KINETICS AND MECHANISM OF THE OXIDATION OF HYDRAZINE DIHYDROCHLORIDE BY AQUEOUS IODINE

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Abstract: The kinetics of the redox reaction of iodine with hydrazinium ion ($N_2H_5^+$) has been studied in aqueous hydrochloric acid at 31.0 ± 1.0^oC and ionic strength, $I = 0.6$ mol dm^{-3} (KCl) and a plausible mechanism proposed. The stoichiometry of the reaction is 1:2 (oxidant/reductant) and follows the rate law: $-d[I_2]/dt = (b + c\,[H^+]^{-1})[I_2][N_2H_5^+]$. The rate of the reaction is inversely dependent on the acid concentration of the reaction medium. Spectroscopic evidence indicates the absence of a pre-electron transfer reaction intermediate. On the basis of the effect of added ions on the rate of reaction and complemented by the nature of the Michaelis-Menten plot, the outer-sphere electron transfer mechanism is proposed for this reaction. [Journal of American Science 2010;6(9):293-296]. (ISSN: 1545-1003).

Key words: hydrazinium ion, stoichiometry, electron transfer, iodine, kinetics, mechanism

1. Introduction

Iodine is an essential micronutrient for mammals including humans. Iodine deficiency, though easily treated, continues to be a problem for approximately a fifth of the world population, goiter, or enlargement of the thyroid, has been recognized for many years as symptoms of iodine deficiency. These pathological conditions have been permitted to be grouped under the common name of Iodine Deficiency Disorders (IDD) Hetzel et al; (1990). Iodine deficiency is in fact the largest preventable cause of mental retardation worldwide Cao et al; (1994). In severe cases, it can result in cretinism, a form of mental retardation. Volatization from oceans and precipitation of ocean water is the origin of most iodine content of the diet is considered critical to compensate for metabolic losses Vought et al; (1964). Goiter surveys so far are limited to clinical symptoms, urinary iodine output and, to some extent, plasma thyroid hormone levels. Thyroxine (T_4, tetraiodothyronine) and triiodothyronine (T_3, liothyronine) are the principal thyroid hormones. These hormones affect fundamental physiological processes including; oxygen consumption, heat production, carbohydrate, fat and protein metabolism, growth and differentiation, promoting action of other hormones such as catecholamines and steroids. Thiourelynes compounds are noted to be antithyroid typically methimazole and propylthiouracil.

Hydrazine dihydrochloride which is a powerful reducing agent have similarity to the thiourelynes by possessing nitrogen in its structure can also be possible inhibitor and similar compounds Cao et al; (1994). The objective of this study is to investigate the kinetics and mechanism of the reduction of iodine by hydrazine dihydrochloride. This will in turn give an insight to the needed kinetic information relating to the reduction of thyroid iodine.

2. Material and Methods

Hydrazine dihydrochloride, (BDH Analar grade) iodine solution, potassium chloride, hydrochloric acid, mercury (II) chloride, copper (II) chloride, Corning Colorimeter 253. Were used for the study

3. Stoichiometry

The stoichiometry was determined by the mole ratio method using Corning Colorimeter at 490 nm. The $[I_2]$ was kept constant at 7.8×10^{-4} mol dm^{-3} and the concentration of hydrazine dihydrochloride varied between 2.5×10^{-5} mol dm^{-3} and 8.0×10^{-4} mol dm^{-3} at $[H^+] = 0.5$ mol dm^{-3} and $I = 0.6$ mol dm^{-3} (KCl).

4. Kinetics

Using Corning Colorimeter 253, the wave length of maximum absorption of iodine in aqueous solution was determined to be 490 nm. This value agrees with what has been reported by other workers Mackowiak, (1999). Kinetic measurements were conducted at this wave length by measuring the

decrease in absorbance of the reaction mixture as the reaction progressed.

The reaction was carried out under pseudo-first order conditions with hydrazine dihydrochloride concentrations in at least 20-fold excess over that of iodine. Ionic strength of the reaction was kept constant at 0.6 mol dm^{-3} (KCl) and [H$^+$] at 0.5 mol dm^{-3}. Plot of log (A$_t$ - A) against time, t, (where A$_t$ and A are the absorbance at time, t and at the end of the reaction respectively) were linear for a greater extent of the reaction. Pseudo-first order rate constants, k$_o$ were determined as the slopes of the plots as given by the equation.

(A$_t$ - A) = (A$_t$ – A$_o$) e$^{ko.t}$ ………….…….. (1)

A$_o$ is the absorbance at the beginning of the reaction. Second order rate constants, k$_2$, were obtained as ratios of k$_o$ to [N$_2$H$_5^+$]

5. Results and discussion

Mole ratio determination showed that for every mole of hydrazine dihydrochloride consumed, 2.0 moles of iodine were reduced. A plot of absorbance versus [N$_2$H$_5^+$] had a sharp break at 4.0 x 10^{-4} mol dm^{-3} hydrazine dihydrochloride corresponding to 7.8 x 10^{-4} mol dm^{-3} [I$_2$] this gives a mole ratio of 1:2 as shown in equation (2).

$$N_2H_4 \, 2HCl + 2I_2 \rightarrow N_2 + 4HI ....(2)$$
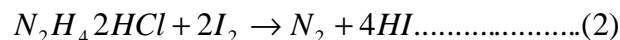
Under pseudo-first order conditions with [N$_2$H$_5^+$] at least 20 fold excess over [I$_2$] and at constant ionic strength, pseudo-first order plots were linear for at least over 90% extent of reaction. This implies that the order of reaction with respect to [I$_2$] is one. Pseudo-first order rate constants, determined as slopes of these plots, are shown in Table 1. Also a plot of log k$_1$ versus log [N$_2$H$_5^+$] was linear with a slope of 1.0, implying first order dependence of rate on [N$_2$H$_5^+$] as shown in Figure 1. The rate law for the reaction is given as equation (3)

$$-\frac{d[I_2]}{dt} = k_2 \, [I_2][N_2H_5^+] ……………..(3)$$

Within the range 0.1 [H$^+$] 0.5 mol dm^{-3} at [I$_2$] = 7.8 x 10^{-4} mol dm^{-3} and constant ionic strength of 0.6 mol dm^{-3}. The rate of reaction increases with decreasing [H$^+$] Table 1. A plot of second order rate constant, k$_2$ against [H$^+$] in the above acid range was linear and fitted equation (4).

k$_2$ = b + c [H$^+$]$^{-1}$ …………………… (4)

Where b and c were determined by the method of least mean square, and were found to be 2.085 dm^3 mol^{-1}s^{-1} and 0.57 dm^6 mol^{-2}s^{-1} respectively, at 31 ± 1 ^{o}C. Substitution of the expression for k$_2$ into equation (3) gives:

-d[I$_2$]/dt =(b+c[H$^+$]$^{-1}$)[I$_2$][N$_2$H$_5^+$] ….. (5)
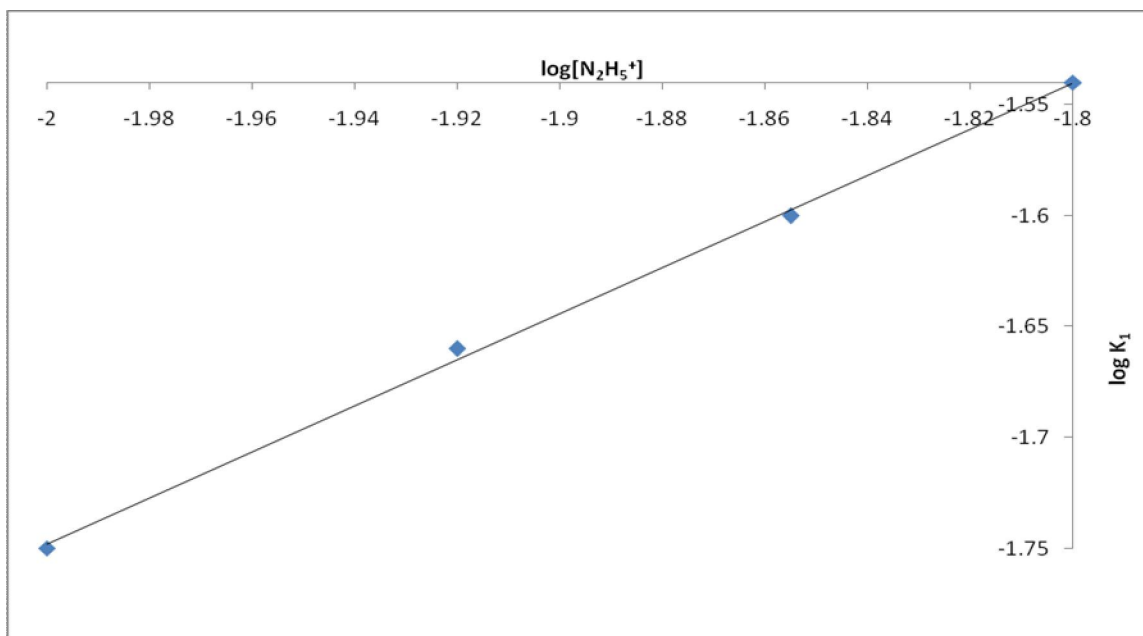
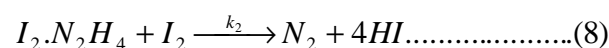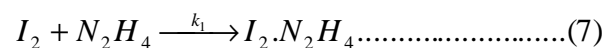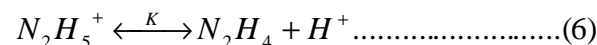**Figure I; plot of log k$_1$ versus log [N$_2$H$_5^+$]**

Table 1: Pseudo-first order and second order rate constants for the reaction of iodine with hydrazine dihydrochloride at; $[I_2] = 7.8 \times 10^{-4}$ mol dm^{-3}, I = 0.6 mol dm^{-3}, T = 31.0 ± 1.0^{o}C and

$_{max}$ = 490 nm

$10^3[N_2H^+]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	I [KCl] moldm^{-3}	$10^3 k_1$ s^{-1}	$10^2 k_2$ dm^3 mol^{-1} s^{-1}
10.0	0.5	0.6	17.89	178.9
12.0	0.5	0.6	21.88	182.3
14.0	0.5	0.6	25.18	179.9
16.0	0.5	0.6	28.78	179.9
16.0	0.4	0.6	29.80	186.3
16.0	0.3	0.6	30.70	191.9
16.0	0.2	0.6	31.44	196.5
16.0	0.1	0.6	32.50	203.1
16.0	0.5	0.7	31.66	197.9
16.0	0.5	0.8	30.62	191.4
16.0	0.5	0.9	29.94	187.1
16.0	0.5	1.0	29.31	183.2

The mechanism below is proposed for the reaction of I_2 with $N_2H_5^+$.

$$N_2H_5^+ \xleftrightarrow{\ K\ } N_2H_4 + H^+ \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$I_2 + N_2H_4 \xrightarrow{\ k_1\ } I_2.N_2H_4 \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

$$I_2.N_2H_4 + I_2 \xrightarrow{\ k_2\ } N_2 + 4HI \ldots\ldots\ldots\ldots\ldots(8)$$

$$N_2H_5^+ + I_2 \xrightarrow{\ k_3\ } I_2.N_2H_5^+ \ldots\ldots\ldots\ldots\ldots(9)$$

$$I_2.N_2H_5^+ \xrightarrow{\ k_4\ } 2HI + N_2 + 3H^+ \ldots\ldots\ldots\ldots(10)$$
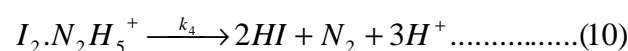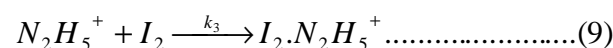
$$Rate = k_1[I_2][N_2H_4] + k_3[N_2H_5^+] \ldots\ldots\ldots\ldots(11)$$

From equation (6)

$$[N_2H_4] = K\frac{[N_2H_5^+]}{[H^+]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Substituting equation (12) into equation (11) gives
Rate
=

$$k_1K\frac{[N_2H_5][I_2]}{[H^+]} + k_3[N_2H_5^+][I_2] \ldots\ldots\ldots(13)$$

Rate
=

$$(k_3 + k_1K[H^+]^{-1})[N_2H_5^+][I_2] \ldots\ldots\ldots\ldots(14)$$

Equation (14) confirms with equation (5) where k_3 = b and k_1K = c.

As to whether the reaction occurs by outer- or inner-sphere mechanism, the following points have to be considered: Michaelis-Menten plot of $1/k_1$ versus $1/[N_2H_5^+]$ was linear without intercept. This suggests that intermediate complex prior to electron transfer step is very unlikely in this reaction.

The cations (Hg^{2+}, Cu^{2+}) were found to increase the reaction rate Table 2. Also the reaction of the partially reacted mixture did not show any shift in absorption maximum ($_{max}$) and there was no enhancement in absorbance, pointing to the absence of intermediate complex in the reaction. The above reasons suggest that the reaction proceeds via outer-sphere path.

Table 2: Rate data for the effect of added cations on the second order rate constants for the reaction of iodine and hydrazine dihydrochloride at: $[I_2] = 7.8 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 0.6$ mol dm^{-3}, $I = 0.5$ mol dm^{-3} (KCl), $[N_2H_4.2HHCl] = 1.6 \times 10^{-4}$ mol dm^{-3}, $_{max} = 490$ nm and $T = 31 \pm 1.0^{o}C$

Cation M^{n+}	$10^3[M^{n+}]$ mol dm^{-3}	10^3k_1, s^{-1}	10^2k_2 dm^3 mol^{-1}s^{-1}
Hg^{2+}	2.0	32.24	201.5
	4.0	36.16	226.0
	6.0	41.45	259.0
	8.0	47.97	299.0
Cu^{2+}	2.0	30.46	190.4
	4.0	31.96	199.8
	6.0	33.32	208.3
	8.0	35.0	218.8

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