.

### 3.7. Effect of temperature

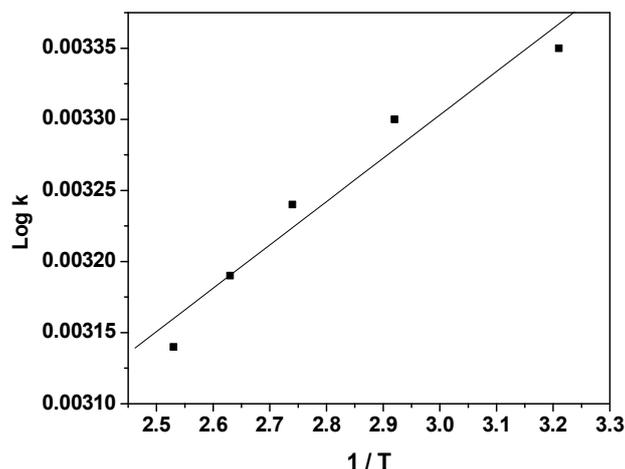
The rate of reaction was evaluated under varying temperature conditions and at constant reactant concentrations, while all other parameters remained unchanged (**Table 2**). As shown in **Figure 3**, as the

temperature increases, the rate of reaction increases. The Arrhenius plot, which depicts the logarithm of the rate constant ( $\log k$ ) as a function of the reciprocal of temperature ( $1/T$ ), exhibits a linear relationship (**Figure 3**). By analyzing the slope and intercept of this plot, the experimental values for the activation energy ( $E_a$ ) and the frequency factor  $\log_{10} A$  were determined. The Eyrings parameters  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta H^\ddagger$  were calculated, and their values are shown in **Table 3**.

**Table 2.** Effect of temperature on the rate of oxidation of TCH by HCF(III) in aqueous  $\text{HClO}_4$  medium.

Temp. (K)	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$
298	6.13
303	12.0
308	17.8
313	23.5
318	29.4

Note:  $[\text{HCF}] = 1.5 \times 10^3 \text{ mol dm}^{-3}$ ,  $[\text{TCH}] = 1.5 \times 10^3 \text{ mol dm}^{-2}$ ,  $[\text{HClO}_4] = 1.0 \times 10^2 \text{ mol dm}^{-3}$ , and  $[\text{KNO}_3] = 1.0 \times 10^2 \text{ mol dm}^{-3}$ .



**Figure 3.** A graph of the Arrhenius plot for temperature dependence.

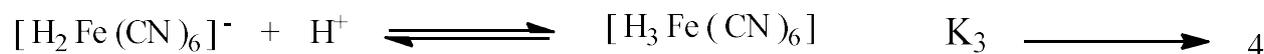
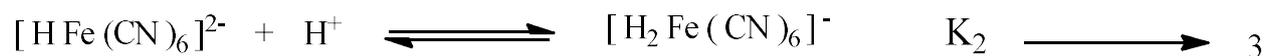
**Table 3.** Activation parameters of oxidation of TCH by HCF(III) in aqueous  $\text{HClO}_4$  medium.

Activation parameters	Values
$E_a$ ( $\text{kJ mol}^{-1}$ )	67.4
$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	50.8
$\Delta S^\ddagger$ ( $\text{kJ mol}^{-1}$ )	-260.78
$\Delta G^\ddagger$ ( $\text{kJ mol}^{-1}$ )	75.4
$\log_{10} A$	4.3

### 3.8. Mechanism

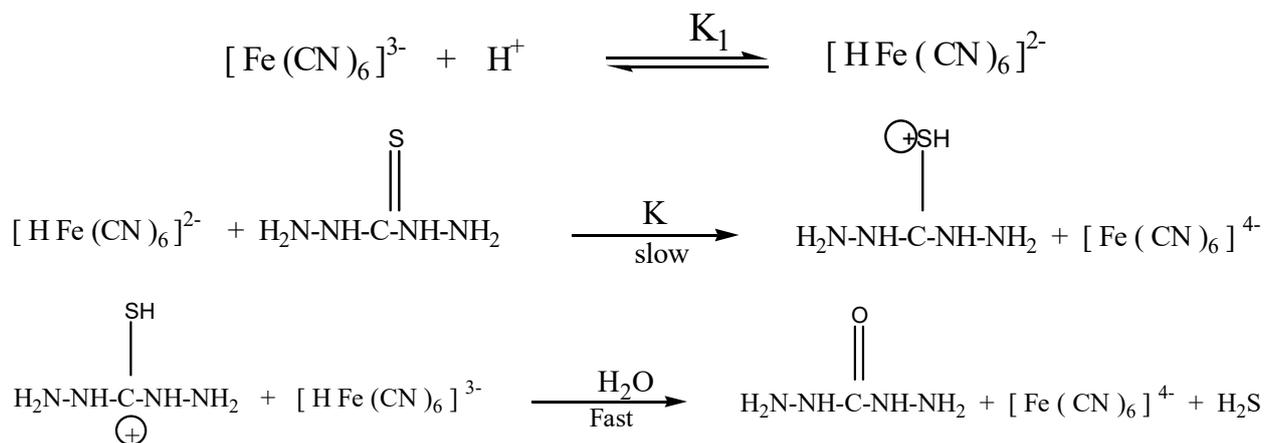
As demonstrated in Equations (2) to (4), HCF(III) generates various protonated species in acid media, with stability constants  $\beta_1 (=K_1)$ ,  $\beta_2 (=K_1K_2)$ , and  $\beta_3 (=K_1K_2K_3)$  corresponding to species with one, two, and three protons, respectively.





The values that have been reported for the equilibrium constants of the various species are as follows:  $K_3 < K_2 < K_1 < 10$ , with the value of  $K_1$  being close to ten in the media that was utilized for the present study. It is expected that the formation of singly protonated species is prevalent in the highly acidic environment employed in this study; the formation of doubly and triply protonated species occurs to a much smaller extent<sup>[18]</sup>.

The method encompasses the formation of the aforementioned species in a prior equilibrium. These species then react with the thiocarbonylhydrazide ion to produce the product, hexacyanoferrate (II), as well as  $\text{H}_2\text{N-NH-C(=S)-NH-NH}_2$ . In subsequent rapid steps, the compound decomposes to yield carbonylhydrazide as another product. Based on the information provided above, a possible mechanism is depicted (**Scheme 3**).



**Scheme 3.** Possible mechanisms of slow-step and fast-step reactions.

$$\text{Rate} = \frac{-dt \text{Fe}(\text{CN})_6^{3-}}{dt} = K [\text{Fe}(\text{CN})_6^{3-}] [\text{TCH}]$$

$$= k K [\text{Fe}(\text{CN})_6^{3-}] [\text{TCH}] [\text{H}^+] \longrightarrow 5$$

The total concentration of hexacyanoferrate (III) is given by

$$\begin{aligned}
 [\text{Fe}(\text{CN})_6]_t &= [\text{Fe}(\text{CN})_6^{3-}]_f + \text{H} [\text{Fe}(\text{CN})_6]^{2-} \\
 &= [\text{Fe}(\text{CN})_6^{3-}]_f \{ 1 + K [\text{H}^+] \}
 \end{aligned}$$

$$[\text{Fe}(\text{CN})_6^{3-}]_f = \frac{[\text{Fe}(\text{CN})_6^{3-}]_t}{1 + K_1 [\text{H}^+]} \longrightarrow 6$$

where “t” and “f” refer to total and free species, similarly.

$$\begin{aligned}
 [H^+]_t &= [H^+]_f + K_1 [HFe(CN)_6^{2-}] \\
 &= [H^+]_f \left\{ 1 + K_1 [Fe(CN)_6^{3-}] \right\}
 \end{aligned}$$

$$[H^+]_f = \frac{[H^+]}{1 + K_1 [Fe(CN)_6^{3-}]} \quad \longrightarrow \quad 7$$

In view of the low concentration of hexacyanoferrate (III) used in the experiment, the term  $K_1 [Fe(CN)_6^{3-}]$  is neglected in Equation (7) in comparison with unity.

Hence,  $[H^+]_f = [H^+]_t$ , substituting Equations (6) and (8) in Equation (5) and omitting subscripts we obtain Equation (9),

$$\text{Rate} = \frac{-d [Fe(CN)_6]}{dt} = \frac{k K_1 [Fe(CN)_6^{3-}] [TCH] [H^+]}{1 + K_1 [H^+]}$$

$$\frac{\text{Rate}}{[Fe(CN)_6]^{3-}} = K_{\text{obs}} = \frac{k K_1 [TCH] [H^+]}{1 + K_1 [H^+]} \quad \longrightarrow \quad 9$$

The rate law in Equation (9) can be rearranged to Equation (10), which is suitable for verification.

$$\frac{[TCH]}{K_{\text{obs}}} = \frac{1}{k K_1 [H^+]} + \frac{1}{k} \quad \longrightarrow \quad 10$$

The graphs of  $1/k_{\text{obs}}$  against  $1/[TCH]$  and  $1/k_{\text{obs}}$  versus  $1/[HClO_4]$  should be linear (Figures 4 and 5), according to Equation (10). From slopes and intercepts,  $k$  and  $K_1$  are  $0.05 \text{ s}^{-1}$  and  $5.5 \times 10^{-5} \text{ M}^{-1}$  were determined at 298 K, respectively. The aforementioned values are utilized in the rate equation, and the calculated experimental values are as shown in Table 1.

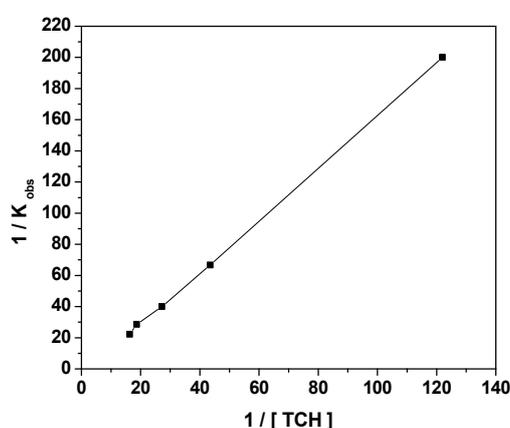


Figure 4. A graph of  $1/k_{\text{obs}}$  against  $1/[TCH]$  for verification of rate law.

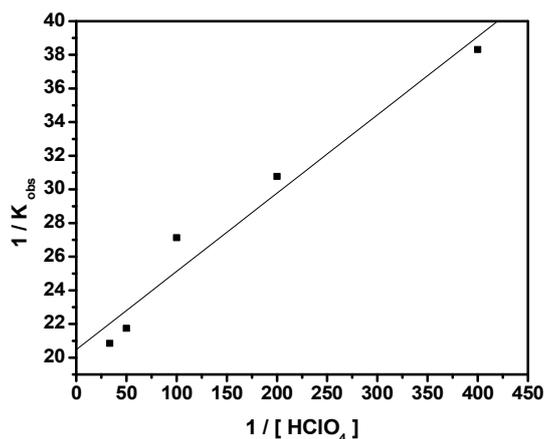


Figure 5. A graph of  $1/k_{\text{obs}}$  against  $1/[\text{HClO}_4]$  for verification of the rate law.

## 4. Conclusion

In the present work, the oxidation of TCH by HCF in an aqueous  $\text{HClO}_4$  medium was investigated spectrophotometrically at 420 nm at a temperature of 298 K. 1:2 in stoichiometry, it was discovered that the reaction was first-order with the oxidant HCF and less than unit-order with the reductants TCH and  $\text{HClO}_4$ . The activation parameters are calculated and tabulated. The overall mechanistic sequence that has been outlined here agrees with product studies, mechanistic investigations, and kinetic studies.

## Author contributions

Conceptualization, RKS and VAS; methodology, RKS and SS; software, SS; validation, RKS, SS and MK; formal analysis, RKS, VAS, SS and MK; investigation, RKS and SS; resources, RKS and SS; data curation, RKS; writing—original draft preparation, RKS and MK; writing—review and editing, RKS and MK; visualization, MK; supervision, VAS. All authors have read and agreed to the published version of the manuscript.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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