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Oxidation of Thiols(II). Kinetics and Mechanism of Oxidation of Diphenylthiocarbazono (dithizone) with Hexacyanoferrate(III) in Acid Medium

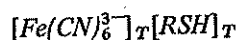
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The oxidation of diphenylthiocarbazono by hexacyanoferrate(III) in acid medium follows the overall rate law(i)

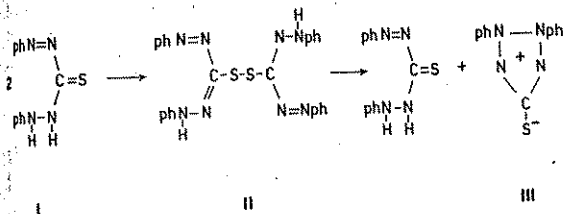
$$\text{Rate} = (k_1 + k_2/[H^+] + k_3[H^+] + k_4[H^+]^2)$$



At pH > 2.5, the reaction appears to proceed by an outer-sphere mechanism and involves the reaction of the two forms RSH and RS⁻ of diphenylthiocarbazono with the Fe(CN)₆³⁻ form of hexacyanoferrate(III). At pH < 2.5, the RSH form is the only active species and is oxidized by the three forms Fe(CN)₆³⁻, HFe(CN)₆²⁻ and H₂Fe(CN)₆ of hexacyanoferrate(III). It is assumed that hydrogen bonding of HFe(CN)₆²⁻ and H₂Fe(CN)₆ to the keto-form of diphenylthiocarbazono activates the reaction. The rate of the reaction is inhibited by the addition of copper(II) ions over the range 5 × 10⁻⁸–6 × 10⁻⁶ M.

Introduction

It is well known that diphenylthiocarbazono (dithizone)(I) is susceptible to oxidation. The mild oxidants, e.g. iodine and hexacyanoferrate(III) produce the disulphide (II) which decomposes to give equimolecular amounts of (I) and (III) [1]



The rate of the spontaneous fission of (II) into (I) and (III) in different solvents was reported and a mechanism was suggested [2]. However, the kinetics and mechanism of oxidation of diphenylthiocarbazono with different oxidizing agents is not yet investigated.

In the present work, the kinetics of oxidation of diphenylthiocarbazono with hexacyanoferrate(III) is studied. It is hoped that this study may give further insight into the mechanism of oxidation of thiols with hexacyanoferrate(III). The copper(II) ion catalytic effect which was assumed [3] in oxidations of thiols with hexacyanoferrate(III) is investigated. Further, the reported [4] formation of complex intermediates by the attack of a thiolate anion on cyano ligands of hexacyanoferrate(III) is also noted.

Experimental

Materials and Reagents

Diphenylthiocarbazono of BDH ANALAR grade was further purified by dissolving it in freshly distilled chloroform and then precipitating with cyclohexane. The product was found to be of high purity as indicated by its absorption spectrum in carbon tetrachloride. The two characteristic peaks of diphenylthiocarbazono at λ = 620 (ε = 34500) and λ = 450 (ε = 20000) are comparable to those reported [5]. Spectroscopically pure ethanol which was freshly distilled prior to use was always used. Hydrochloric acid-sodium acetate buffers were made up from ANALAR grade chemicals and were further freed of metals ions by shaking with a concentrated solution of diphenylthiocarbazono in chloroform. This step was followed by washing the buffer with pure aliquots of chloroform to remove traces of diphenylthiocarbazono. NaOH was prepared from concentrated carbonate-free solution. Copper nitrate stock solution from which all dilute solutions were made up, was standardized iodometrically [6]. Potassium hexacyanoferrate(III) was recrystallized and dried. A stock solution was prepared by weight and standardized spectrophotometrically (ε = 1030 M⁻¹ cm⁻¹ at 420 nm).

Doubly distilled deionized water was always used.

Instruments

The acid dissociation constant of diphenylthiocarbazono as well as the identification of the products

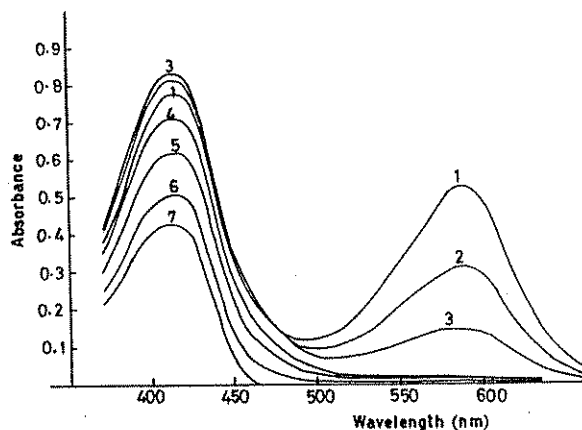


Figure 1. Effect of time on the absorption spectrum of a solution containing $[RSH] = 2.5 \times 10^{-5} M$, $[Fe(CN)_6^{3-}] = 4 \times 10^{-4} M$ at $pH = 1.48$ and $temp. = 25^\circ C$. Curves 1 and 7 represent the first one recorded after mixing and at infinity respectively.

of its reaction with $Fe(CN)_6^{3-}$ were determined using a Unicam Sp 8000 spectrophotometer. A Radiometer pH meter (type 63) equipped with a combined glass electrode type GK 2311c was used in measuring the pH of solutions. Kinetic runs were performed with a Unicam SP 700 spectrophotometer equipped with thermostated cell holders.

Determination of the Acid Dissociation Constant of Diphenylthiocarbazonone in 50% Ethanol-Water Mixture

The change in the spectrum of diphenylthiocarbazonone in 50% ethanol-water mixture was recorded with change in the pH of the solution. In a typical experiment, several solutions were prepared by mixing 12.5 ml of diphenylthiocarbazonone in ethanol and 12.5 ml of an aqueous solution prepared by mixing different ratios of equimolar (0.2 M) solutions of HCl and sodium acetate. The pH of each solution was read and its spectrum recorded. The titration was repeated twice. The pH meter readings were calibrated prior to titration against a standard Radiometer buffers of pH 4.01 ± 0.01 and 7.01 ± 0.01 . The pH values in 50% ethanol-water mixture were converted into $[H^+]$ without being corrected.

Kinetic Measurements

All kinetic runs were performed under pseudo-first order condition with hexacyanoferrate(III) in large excess (more than tenfold). The ethanolic solution of diphenylthiocarbazonone was added to one side of an indented flask and in the other hexacyanoferrate(III), buffer and potassium chloride (to adjust ionic strength) solutions were added. The flask, after being kept for at least 20 minutes in a thermostat controlled at $25^\circ C$, was shaken well to mix the two solutions and an aliquot was placed in a 1 cm

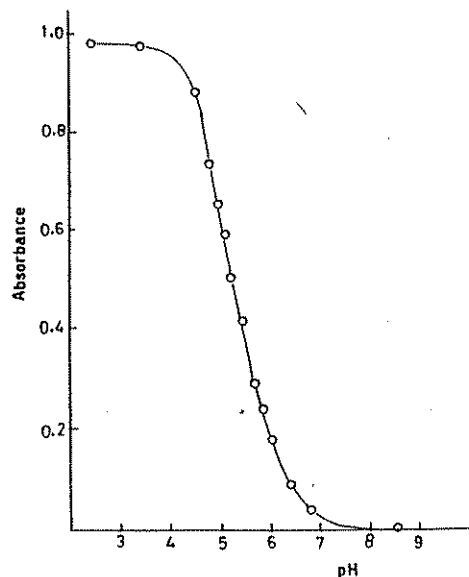


Figure 2. Dependence of absorbance of diphenylthiocarbazonone on pH.

quartz cell which was kept in the thermostated cell holder of the spectrophotometer. The change in absorbance as a function of time was monitored at 595 nm (wavelength of maximum absorption of diphenylthiocarbazonone in 50% ethanol-water mixture). The pH of each reaction solution was then measured.

Results

Identification of the Products

The reaction products were identified by observing the change of the spectrum of a solution prepared under the pseudo-first order conditions described. Fig. 1 shows that the absorbance at 595 nm (where diphenylthiocarbazonone is the only absorbing species) decreases in intensity until it completely disappears. However, at $\lambda = 420$ nm the absorbance increases with time until it reaches a maximum value (A_m) at almost the same time when the absorbance at 595 nm is zero and then start to decrease. From the difference between A_m and that due to hexacyanoferrate(III), the molar absorptivity of the product was calculated to be around 50,000 which is comparable to that obtained by dissolving an authentic sample of the disulphide(II), which has been previously prepared [2], in the same solvent. Thus, the disulphide(II) is the oxidation product of the first step of the oxidation-reduction reaction of diphenylthiocarbazonone with hexacyanoferrate(III). The nature of the oxidation product of the disulphide(II) (the kinetics and mechanism of which will be reported later on) with $Fe(CN)_6^{3-}$ is investigated by observing the decrease in

TABLE I. Dependence of k_{obs} on $[RSH]_T$.

$[RSH]_T \times 10^5$	pH	$k_{obs} \times 10^3$
0.5	3.88	5.6
0.75	3.88	5.65
1.00	3.88	5.55
1.5	3.88	5.62
0.5	1.56	9.2
0.75	1.56	9.15
1.00	1.56	9.22
1.5	1.56	9.17

$[Fe(CN)_6^{3-}] = 1 \times 10^{-3} M$; $I = 0.2 M$; $T \text{ } ^\circ C = 25$

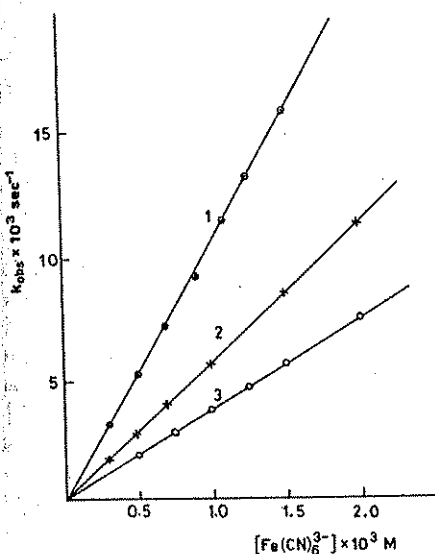


Figure 3. Variation of k_{obs} with $[Fe(CN)_6^{3-}]$ at pH: 4.25, 3.88 and 3.5 for curves 1, 2, and 3 respectively.

A_m with time. At the completion of the reaction, the molar absorptivity of the product ($\lambda_{396} = 1150$) was calculated from A_∞ and that due to hexacyanoferrate(III). Further, the product was isolated from a solution obtained by reacting appreciably concentrated solutions of $Fe(CN)_6^{3-}$ and diphenylthiocarbazone. The physical and chemical properties were identical with those reported for 2,3-diphenyl-2H-tetrazolium-5-thiolate(I).

Acid Dissociation Constant

The absorbance at $\lambda = 595 \text{ nm}$ is plotted vs. pH as shown in Fig. 2. The pK_a value (5.33 ± 0.01) was calculated by applying the equation [7]: $pK_a = pH + \log(A_x - A_a)/(A_\mu - A_x)$ where A_x is the absorbance at pH_x , A_a is the absorbance of the anion and A_μ is that of the unionized form of diphenylthiocarbazone.

Kinetics

Plots of $\log(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances at time t and infinity, respectively,

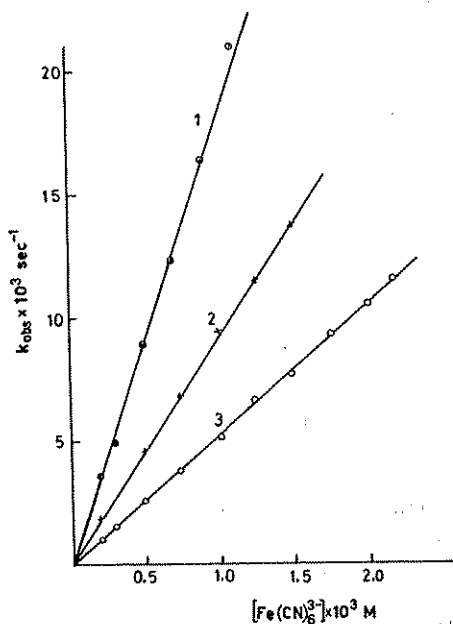


Figure 4. Variation of k_{obs} with $[Fe(CN)_6^{3-}]$ at pH: 1.37, 1.57 and 1.77 for curves 1, 2 and 3 respectively.

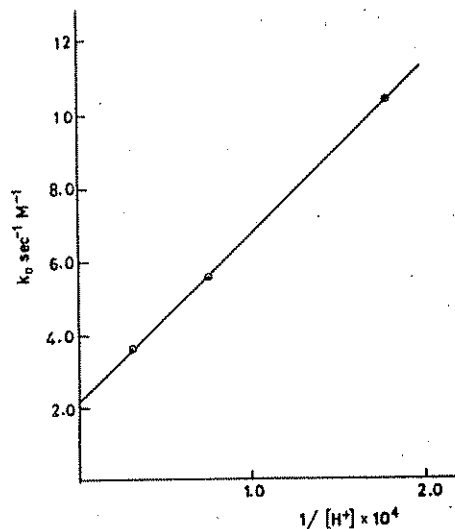


Figure 5. Dependence of k_o on $[H^+]$ over the pH range 4.25-3.5.

ly, showed typical first order kinetics to beyond 80% of the reaction. The magnitude of the pseudo-first order rate constant is independent of the concentration of diphenylthiocarbazone as shown in Table I.

Figs. 3 and 4 show that k_{obs} varies linearly with $Fe(CN)_6^{3-}$ at all pH values and the dependence is described in eqn. 1:

$$k_{obs} = k_o [Fe(CN)_6^{3-}] \tag{1}$$

where k_o corresponds to the slope. From Figs. 5 and 6 k_o is acid dependent.

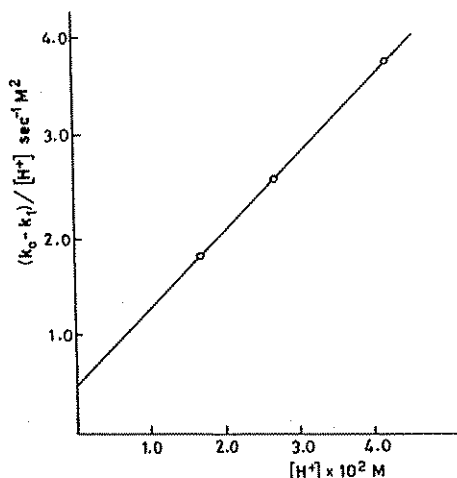


Figure 6. Plot of $(k_o - k_1)/[H^+]$ vs. $[H^+]$ over the pH range 1.37-1.77.

In the pH range above 2.5, the plot of k_o vs. $1/[H^+]$ (Fig. 5) is represented by eqn. 2

$$k_o = k_1 + k_2/[H^+] \quad (2)$$

where k_1 and k_2 correspond to the intercept and the slope respectively and have the values $2.2 \text{ sec}^{-1} M^{-1}$ and $4.6 \times 10^{-4} \text{ sec}^{-1}$ respectively. Hence, the rate equation at $\text{pH} > 2.5$ is written as in eqn. 3.

$$\text{Rate} = (k_1 + k_2/[H^+])[\text{Fe}(\text{CN})_6]_T [\text{RSH}]_T \quad (3)$$

where $[\text{Fe}(\text{CN})_6]_T$ and $[\text{RSH}]_T$ are the total hexacyanoferrate(III) and diphenylthiocarbazono respectively.

In the pH range below 2.5, the plot of $(k_o - k_1)/[H^+]$ vs. $[H^+]$ (Fig. 6) gives the best fit of the kinetic data and is represented by eqn. 4.

$$k_o = k_1 + k_3[H^+] + k_4[H^+]^2 \quad (4)$$

where k_3 and k_4 are the intercept and the slope respectively and have the values $47.5 \text{ sec}^{-1} M^{-2}$ and $7.8 \times 10^3 \text{ sec}^{-1} M^{-3}$ respectively. Hence, the rate equation at $\text{pH} < 2.5$ is written as in eqn. 5

$$\text{Rate} = (k_1 + k_3[H^+] + k_4[H^+]^2) [\text{Fe}(\text{CN})_6]_T [\text{RSH}]_T \quad (5)$$

By combining eqns. 3 and 5 the overall rate equation is then written as in eqn. 6

$$\text{Rate} = (k_1 + k_2/[H^+] + k_3[H^+] + k_4[H^+]^2) [\text{Fe}(\text{CN})_6]_T [\text{RSH}]_T \quad (6)$$

Kinetics in the presence of Copper(II) Ions

The effect of copper impurities which may catalyse the reaction is not tested by the addition of EDTA as a masking agent to the reaction medium because

TABLE II. Dependence of k_{obs} on Copper(II) Ion Concentration.

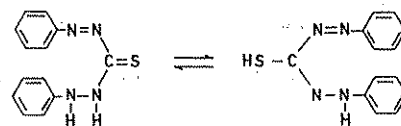
$[\text{Cu}^{2+}]_{\text{added}}$	$k_{\text{obs}} \times 10^3$
0	3.20
5.78×10^{-8}	2.95
2.1×10^{-7}	2.84
4.2×10^{-7}	2.42
8.4×10^{-7}	2.26
1.68×10^{-6}	2.4
3.36×10^{-6}	2.45
5.25×10^{-6}	2.58
7.75×10^{-6}	3.2
9.45×10^{-6}	3.9
1.15×10^{-5}	5.86
1.28×10^{-5}	8.63

$[\text{Fe}(\text{CN})_6]^{3-} = 6.5 \times 10^{-4} M$; $[\text{RSH}] = 2.2 \times 10^{-5} M$; $\text{pH} = 1.85$; $I = 0.2 M$; $T^\circ\text{C} = 25$.

diphenylthiocarbazono is known [8, 9] to form more stable complexes than EDTA in the reaction conditions. However, the deliberate addition of varying concentrations of Cu^{2+} ions, where other conditions were maintained, showed a gradual decrease in the value of k_{obs} over the $[\text{Cu}^{2+}]$ range 5×10^{-8} - $1.5 \times 10^{-6} M$ (Cu^{2+} was always added to one compartment of the reaction vessel and diphenylthiocarbazono in the other). Further, the value of k_{obs} over the $[\text{Cu}^{2+}]$ range 5×10^{-8} - $6 \times 10^{-6} M$ which is far in excess than the value determined [3] for copper impurities is smaller than that determined in absence of Cu^{2+} ions (Table II). The inhibition of the rate of the reaction over the range of $[\text{Cu}^{2+}]$ 5×10^{-8} - $6 \times 10^{-6} M$ may be due to the formation of $\text{CuFe}(\text{CN})_6$ which may be less reactive than $\text{Fe}(\text{CN})_6^{3-}$ or any of its protonated forms. However, it is worth mentioning that the rate of the reaction was catalysed at $[\text{Cu}^{2+}] > 6 \times 10^{-6} M$ and this may be due to the formation of $\text{Cu}(\text{RS})_2$ which is known [10] to be formed under the reaction conditions. Hence, the increase in the value of k_{obs} may be due to the higher reactivity of the coordinated diphenylthiocarbazono anion.

Discussion

Diphenylthiocarbazono is known to exist in organic and neutral aqueous solution as a mixture of keto-enol tautomers [10]



However, in alkaline medium, the thiolate anion(IV) exists. Fig. 2 shows



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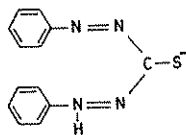
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(I) Ion Concentrations

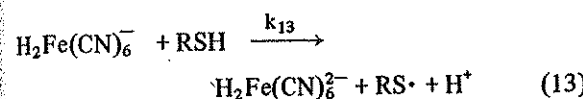
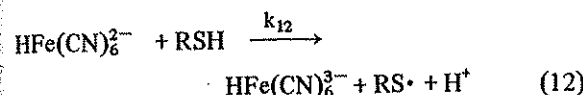
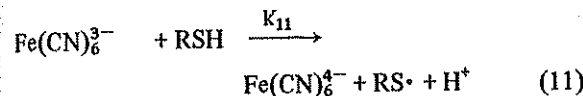
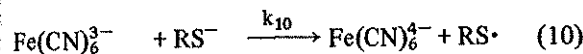
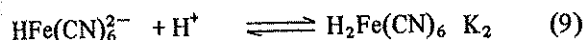
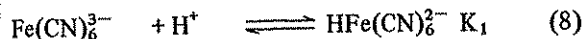
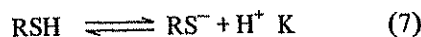


IV

that the ionization is negligibly small below pH = 2.5 and increases with the increase of the pH of the solution. At pH > 2.5, both RSH and RS⁻ are available and may react with hexacyanoferrate(III). However, in the pH range 0.6–2.5 the only species available is RSH. Diphenylthiocarbazonate is not protonated in this pH range as indicated by the constancy of the values of λ_{595} , λ_{450} , ϵ_{595} , ϵ_{450} and $\epsilon_{595}/\epsilon_{450}$.

The oxidizing agent, hexacyanoferrate(III), is known [11] to be only slightly protonated above pH 1.3 and it is expected that the only active species at pH > 2.5 is $\text{Fe}(\text{CN})_6^{3-}$. Hence, the increase of the rate of the reaction with pH over the range of pH > 2.5 is an indication that the thiolate anion, RS⁻, is the more reactive species. At pH < 2.5, hexacyanoferrate(III) may be present in the forms $\text{Fe}(\text{CN})_6^{3-}$, $\text{HFe}(\text{CN})_6^{2-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^-$. This is also inferred from the increase in the rate of the reaction with [H⁺]. $\text{HFe}(\text{CN})_6^{2-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^-$ are expected to be more reactive than $\text{Fe}(\text{CN})_6^{3-}$ because they can form hydrogen bonding with the keto-form of diphenylthiocarbazonate.

The reaction sequence for the oxidation of diphenylthiocarbazonate with hexacyanoferrate(III) may be generally represented by the following eqns:



and the rate law is given by eqn. 15.

$$\frac{-d[\text{RSH}]}{dt} = \frac{(k_{10}K + k_{11}[\text{H}^+] + k_{12}K_1[\text{H}^+]^2 + k_{13}K_1K_2[\text{H}^+]^3)}{K + K_1K[\text{H}^+] + [\text{H}^+] + K_1[\text{H}^+]^2 + K_1K_2K[\text{H}^+]^2 + K_1K_2[\text{H}^+]^3} \times [\text{Fe}(\text{CN})_6]_T [\text{RSH}]_T \quad (15)$$

Thus from eqn. 15 the reaction shows first order dependence on both hexacyanoferrate(III) and diphenylthiocarbazonate. The dependence of the second order rate constant k_2 on [H⁺] can be written as in eqn. 16.

$$k_2 = \frac{k_{10}K + k_{11}[\text{H}^+] + k_{12}K_1[\text{H}^+]^2 + k_{13}K_1K_2[\text{H}^+]^3}{K + K_1K[\text{H}^+] + [\text{H}^+] + K_1[\text{H}^+]^2 + K_1K_2K[\text{H}^+]^2 + K_1K_2[\text{H}^+]^3} \quad (16)$$

At pH > 2.5 eqn. 16 reduces to eqn. 17 (assuming only reactions 10 and 11 are rate determining)

$$k_2 = \frac{1}{[\text{H}^+] + K} (k_{10}K + k_{11}[\text{H}^+]) \quad (17)$$

Eqn. 17 would take the form of eqn. 2 if [H⁺] >> K in the range of [H⁺] covered, whereby eqn. 18 is obtained:

$$k_2 = k_{11} + \frac{k_{10}K}{[\text{H}^+]} \quad (18)$$

By comparing eqns. 2 and 18, we can see that $k_{11} = k_1 = 2.2 \text{ sec}^{-1} M^{-1}$, $k_{10}K = k_2 = 4.6 \times 10^{-4} \text{ sec}^{-1}$ and $k_{10} = 4.6 \times 10^{-4}/K = 98.3 \text{ sec}^{-1}$. At pH < 2.5 eqn. 16 reduces to eqn. 19 (neglecting reaction 10):

$$k_2 = \frac{k_{11}[\text{H}^+] + k_{12}K_1[\text{H}^+]^2 + k_{13}K_1K_2[\text{H}^+]^3}{K + K_1K[\text{H}^+] + [\text{H}^+] + K_1[\text{H}^+]^2 + K_1K_2K[\text{H}^+]^2 + K_1K_2[\text{H}^+]^3} \quad (19)$$

If the factors K , $K_1K[\text{H}^+]$, $K_1[\text{H}^+]^2$, $K_1K_2K[\text{H}^+]^2$ and $K_1K_2[\text{H}^+]^3$ are small compared to [H⁺] eqn. 19 would take the form of eqn. 4 and eqn. 20 is obtained:

$$k_2 = k_{11} + k_{12}K_1[\text{H}^+] + k_{13}K_1K_2[\text{H}^+]^2 \quad (20)$$

By comparing eqns. 4 and 20, we can see that $k_{12}K_1 = k_3 = 47.5 \text{ sec}^{-1} M^{-2}$ and $k_{13}K_1K_2 = k_4 = 7.8 \times 10^3 \text{ sec}^{-1} M^{-3}$.

The copper(II) ions catalytic effect which results from impurities available in reagents is not operative in the oxidation of diphenylthiocarbazon with hexacyanoferrate(III). This is concluded from the inhibition of the rate of the reaction by the deliberate addition of copper(II) ions. Further, the kinetic data plotted in Figs. 3 and 4 show that the formation of intermediates by the attack of diphenylthiocarbazon anion on a cyano-ligand of hexacyanoferrate(III) may be excluded.

Acknowledgement

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