RESEARCH ARTICLE

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Investigation of The Chemical Reactions of 2, 4, 6-Trinitrophenol with Thiocyanate Ion in Acidic Condition: Kinetic Approach

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ABSTRACT

The rate and overall observed chemical change of the redox reaction between 2, 4, 6-trinitrophenol (TNP) and thiocyanate ion (SCN^{-}) was investigated under a constant concentration of ionic strength, $[H^{+}]$ and λ_{max} = 360 nm using a spectrophotometric titration method. The research aim is to study stoichiometry, order of reaction, the influence of acid, and the effect of change in ionic concentration on the reaction speed. The stoichiometry discovered gave a 1:2 molar proportion of TNP against SCN^{-}. The reaction is 1st - order in relation to TNP and 1st – order in relation to SCN^{-} hence, a 2nd -order overall for the system. An acid-dependence rate constant on TNP was positive for the TNP and SCN^{-} system. A positive salt effect was observed for the system. An increase in the concentration of added cations and anions (Mn^{2+}, NO_3^{-} and PO_4^{3-}) had no influence on the speed of the reaction. The spectroscopic and kinetic results did not show any intermediate complex emergence all through the reaction. On grounds of the experimental results attained, a presumptive mechanism in favor of an outer-sphere mechanism has been recommended.

Keywords: Acidic Condition, Chemical, Reactions, Thiocyanate, 2, 4, 6-Trinitrophenol.

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I. INTRODUCTION

The main aim of chemical reactions is to enable us foretell the extent at which certain chemicals react, and to alter it to our advantage; on the other hand, it makes it possible for us to adjust chemical reactions to produce products with distinctive chemical properties in a tractable procedure, including choice of a suitable catalyst [1]. In spite of the days great computers, however, we have not been able to do this generally, and we must investigate experimentally each individual reacting system of concern to garner a quantitative kinetic representation of it. Chemical method of reactions is preferred for their high susceptibility, superlatively low detection limit, swift analysis rate, low-priced instruments, adequate selectivity, and equally permits for the concurrent analysis of species devoid of any separation [2].

TNP is associated to a group of very acidic phenols. It is oftentimes talked about as a pollutant that is distinctly dangerous to the human body like trinitrotoluene [3]. Trinitrophenol is to a great extent used in many industries such as fuel cells, leathers, pharmaceuticals, explosives, agriculture, and polymer. It is immensely dangerous to the liver, eyes, kidney, and respiratory system [4]. It is a highly sensitive and unstable material that could be triggered by sparks, heat, and flames. Dried-out TNP may shatter if prone to friction, heat, shock or flame, hence an explosive [5].

Thiocyanate plays a vital role in the oxidative host defense system of the body; therefore, its absence could pose harm to the human defense system [6]. Thiocyanate is often used for the discovery of Re, Mo, Fe (III), W, Nb, Ti, Co, and U [7]. TNP has wide usage by the military and terrorist groups and it has been observed over time that this explosive is mostly detonated on the earth's surface.

The use of TNP for medicinal purposes and its application on the soil has prompted the study of the reaction between TNP and thiocyanate found in the human body and the soil to get relevant data that will provide deep knowledge of the reaction path.

II. Materials And Methods

A. Materials

High-purity reagents were used without additional purification all throughout this work. Distilled water was used to prepare each of the solutions.

B. Determination of Maximum Absorbance (λ_{max})

The absorption spectrum of 2, 4, 6-trinitrophenol (TNP) solution was obtained by scanning its absorbance using a UV-visible spectrophotometer, within a UV range of 200-800 nm. The maximum absorption of 360 nm was obtained from the spectrum.

C. Stoichiometric Exploration

The stoichiometry of the reaction was established by spectrophotometric titration employing the mole ratio method by keeping the concentration of TNP steady at 1.0×10^{-5} mol dm^{-3}, $[H^+] = 1 \times 10^{-3}$, I = 1.0 mol dm^{-3}, λ_{max} = 360 nm, and T = 28 ± 1 ºC while $[SCN^-]$ was varied from $3.0–6.0 \times 10^{-5}$ mol dm^{-3}. The absorbance of the reacting mixture was evaluated after the reaction had reached completion over 48 hours. The mole ratio of the reactants was gotten from the point of inflection on the curve of absorbance versus $[SCN^-]$ [8]

D. Kinetic Consideration

The reaction kinetics was observed using a UV-Vis spectrophotometer (UV 752s) at T = 28 ± 1 ºC, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, and I = 1.0 mol dm^{-3}. All of the kinetic measurements were performed under pseudo-first-order conditions with the concentration of SCN^-at least 42 times greater than that of TNP. The progress of the reaction was observed by following the decline in absorbance of TNP at 360 nm. The pseudo-first-order plots of the log ($A_t - A_\infty$) versus time (t) in seconds were made (where A_t and A_∞ are the absorbance at time t and infinity respectively). The pseudo-first-order rate constant (k_1) was established from the slope of the plots [9]. The second-order rate constant was then determined from the relation in (1).

$$k_2 = \frac{k_1}{[SCN^-]} \tag{1}$$

1) Effect of hydrogen Ion concentration

The effect of change in $[H^+]$ on the rate of the reaction was studied at 28 ± 1 ºC by varying $[H^+]$ between $(0.4–1.0) \times 10^{-3}$ mol dm^{-3} while the concentration of the TNP, SCN^- and ionic strength were kept steady at 1.0×10^{-5} mol dm^{-3}, 4.4×10^{-3} mol dm^{-3}, and 1.0 mol dm^{-3} respectively. A plot of k_2 vs $[H^+]$ was made [10].

E. Effect of Change in Ionic Strength

The effect of NaCl on the rate reaction was studied between the range of 0.4 – 1.0 mol dm^{-3} keeping the concentration of all other reactants stable at 28 ± 1 ºC, TNP, SCN^- and $[H^+]$ at 1.0×10^{-5} mol dm^{-3}, 4.4×10^{-3} mol dm^{-3}, and 1.0×10^{-3} mol dm^{-3} respectively. Plots of log k_2 versus $\sqrt{I}$ was made [11].

F. Effect of Added Ions on Rate of Reaction

The influence of added ions on the rate of reaction was studied by adding $(1.5 – 3.0) \times 10^{-3}$ mol dm^{-3} of Mn^{2+}, PO_4^{3-} and NO_3^- while keeping the concentration of other reactants steady at 28 ± 1 ºC, [TNP] = 1.0×10^{-5} mol dm^{-3}, $[SCN^-] = 4.4 \times 10^{-3}$ mol dm^{-3} and I = 1.0 mol dm^{-3}.

G. Test for Intermediate Complex

The electronic spectra of the incompletely reacted mixture were obtained at 3 mins interval after the initiation of the reaction, in the wavelength range of 200–800 nm. This was matched with the spectra of the explosive alone within the same range. Michaelis - Menten plot of $1/k_2$ verses $1/[SCN^-]$ was made [12].

H. Test for Free Radicals

Acrylamide solution (4 ml) was added to the relatively reduced reaction mixture and soon after by an excess of methanol to trigger off free radical polymerization. Acrylamide was also added to all of the reactants singly to serve as a control [13].

I. Examination of Product

The reaction product at the end of the reaction as indicated with zero absorbance value was determined using a modified qualitative method of analysis by [14] which involved the addition of 2 cm^3 of dilute lead (II) nitrate solution followed by the addition of 1 cm^3 of bromine in 5 cm^3 glacial acetic acid.

III. RESULTS AND DISCUSSION

A. Determination of UV Wavelength

Maximum absorbance of TNP at 360 nm was observed after scanning the solution within a wavelength span of 200-800 nm (Fig. 1). The value obtained was close to that reported by [15] and [16] at 350 nm and 395 nm respectively.

B. Stoichiometry Exploration

The stoichiometry of the reaction was deduced from the spectrophotometry graph (Fig. 2). The result revealed that 1 mole of TNP was depleted by 2 moles of SCN^-. Based on the stoichiometry observed, the overall equation for the redox reaction is put forward in (2).

$$TNP + 2SCN^- + 2H^+ \rightarrow TNPW + (SCN)_2 + H_2 \tag{2}$$

where $TNPW$ = colorless TNP

In 2019, Umoru reported a mole ratio of 1:3 for the reaction between $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ and SCN^- [11]. Babatunde and Nwaji also investigated the reduction of (7–amino–8–methyl–phenothiazine–3–ylidene) – dimethyl–ammonium chloride by thiocyanate ion and reported a mole ratio of 1:1 [17].

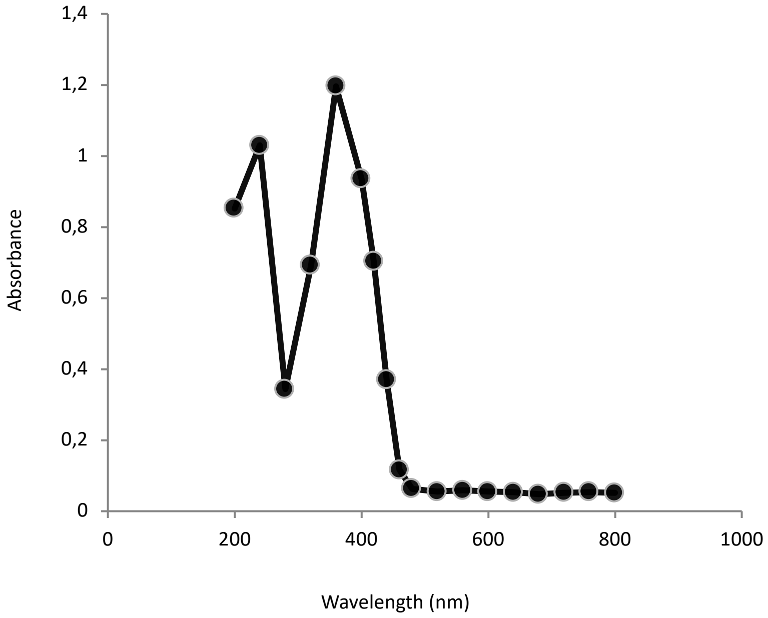

Fig. 1. Spectrum for TNP showing Absorption Maxima.

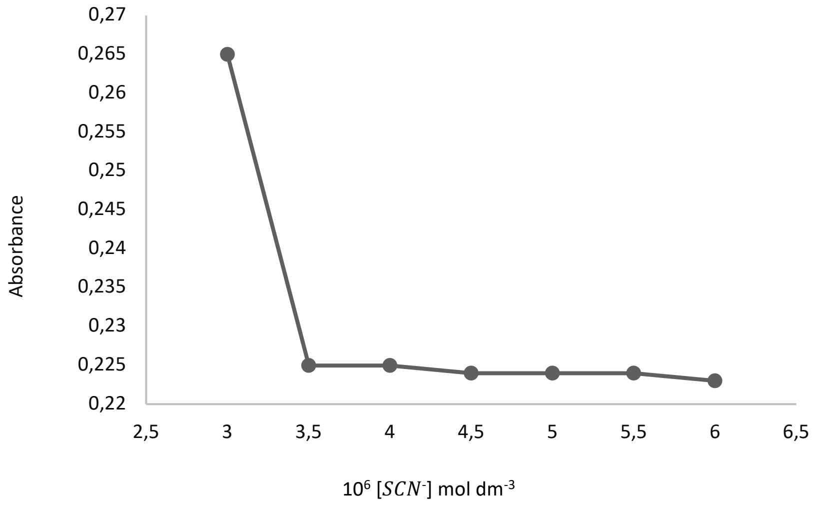

Fig. 2. Plot of Absorbance versus [SCN^-] for the Determination of Stoichiometry of TNP and SCN^-

C. Kinetics Consideration

The pseudo-1st-order plot of the log of Absorbance at time t – Absorbance at infinity versus time (t) for the reaction was extended in a straight line for over 80% extent of the reaction (Fig. 3). The unbending of the plot shows that the reaction is 1st - order in relation to [TNP]. From the slope of the graph, the pseudo-1st -order rate constant (k_1) was calculated. The plot of log k_1 versus log [SCN^-] was linear with a slope of 0.93. This implies that the reaction is 1st – order in relation to the concentration of the SCN^- (Fig. 4) thereby indicating an overall 2nd - order. The 2nd -order rate constant k_2 was calculated from the relation $k_2 = k_1/[SCN^-]$ and was discovered to be fairly equable (Table I). The homogeneity in k_2 values again re-affirms the order one to the [SCN^-]. The rate law for the reaction is shown in (3).

$$\frac{-d[TNP]}{dt} = k_2[\mathrm{TNP}][SCN^-] \tag{3}$$

Where $k_2 = 16.61 \pm 0.29$ dm^3 mol^{-1} s^{-1} at [TNP] = 1.0×10^{-5}, $[SCN^-] = (4.2–5.0) \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3}, λ_{max} = 360 nm and T = 28 ± 1 °C.

This result corresponds with the results declared by Lohdip and Iyun [8]; Babatunde and Nwaji [17] for the study of the kinetics of the oxidation of iodide and Thiocyanate ions by 12-tungstocobaltate (III) and the reduction of (7–Amino–8–Methyl–Phenothiazin–3–Ylidene) – Dimethyl – Ammonium Chloride by thiocyanate ion respectively.

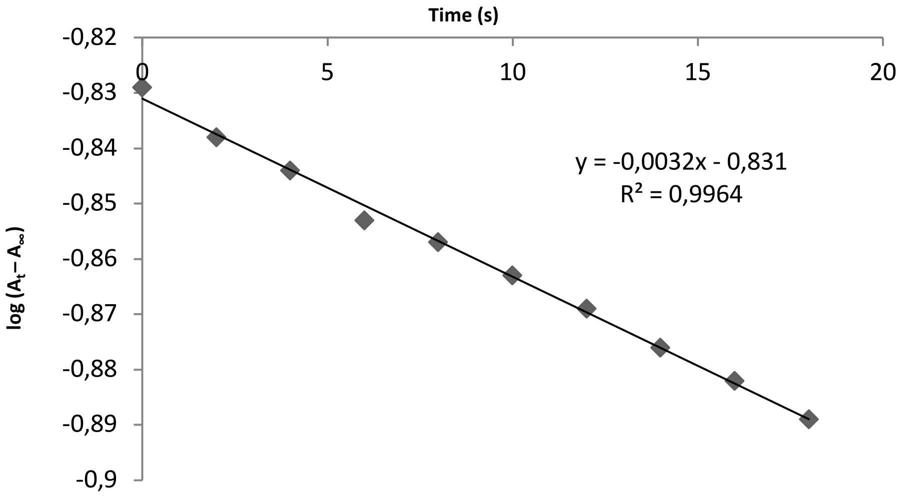

Fig. 3. Pseudo-1st - Order Plot for the Reaction of TNP by SCN^-

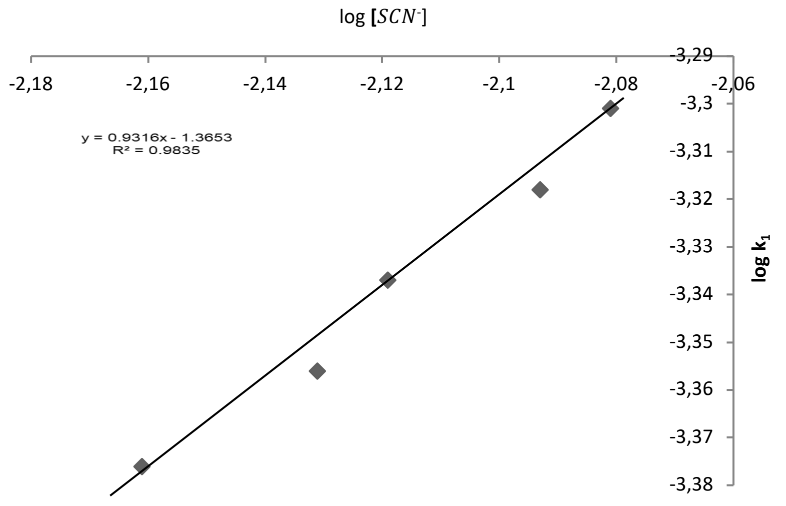

Fig. 4. Plot of log k_1 versus log [SCN^-]

A. Effect of Change in the Concentration of Hydrogen Ion

The reaction rate constants increased with increase in $[H^+]$ in the range of (0.4 - 1.0) × 10^{-3} at 28 ± 1 °C and I = 1.0 mol dm^{-3} (Table I). The plot of k_2 versus $[H^+]$ gave a straight line with a slope and an intercept of 7.65 and 8.89 respectively (Fig. 5). Similar acid dependence was reported by Hamza *et al.*, [18] and Onu *et al.*, [19]. The rate constant as influenced by the acid is represented in (4).

$$k_2 = (a + b[H^+]) \tag{4}$$

The rate is represented in (5).

$$\frac{-d[TNP]}{dt} = (\mathrm{a} + \mathrm{b}[H^+])[\mathrm{TNP}][SCN^-] \tag{5}$$

where a = 7.65 mol^{-1} dm^3 s^{-1}, b = 8.89 × 10^{-3} mol^{-1} dm^3 s^{-1} a = intercept and b = slope.

TABLE I: PSEUDO-1ST - ORDER AND 2ND - ORDER RATE CONSTANTS FOR THE REACTION OF TNP AND SCN^-.

$[SCN^-]$ = 1.0 × 10^{-3} mol dm^{-4}	I = 1.0 mol dm^{-3}	$[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}	10^3 k_1 s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
4.2	1.0	1.0	6.90	16.43
4.4	1.0	1.0	7.36	16.73
4.6	1.0	1.0	7.59	16.50
4.8	1.0	1.0	8.06	16.79
5.0	1.0	1.0	8.29	16.58
4.4	1.0	1.0	5.30	12.05
4.4	1.0	1.0	5.53	12.57
4.4	1.0	1.0	6.45	14.66
4.4	1.0	1.0	7.36	16.73
4.4	0.4	1.0	5.07	11.52
4.4	0.6	1.0	5.53	12.57
4.4	0.8	1.0	6.45	14.66
4.4	1.0	1.0	7.36	16.73

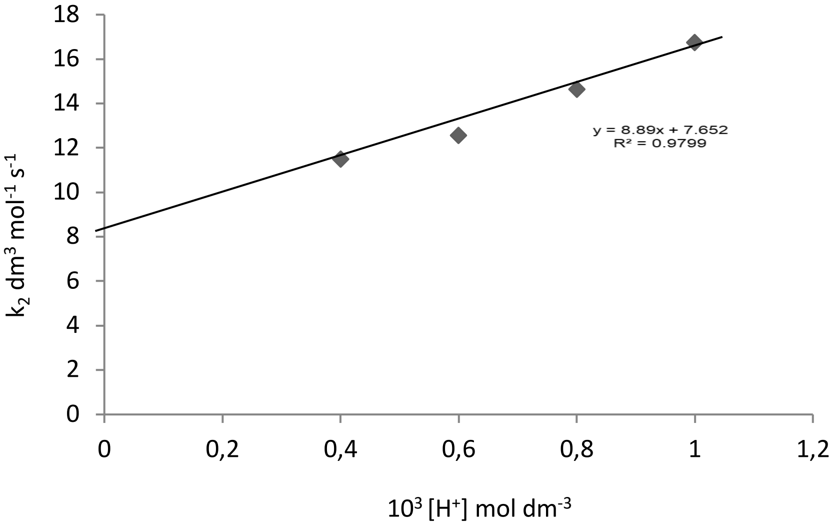

Fig. 5. Plot of k_2 versus $[H^+]$ for the Reaction of TNP and Thiocyanate Ion.

B. Effect of Change in Ionic Strength

The reaction rate increases with an increase in the concentration of NaCl between the range of (0.4 - 1.0) mol dm^{-3} (Table I). This shows that the activated complex is made from two ions of like charges. A plot of k_2 versus √I was linear (Fig. 6). Umoru [11] reported a decrease in rate with an increase in ionic strength in the study of the kinetics of $[(bipy)_2\,Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ by thiocyanate ion.

C. Effect of Added Ions

The addition of Mn^{2+}, NO_3^-, and PO_4^{3-} did not affect the reaction rate (Table II). Added ions did not speed up or retard the reaction may be due to the formation of ion-pair before electron transfer. Since the ion complex does not have a formal charge, interactions with added ions may be implausible [20].

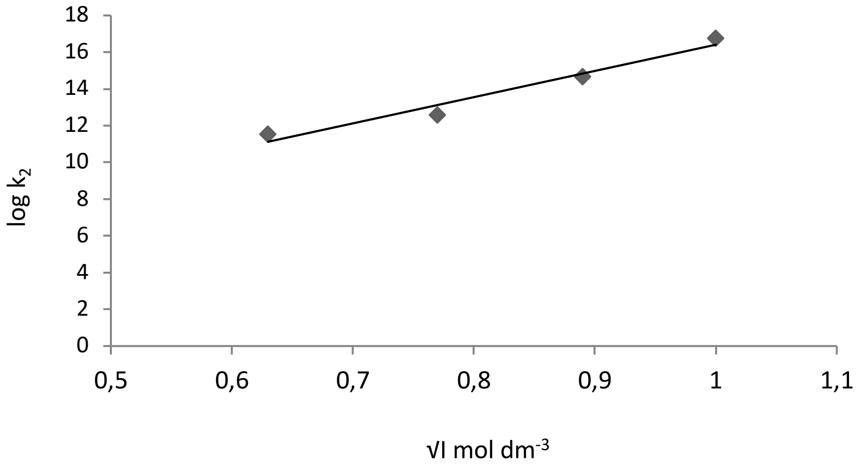

Fig. 6. Plot of log k_2 versus √I for the Reduction of TNP by SCN^-

TABLE II PSEUDO-1ST - ORDER AND 2ND - ORDER RATE CONSTANTS FOR THE INFLUENCE OF ADDED CATIONS AND ANIONS UPON REACTION OF TNP AND SCN^-

Ion	[Ion] = 1.0 × 10^{-3} mol dm^3	$10^3 k_1 s^{-1}$	$k_2 dm^3 mol^{-1} s^{-1}$
Mn^{2+}	1.5	8.75	19.89
	2.0	8.75	19.89
	2.5	8.75	19.89
	3.0	8.75	19.89
NO_3^-	1.5	6.90	15.70
	2.0	6.90	15.70
	2.5	6.90	15.70
	3.0	6.90	15.70
PO_4^-	1.5	8.06	18.32
	2.0	8.06	18.32
	2.5	8.06	18.32
	3.0	8.06	18.32

D. Test for Free Radicals

The introduction of acrylamide (4 ml) followed by a great excess of methanol to the partially reactive mixture showed no cloggy precipitate. This implies that free radicals were not present in the reaction or that they reacted so quickly that it was not detected experimentally [13].

E. Test for Intermediate Complex

The outcomes of the spectroscopic studies showed no slip from the lambda max of 360 nm. This indicates that there was no emergence of an intermediate complex during the reaction process. Additionally, the plot of $1/k_1$ versus $1/[SCN^-]$ was linear and passed through the origin (Fig. 7). This as well suggests the absence of formation of an intermediate complex and upholds the probable dominance of an outer-sphere mechanism [21].

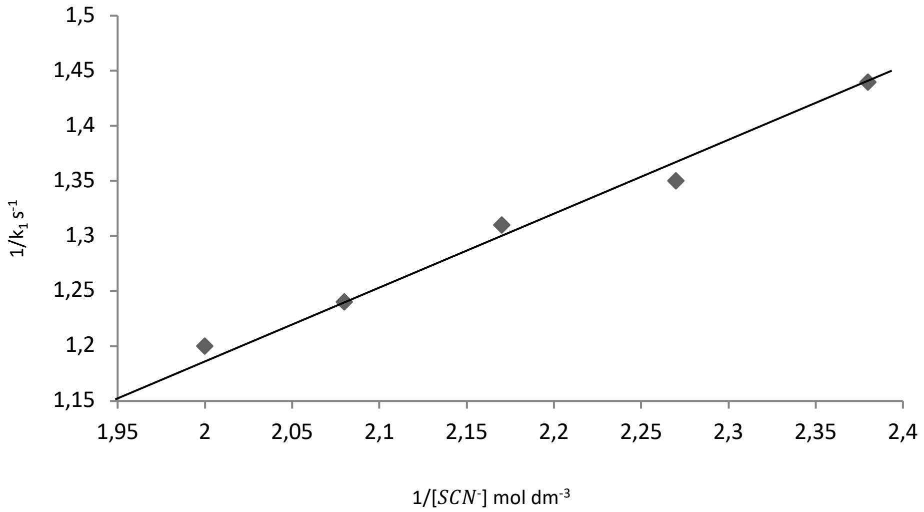

Fig. 7. Plot of $1/k_1$ versus $1/[SCN^-]$.

F. *Examination of Product*

The inclusion of 2 cm^3 of dilute lead (II) nitrate solution gave a white precipitate and on addition of bromine in glacial acetic acid, a clear solution was formed indicating the presence of thiocyanogen $(SCN)_2$ which was stable for several days. Based on the experimental results obtained, the following reaction mechanism was proposed:

$$SCN^- + H^+ \overset{K}{\leftrightarrow} HSCN \tag{6}$$

$$HSCN + H_2O \overset{k_1}{\rightarrow} H_3SOCN \tag{7}$$

$$H_3SOCN + H^+ \overset{k_2}{\rightarrow} H_2SCN^+ + H_2O \tag{8}$$

$$H_2SCN^+ + H_2O \overset{k_3}{\rightarrow} Product \tag{9}$$

$$TNP + SCN^- \overset{k_4}{\rightarrow} Product \tag{10}$$

From (6), we derive:

$$HSCN = K[SCN^-][H^+] \tag{11}$$

$$Rate = k_1[HSCN^-][H_2O] + k_4[TNP][SCN^-] \tag{12}$$

Substituting (11) into (12):

$$Rate = k_1K[SCN^-][H^+][H_2O] + k_4[TNP][SCN^-] \tag{13}$$

Rearranging (13) gives:

$$Rate = k_4 + k_1K[H^+][TNP][SCN^-] \tag{14}$$

Equation (14) is similar to (5), where k_4 = intercept “a” = 7.65 $mol^{-1}\ dm^3\ s^{-1}$
k_1K = slope “b” = 8.89×10^{-3} $mol^{-1}\ dm^3\ s^{-1}$

IV. CONCLUSION

The reactions of 2, 4, 6-trinitrophenol (TNP) with $[SCN^-]$ were investigated. The maximum absorbance of TNP was found to be 360 nm. A stoichiometry of 1:2 was observed between TNP and SCN^-. The reaction was catalyzed by acid. Spectroscopic studies did not show an intermediate complex was formed. The introduction of acrylamide solution to the not completely reacted mixture did not show any cloggy precipitate, indicating the absence of free radicals. Added ions did not affect the reaction rate. An outer sphere mechanism has been proposed based on the experimental results obtained.

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CONFLICT OF INTEREST

I wish to inform you that there is no conflict of interest amongst the authors.

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