



Kinetics and mechanism of electron transfer to Sodiumhexachloroiridate (IV) from N, N- ethylenethiourea in aqueous perchlorate media

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Abstract: The kinetics of the oxidation of N,N-ethylene thiourea by IrCl_6^{2-} in aqueous perchlorate solution followed a third order rate law, second order which respect to [N,N-ethylenethiourea] and first order with respect to $[\text{IrCl}_6^{2-}]$. The third order rate constants were obtained from the slopes of k_{obs} versus $[\text{N,N-ethylenethiourea}]^2$ plots under the following reaction condition, $[\text{IrCl}_6^{2-}] = 1.026 \times 10^{-4}$, $[\text{N,N-ethylenethiourea}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ to $6.0 \times 10^{-3} \text{ mol dm}^{-3}$, pH=5.8, in the temperature range 290K - 305K. The reaction between Na_2IrCl_6 (IV) and N,N-ethylenethiourea which has been carried out in acid medium is pH sensitive in the pH range 3.5 to 6.5. The product of the reaction was found to be a dimeric N,N-ethylenethiourea. The reaction is showing first order dependence in the concentration of the [oxidant] and second order dependence in the concentration of the [reductant]. The outer sphere electron transfer process is passing through an ordered transition state which is indicated by highly negative activation entropy value.

Keywords: N,N-ethylene thiourea, hexachloroiridate (IV), Kinetic Study.

I. Introduction

Ethylenethiourea is a white crystalline solid used extensively in the rubber industry as an accelerator in the vulcanization of elastomer. It is also a trace contaminant and metabolic degradation product of a widely used class of ethylene bisdithiocarbamate fungicides. Ethylene thiourea is known to produce thyroid neoplasm in rats and liver neoplasm in mice following long-term administration. Due to this reason it was chosen by the National Toxicology program in an investigation of the potential value of perinatal exposures in assessing chemical carcinogenicity. Iridium has been widely employed as a useful oxidant. The oxidation of many organic and inorganic compounds by hexachloroiridate has been reported [1-18]. The present investigation deals with the oxidation of N, N ethylenethiourea by hexachloroiridate (IV) ion which will be helpful to understand the role of this reducing agent in the biological domain.

II. Experimental

A. Materials

Chemicals used were of Analytical grade. Stock solutions of Na_2IrCl_6 were prepared by dissolving a known mass of Na_2IrCl_6 (Merck) in HCl (1 mol dm^{-3}). The molar extinction coefficient $\epsilon_{488} = 4060 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for Na_2IrCl_6 in 1M HCl. By using the above data, the IrCl_6^{2-} N,N-ethylene thiourea (Merck) was used without further purification. Ionic strength of the solution was maintained at $I = 0.5 \text{ mol dm}^{-3}$ by using freshly prepared standard NaClO_4 solution. Solutions of oxidants and reductants of different concentrations were prepared by proper dilution of the stock solution, fresh solutions were used for kinetic measurements. The strength of stock NaClO_4 solution was estimated by a combined ion-exchange alkali metric procedure. The resin Dowex 50 W x 8 (Na^+ form) was used for ion – exchange experiments. Fresh solutions were prepared using double distilled water prepared in an all-quartz distillation apparatus containing KMnO_4 solution. The pH of the reacting solution was adjusted with an appropriate amount of perchloric acid.

B. Kinetic Measurements

The kinetics of the reaction between N,N-ethylene thiourea and Sodium Hexachloro Iridate (IV) in aqueous medium were studied spectrophotometrically under pseudo-first order conditions with excess of [N,N-ethylenethiourea] using a CECIL 7200 (UK) UV-Visible spectrophotometer with a thermostatic bath for temperature control with an accuracy $\pm 0.1^\circ\text{C}$. The concentration of N,N ethylenethiourea was varied from 1.0×10^{-3} to $6.0 \times 10^{-3} \text{ mol dm}^{-3}$. The progress of the reaction was monitored by following decrease in absorbance (A_t) at 488 nm using conventional mixing technique. A_∞ was measured after completion of the reaction (approximately after 24 hours of mixing) when the absorbance became almost constant. Plot of $\ln(A_t - A_\infty)$ versus t was found to be linear as indicated in equation (1).

Figure 1: FTIR Spectra of N,N ethylene thiourea

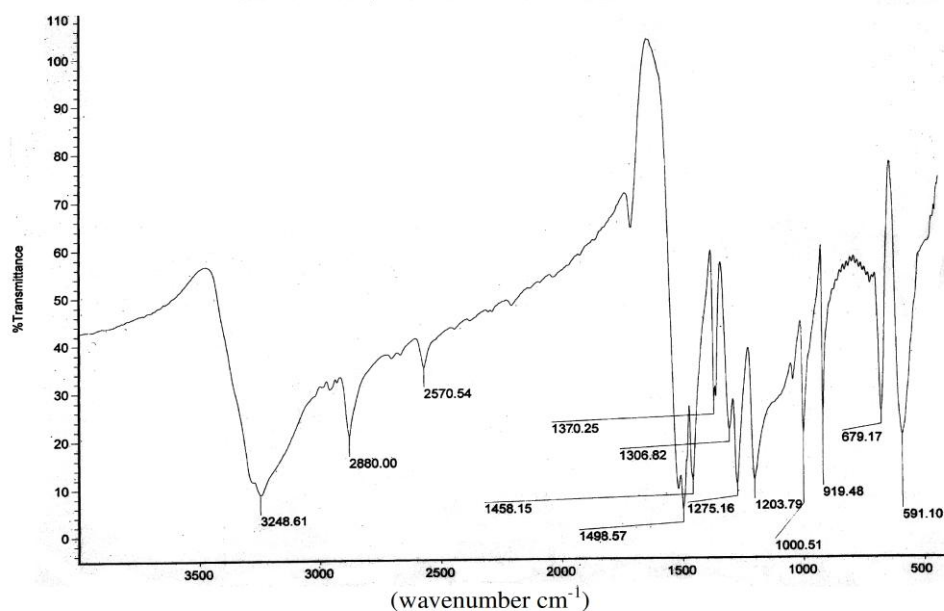


Figure 2: FTIR Spectra of the disulphide product

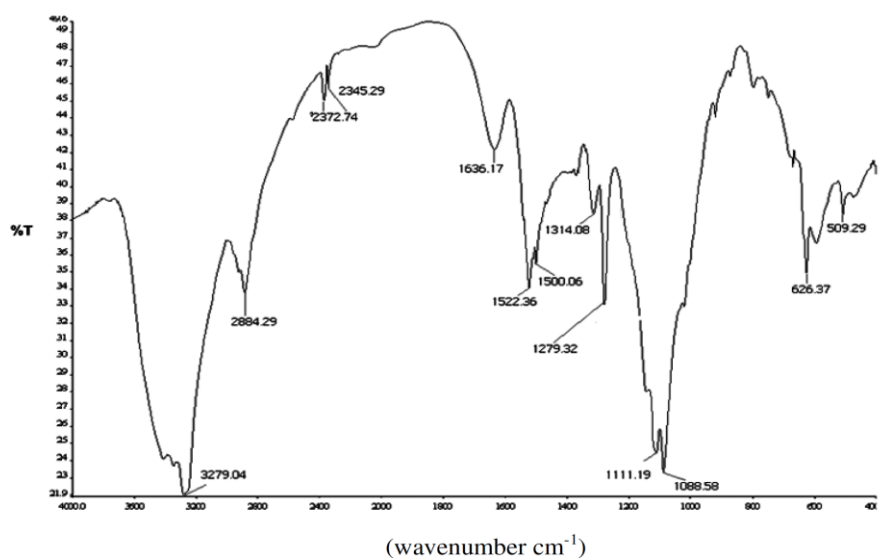


Figure 3: ^1H NMR spectra of disulfide product

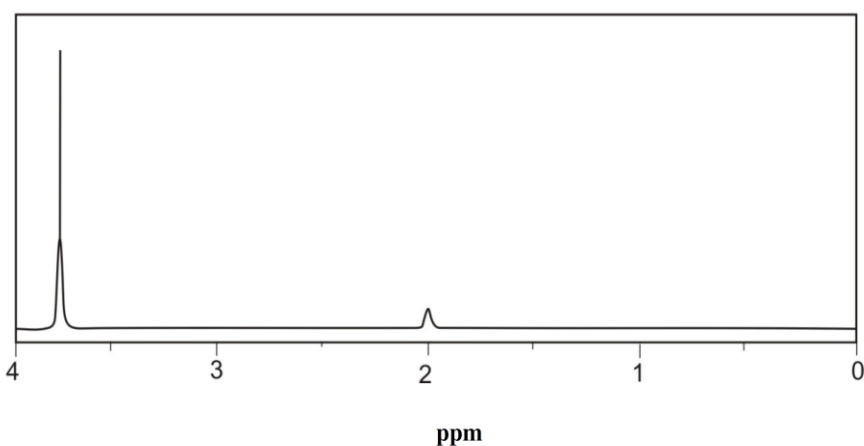
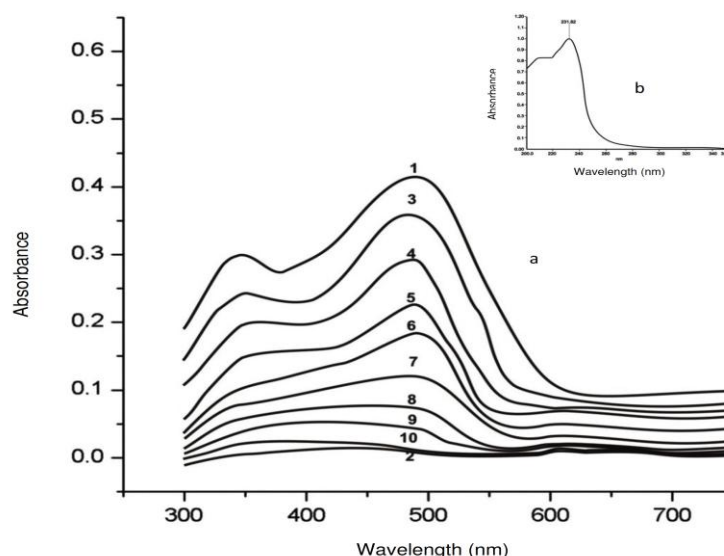


Figure 4 (a) UV-Vis Spectral scan for oxidation of N,N-ethylenethiourea by IrCl_6^{2-} in aqueous perchlorate medium at pH = 6.0, $I = 0.5 \text{ mol dm}^{-3}$, Temp. = 300K (1) $[\text{IrCl}_6^{2-}] = 2 \times 10^{-5} \text{ mol dm}^{-3}$ (2) $[\text{N,N-ethylenethiourea}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$ (3) Immediately after mixing, curve (4-10), $\Delta t = 5 \text{ min.}$ (b) UV-Vis Spectral scan of the reaction mixture after 24 hrs.



The UV-VIS spectral scan (Fig.3) of the reaction mixture of N,N-ethylenethiourea and Na_2IrCl_6 shows a steady decrease of absorbance with time over the range $300 \leq \lambda(\text{nm}) \leq 600$. The curve shows a continuous decrease of absorbance at 488 nm. Kinetics of the reaction has been studied at 488 nm measuring the decrease of absorbance at different time interval and the value of k_{obs} were calculated from the slope of $\log (A_t - A_{\infty})$ versus time plots. The plot of k_{obs} versus $[\text{N,N-ethylene thiourea}]^2$ at 295 K shows linear line passing through origin (Fig.4) indicating the second order rate dependence with respect to $[\text{N,N-ethylenethiourea}]$. Hence the observed rate law for the system is expressed as

$$-\frac{d[\text{IrCl}_6^{2-}]}{dt} = k_3 [\text{IrCl}_6^{2-}] [\text{N,N-ethylenethiourea}]^2 \quad (2)$$

The overall reaction is of third order. The third order rate constant k_3 was measured at four different temperatures (290K-305K) with varying substrate concentration keeping other variables constant and presented in Table-1. It was found to increase with increasing temperature. The effect of pH on the rate of the reaction was studied and found to appear unchanged in the pH range 0.1 to 2.5. However increase in the rate was observed by increasing the pH of the solution from 5.8 to 6.5 (Please see Table –2).

Table 1 Pseudo first order rate constants of the redox reaction of N,N-ethylene thiourea with sodium hexachloroiridate (IV) at different temperatures.

pH	$[\text{N,N-ethylene thiourea}] \times 10^3$ (mol dm^{-3})	$k_{\text{obs}} \times 10^{-4} (\text{sec}^{-1})$			
		290K	295K	300K	305K
5.80	1.0	0.205	0.303	0.420	0.505
	2.0	0.400	0.505	0.720	1.000
	3.0	0.720	1.000	1.230	1.750
	4.0	1.100	1.423	1.800	2.530
	5.0	1.400	1.750	2.750	3.700
	6.0	1.897	2.670	3.703	5.090

$$[\text{Ir}^{\text{IV}}] = 1.026 \times 10^{-4} \text{ mol dm}^{-3}, I = 0.5 \text{ mol dm}^{-3}, \text{pH} = 5.80$$

Table 2 Pseudo-first order rate constants for the redox reaction of N, N- ethylene thiourea with sodium hexachloroiridate (IV) at different pH.

$[\text{N,N-ethylene thiourea}] \times 10^3$ mol dm^{-3}	$10^4 k_{\text{obs}} (\text{sec}^{-1})$		
	pH=5.8	pH=6.2	pH=6.5
1.0	0.42	0.93	0.96
2.0	0.72	1.34	1.40
3.0	1.23	1.69	1.80
4.0	1.80	1.99	2.10
5.0	2.75	2.80	3.40
6.0	3.70	3.88	4.40

$$[\text{Ir}^{\text{IV}}] = 1.026 \times 10^{-4} \text{ mol dm}^{-3}, I = 0.5 \text{ mol dm}^{-3}, T = 300\text{K}$$

Table 3 Third order rate constant k_3 and its activation parameters

Parameter	Temperature (K)			
	290	295	300	305
$k_3(\text{mol}^{-2} \text{sec}^{-1})$	4.744	6.472	9.400	12.89
$\Delta H^\ddagger$ (kJ mol ⁻¹)	47.23±0.095			
$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	-325.88±6.43			

Activation parameters were calculated by using Eyring equation and given in Table-3. The moderate values of activation parameters, $\Delta H^\ddagger = 47.23 \pm 0.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -325.88 \pm 6.4 \text{ JK}^{-1} \text{ mol}^{-1}$ are favorable for the electron transfer reaction.

The overall third order reaction indicates a rapid preequilibrium and an intermediate formation before the rate determining step in the mechanism. Basing on stoichiometry and identification of the product, the probable mechanism may be delineated as follows.



Where Tu is the simplified representation for N, N-ethylenethiourea, Ir^{IV} and Ir^{III} represent hexachloroiridate (IV) and (III) Tu_2 is the disulphide product. N, N-ethylenethiourea reacts with iridium (IV) forming a binuclear intermediate radical. It is unstable and reacts with Ir (IV) to produce Ir (III).

The rate law corresponding to the above mechanism is derived as

$$\frac{d[\text{Int}]}{dt} = k_1 [\text{Tu}] [\text{Ir}^{\text{IV}}] - k_{-1} [\text{Tu} \cdot \text{Ir}^{\text{IV}}] - k_2 [\text{Tu} \cdot \text{Ir}^{\text{IV}}] [\text{Tu}] \quad (6)$$

Applying steady state condition

$$k_1 [\text{Tu}] [\text{Ir}^{\text{IV}}] = [\text{Tu} \cdot \text{Ir}^{\text{IV}}] \{k_{-1} + k_2 [\text{Tu}]\}$$

$$[\text{Tu} \cdot \text{Ir}^{\text{IV}}] = \frac{k_1 [\text{Tu}] [\text{Ir}^{\text{IV}}]}{k_{-1} + k_2 [\text{Tu}]} \quad (7)$$

$$\text{Rate} = k_2 [\text{Tu} \cdot \text{Ir}^{\text{IV}}] [\text{Tu}]$$

$$\text{Rate} = k_2 \frac{k_1 [\text{Ir}^{\text{IV}}] [\text{Tu}]^2}{k_{-1} + k_2 [\text{Tu}]} \quad (8)$$

$$\frac{dp}{dt} = -d \frac{[\text{Ir}^{\text{IV}}]}{dt} \frac{1}{2}$$

$$\frac{-d[\text{Ir}^{\text{IV}}]}{dt} = \frac{2dp}{dt} = \frac{2k_1 k_2 [\text{Ir}^{\text{IV}}] [\text{Tu}]^2}{k_{-1} + k_2 [\text{Tu}]} \quad (9)$$

$$\text{Rate} = \frac{2k_1 k_2 [\text{Ir}^{\text{IV}}] [\text{Tu}]^2}{k_{-1} + k_2 [\text{Tu}]} \quad (10)$$

$$\text{Rate} = k_{\text{obs}} [\text{Ir}^{\text{IV}}]$$

$$k_{\text{obs}} = \frac{2k_1 k_2 [\text{Tu}]^2}{k_{-1} + k_2 [\text{Tu}]} \quad (11)$$

Assuming $k_{-1} \gg k_2$ [Tu] the above equation reduces to

$$k_{\text{obs}} = \frac{2k_1k_2}{k_{-1}} [\text{Tu}]^2 \quad (12)$$

$k_{\text{obs}} = k_3 [\text{Tu}]^2$ where k_3 is the composite rate constant. The k_{obs} value at for different temperature were plotted against $[\text{Tu}]^2$. From the slope of the curve the composite rate constant [k_3] at for different temperatures were calculated. The activation parameters of the composite rate constant were calculated using Eyring equation and listed in table-3. These values appear to be more or less compatible with the mechanism proposed.

V. Conclusion

The reaction between Na_2IrCl_6 (IV) and N,N-ethylenethiourea which has been carried out in acid medium is pH sensitive in the pH range 5.8 to 6.5. The product of the reaction was found to be a dimeric N,N-ethylenethiourea. The reaction is showing first order dependence in the concentration of the [oxidant] and second order dependence in the concentration of the [reductant]. The outer sphere electron transfer process is passing through an ordered transition state which is indicated by highly negative activation entropy value.

VI. References

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