ELECTRON TRANSFER REACTION OF THEOBROMINE AND PERMANGANATE ION IN AQUEOUS ACIDIC MEDIA

ABSTRACT

Electron transfer reaction of theobromine (hereafter referred to as TB) and permanganate ion has been studied using spectrophotometric technique under pseudo first-order conditions at T = 24± 0.1℃, $[H^+]$ = 3.2 × 10^{-1} mol $dm^{-3}$and I = 1.0 mol dm^{-3} (Na_2SO_4). Stoichiometric study depicted that two moles of TB were consumed by one mole of permanganate ion. The rate of the reaction is first order in both [TB] and $[MnO_4^-]$ and second order overall. It was observed that, $[H^+]$ and ionic strength respectively enhanced the rate of the reaction in the range studied. Michaelis-Mentens analysis showed no evidence of intermediate complex formation. Added anions and cations were observed to catalyze the reaction rate. The reaction conforms to the rate law as shown below:

$-d[MnO_4^-]/dt = (a+b[H^+])[TB][MnO_4^-]$

where a = 0.041 $dm^3 mol^{-1} s^{-1}$ and b= 0.028 $dm^3 mol^{-1} s^{-1.}$

The reaction thus occurs by an outer-sphere pathway and plausible mechanism is proposed for the reaction.

Keywords: Electron transfer, theobromine, permanganate ion and spectrophotometric

1. INTRODUCTION

"Electron transfer (ET) is one of the unique chemical processes which have received considerable attention due to its role in physical and biochemical systems" [1]. "It occurs when an electron moves from an atom or a chemical species (e.g. a molecule) to another atom or chemical species. The development of the field, experimentally and theoretically, as well as its relation to the study of other kinds of chemical reactions, presents an intriguing history, one in which many threads have been brought together" [2]. "The process is a mechanistic description of the thermodynamic concept of redox, wherein the oxidation states of both reaction partners changed. Numerous biological processes involve ET reactions, these processes include oxygen binding, photosynthesis, respiration, and detoxification. ET reactions commonly involve transition metal complexes, but there are now many examples of ET in organic chemistry and other discipline or field of study" [3-5]. "Moreover, many reactions in bioinorganic systems involve the electron transfer at one stage or the other and proper understanding of these electron transfer processes would help in the understanding development and eventual effective control of a wide area of science and technology" [6].

"Theobromine also known as xantheose is an alkaloid of the methylxanthine family which can be found in chocolate, kolanuts, tea leaves and other food substances. In modern medicine, it is used as a vasodilator, a diuretic and as a heart stimulant" [7]. "It is also known to exhibit antioxidant and pro-oxidant properties" [8]. "It is slightly water soluble but more fat soluble" [9]. "Theobromine is a purine alkaloid which can be derived from a nucleoside called xanthosine. Cleavage of the ribose and N-methylation yields 7-methylxanthosine. 7-methylxanthosine in turn is the precursor to theobromine" [10].

The electron transfer reactions of permanganate ion have been reported by several authors [11-15]. Permanganate undergoes several electron transfer reactions with organic and inorganic compounds in both acidic and alkaline medium [16]. The extent of oxidation by permanganate ion depends on the nature of the reductant and the pH of the reaction medium. In acidic medium Mn VII exists as $HMnO_4$, $H_2MnO_4^+$, $HMnO_3$, and Mn_2O_7. There exist paucity of data on electron transfer reaction between permanganate ion and theobromine and it is hopeful that the data that shall be generated from this study will provide more information about theobromine (alkaloid).

2. MATERIALS AND METHODS

2.1 Materials

Accurately, 3.60g (BDH) of theobromine was dissolved in 200 cm^3 of distilled water to give $1.0x10^{-1}$ mol dm^{-3} solution. Standard solutions of potassium permanganate ($KMnO_4$) and sulfurric acid (H_2SO_4) were also prepared, and standardized. Standard solutions of sodium sulfate (Na_2SO_4), sodium formate (HCOONa),magnesium sulfate ($MgSO_4$), calcium sulfate ($CaSO_4$) and sodium nitrate ($NaNO_3$) were prepared by dissolving accurately weighed quantity of the solute in a given volume of distilled water.

2.2 METHODS

2.2.1 Stoichiometry

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method[17-21] .Permanganate concentration was kept constant while that of the TB was varied in the range, [TB] = $(1.0 - 3.8) \times 10^{-2}$ mol dm^{-3} at $[MnO_4^-] = 2.0x10^{-4}$ mol dm^{-3} , $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm^{-3} (Na_2SO_4) and $\lambda_{max} =$ 530nm .The reactions were allowed to go to completion, when the absorbances of the solutions of the reaction mixture remained constant. The stoichiometry was indicated by the point of inflexion, was evaluated from the plots of absorbance versus mole ratio ($[TB]/[MnO_4^-]$) [22].

2.2.2 Kinetic studies

The rate of the reaction was monitored by measuring decreased in absorbances of the permanganate at 530nm using Corning Colorimeter 252 model. Kinetic measurements were made under pseudo-first order conditions with [TB] at least 10-folds excess of $[MnO_4^-]$. The pseudo first order rate constant (k_{obs}) in each case was obtained from the slope of the plots of (log $A_t - A_\infty$) versus time [23, 19, 24]. The second order rate constant (k_2) was obtained as k_{obs}/ [TB] at [TB] = $4.0 x10^{-3} – 2.8 x10^{-2}$ mol dm^{-3}, $[H^+] = 3.2 x10^{-1}$ mol dm^{-3}. I = 1.0 mol dm^{-3} (Na_2SO_4) and $[MnO_4^-] = 2.0 x10^{-4}$ mol dm^{-3}.

2.2.3 Effect of change in hydrogen ion concentration, $[H^+]$ on the reaction rate

The effect of $[H^+]$ on the rate of the reaction was investigated using sulfuric acid in the range $[H^+]$ = 0.24 - 0.64 mol dm^{-3}, while the concentrations of other reactants were kept constant at, I = 1.0 mol dm^{-3} (Na_2SO_4) and λ_{max} = 530nm [19, 20].

2.2.4 Effect of ionic strength (I) on the rate

The effect of ionic strength of the reaction medium was investigated by keeping the concentration of TB and MnO_4^- constant and varying the ionic strength of the reaction medium in the range I = 0.2-1.4 mol dm^{-3} (Na_2SO_4) and λ_{max} = 530nm [25-27, 24].

2.2.5 Effect of added cations and anions on the rate of reaction

The effect of added ions in the reaction medium was carried out by adding various concentrations of Mg^{2+}, Ca^{2+}, NO_3^- and $HCOO^-$ to the reaction medium while all other conditions remained constant [28, 25, 19], at I = 1.0 mol dm^{-3} (Na_2SO_4) , [MnO_4^-] = 2.0 $x10^{-4}$ mol dm^{-3}, [TB] = 2.0 x 10^{-2} mol dm^{-3} and [H^+] = 3.2 × 10^{-1} mol dm^{-3}.

2.2.6 Free radical test

About 5cm^3 of acrylamide was added to partially oxidized reaction mixture containing various concentrations of solution of theobromine, permanganate ion and hydrogen ion. This was followed by a large excess of methanol [29-30]. The acrylamide was also added to the solution of theobromine and permanganate ion separately, serving as control.

2.2.7 Test for intermediate complex formation

Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture 20 minutes after the start of the reaction with that of the permanganate ion within a wavelength of 400-700nm. Kinetic test was also investigated using Michaelis-Mentens plot of 1/k_{obs} versus 1/[TB] [12, 13].

3. RESULTS AND DISCUSSION

3.1 Stoichiometry and Product Analysis

The stoichiometry studies showed that one mole of $MnO_4^-$was consumed by two moles of TB as represented by the equation 1.

$2C_4H_8N_4O_2 + MnO_4^- + H^+ \rightarrow$ Other product + $Mn^{2+} + H_2O$ (1)

Similar stoichiometry has been reported for the oxidation of DL-alanine by permanganate ion [9] However, in the reaction of permanganate ion with malachite green, nicotinic acid, and L-tryptophan one mole of permanganate was consumed by one mole of each reductant [22, 11, 12, 14]. Mn^{2+}, a product of oxidation of MnO_4^- was confirmed qualitatively by reacting the product with indole [31]. Formation of white precipitate is an indication of the presence of Mn^{2+}.

3.2 Kinetic Study

The plots of ($logA_t$-A_∞) versus time were linear to more than 80% extent of reaction indicating that the reaction is first order dependence on [MnO_4^-]. A typical pseudo-first order plot is presented in Figure 1. The pseudo-first order rate constants were determined at different initial concentrations of TB. Plot of log k_{obs} versus log [TB] at, I = 1.0 mol dm^{-3}, [H^+] = 3.2 × 10^{-1} mol dm^{-3} gave a slope of 0.94 (Fig.2). This suggests a first order dependence on [TB]. The values of second order rate constant $k_2 = k_{obs}$/[TB] were constant (Table 1.) suggesting that the reaction is also first order in [TB] and that the reaction is second order overall, therefore conforming to the rate equation below:

$$– d [MnO_4^-]/dt = k_2[MnO_4^-][TB]. \quad (2)$$

Similar order kinetics have been reported in the reduction reactions of permanganate ion by aliphatic aldehydes[32], acetadelhydes [16], DL- alanine [33], L- asparaginase [34]) and L-tryptophan [14].

3.3. Effect of [H^+] on the Rate of the Reaction: The rate of the reaction was enhanced by increase in [H^+] at [H^+] = 0.24 – 0.0.64 mol dm^{-3}, [TB] 2.0$x10^{-2}$ mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4), [MnO_4^-] = 2.0 $x10^{-4}$ mol dm^{-3} and λ_{max} = 530nm

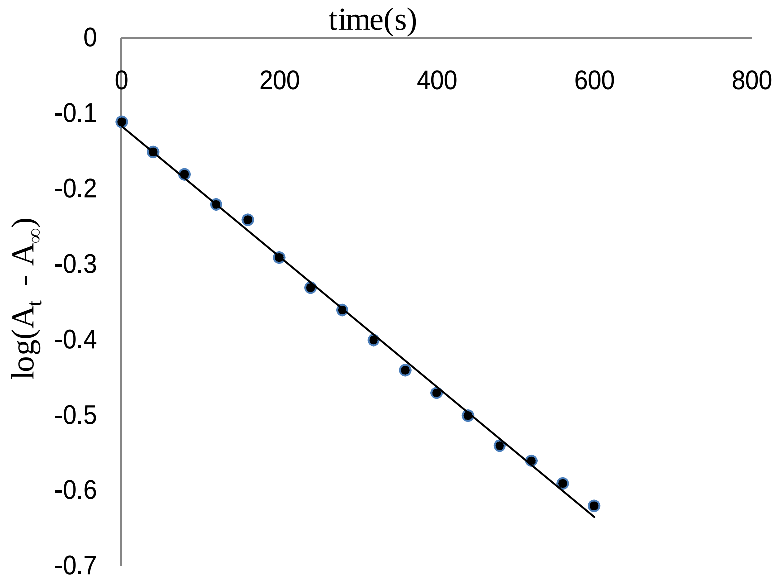

Figure 1: Typical pseudo–first order plot for the redox reacton of TB with MnO_4^-, [TB] = 1.0×10^{-2} mol dm^{-3}, [MnO_4^-] = 2.0×10^{-4} mol dm^{-3}, [H^+] = 1.0×10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, λ_{max} = 530nm and T =23.0 ± 0.1°C.

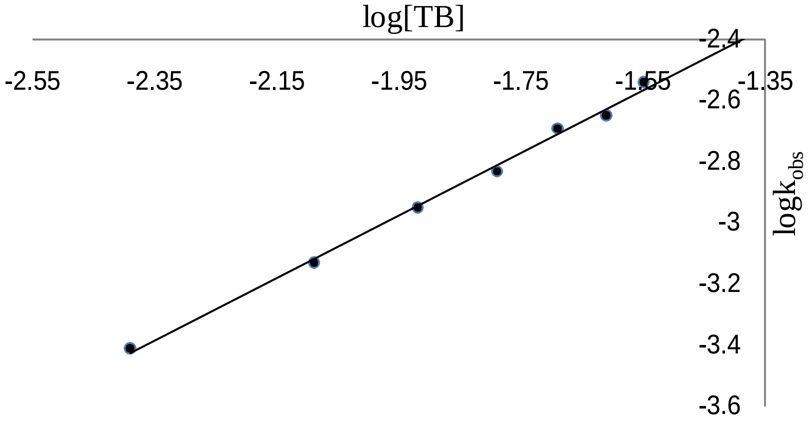

Figure 2: Plot of log k_{obs} versus log [TB] at [MnO_4^-] = 2.0×10^{-4} mol dm^{-3}, [TB] = (2.0 – 3.8) $\times 10^{-2}$ mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4) and T = 24 ± 0.1°C

Table 1: Pseudo–first order and second order rate constants for the reaction of TB and MnO_4^- at [TB] = 2.0×10^{-2} mol dm^{-3} [MnO_4^-] = 2.0×10^{-4} mol dm^{-3}, T = 24.0 ± 0.1°C, I = 1.0 mol dm^{-3} and λ_{max} = 530 nm

10^3 [TB], mol dm^{-3}	10^1 [H^+], mol dm^{-3}	10 [I], mol dm^{-3}	10^3 k_{obs}, s^{-1}	k_2, dm^3 $mol^{-1}s^{-1}$
4.00	3.20	1.00	0.380	0.095
8.00	3.20	1.00	0.736	0.092
12.0	3.20	1.00	1.100	0.092

16.0	3.20	1.00	1.470	0.092
20.0	3.20	1.00	2.020	0.101
24.0	3.20	1.00	2.200	0.091
28.0	3.20	1.00	2.820	0.100
20.0	2.40	1.00	1.590	0.079
20.0	3.20	1.00	2.300	0.110
20.0	4.00	1.00	3.070	0.153
20.0	4.80	1.00	3.720	0.186
20.0	5.60	1.00	4.790	0.239
20.0	6.40	1.00	5.860	0.293
20.0	3.20	0.20	1.220	0.060
20.0	3.20	0.60	1.480	0.074
20.0	3.20	0.80	1.660	0.083
20.0	3.20	1.00	2.490	0.120
20.0	3.20	1.40	3.260	0.160

and T = 24 ± 0.1°C. Plot of $\log k_{obs}$ versus $\log[H^+]$ gave a slope of 1.31, indicating that the reaction is first order with respect to $[H^+]$. Plot of k_2 versus $[H^+]$ was linear with positive intercept. The rate equation of the reaction as a function of H^+ can be represented by equation 3

$$-d\,[MnO_4^-]/dt = (a+b\,[H^+])\,[TB]\,[MnO_4^-] \qquad (3)$$

where a= 0.041 $dm^3mol^{-1}\,s^{-1}$ and b= 0.028 $dm^3mol^{-1}\,s^{-1}$.

The rate of the reaction showed two parallel pathways of reaction; one involving the protonated and the other the unprotonated species both reacting to give a product [35]. Similar results were reported in the reaction of permanganate ion with L- ascorbic acid [36], and malachite green [22].

3.4.The Effect of Ionic Strength on the Rate of the Reaction

The increase in ionic strength of the reaction medium resulted in increase in the rate of the reaction within the concentration range studied, the positive salt effect observed for the reaction showed the interaction of like charges (Bronsted- Debye positive salt effect) in the activated complex. Similar results were obtained by [17, 36]). Linear plot was obtained for $\log k_2$ versus $I^{1/2}$ (Fig. 3).

3.5.Effect of Added Ions on the Rate of the Reaction

The added ions NO_3^-, $HCOO^-$, Mg^{2+} and Ca^{2+} increased the rate of the reaction as shown on Table 2 below. “Catalysis of the reaction by these added anions and cations is possibly due to the coulombic bridging in which the closeness of approach of the reactant ions in the activated complex is such as to allow added ions to come in between them, thereby affecting the rates of reaction. This is when the reaction proceeding through the outer-sphere pathway in in which the reactant ions maintain their coordination integrity in the activated complex prior to and during electron transfer” [37].

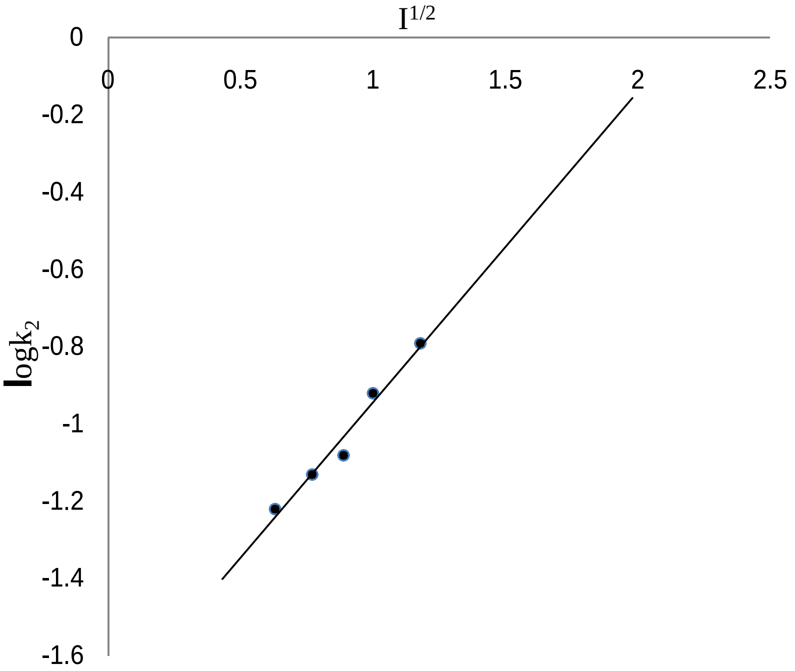

Figure 3: Logk$_2$ versus I$^{1/2}$ plot for the oxidation of TB by MnO_4^- at [TB] = 1.0 × 10^{-2} mol dm^{-3},[MnO_4^-] = 2.0 × 10^{-4} mol dm^{-3} ,[H^+] = 3.2 × 10^{-1} mol dm^{-3}, I = 0.2 – 1.4 mol dm^{-3} (Na_2SO_4) and T = 24 ± 0. 1℃

3.6.Test for Intermediate Complex Formation

The Michaelis-Menten plot of 1/k$_{obs}$ versus 1/[TB] showed no intercept on the 1/k$_{obs}$ axis (Fig. 4), suggesting the absence of an intermediate complex formation. Spectrophotometric measurement showed no clear shift in the λ_{max} from 530nm when reactants were mixed and the electronic spectrum was recorded after 20 minutes of mixing. This further suggests the absence of intermediate complex formation [13, 15].

3.7. Reaction Mechanism

The mechanism can be explained as follows: protonation of MnO_4^- by H^+ occurred at equation 4 to form $HMnO_4$. TB reacted with $HMnO_4$ to form to form $Mn^{2+}$and other product that were not determined in equation 5. TB further reacted with MnO_4^- in equation 6, moreover equation 5 and 6 are the rate determining steps. The mechanism is as follows:

Table 2: Rate constants for the effect of cations and anions in the oxidation reaction of theobromine and permanganate ion at [TB] = 2.0 × 10^{-2} mol dm^{-3}, T = 24. 0 ± 0.1℃ dm^{-3}, λ_{max} = 530 nm, [MnO_4^-] = 2.0 × 10^{-4} mol dm^{-3} and I = 1.0 mol dm^{-3} (Na_2SO_4)

Zn	**10^3 [Z], mol dm^{-3}**	**10^3 k_1, s^{-1}**	**k_2, dm^3 $mol^{-1}s^{-1}$**
Mg^{2+},	0.00	2.26	010
	5.00	2.68	0.13
	10.0	3.07	0.15
	20.0	3.83	0.19
	30.0	4.20	0.21
	40.0	4.79	0.25
Ca^{2+}	0.00	2.11	0.10
	5.00	3.45	0.13
	10.0	3.64	0.16
	20.0	3.83	0.19
	30.0	4.03	0.22
	40.0	4.41	0.23
$HCOO^-$	0.00	2.03	0.10
	5.00	3.26	0.14
	10.0	3.45	0.17
	20.0	3.83	0.19
	30.0	4.41	0.22
	40.0	4.98	0.24
NO_3^-	0.00	2.73	0.11
	5.00	3.64	0.15
	10.0	4.03	0.18
	20.0	4.41	0.21
	30.0	4.60	0.23
	40.0	5.37	0.26

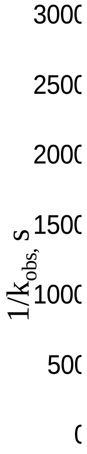

Figure 4: **Michealis–Mentens plot of 1/ k_{obs} versus 1/ [TB] at [MnO_4^-] = 2.0 × 10^{-4} mol dm^3, [TB] = 4.0 × 10^{-3} – 2.8 × 10^{-2} mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4) and T = 24 ± 0.1℃.**

$$MnO_4^- + H^+ \xrightarrow{K} HMnO_4 \qquad (4)$$

$$TB + HMnO_4 \xrightarrow{k_1} Mn^{2+} + \text{other products} \qquad (5)$$

$$MnO_4^- + TB \xrightarrow{k_2} Mn^{2+} + \text{other products} \qquad (6)$$

$$\text{Rate} = k_1[TB][HMnO_4] + k_2[TB]\,[MnO_4^-] \qquad (7)$$

$$\text{But, } [HMnO_4] = K[H^+]\,[MnO_4^-] \qquad (8)$$

$$\text{Rate} = Kk_1\,[TB]\,[MnO_4^-]\,[H^+] + k_2\,[TB]\,[MnO_4^-] \qquad (9)$$

$$\text{Rate} = (Kk_1[H^+] + k_2)\,[TB]\,[MnO_4^-] \qquad (10)$$

$$\text{Rate} = (Kk_1 + [H^+])\,[TB][MnO_4^-] \qquad (11)$$

4. CONCLUSION

The electron transfer reaction of permanganate ion and theobromine in aqueous sulfuric acid media showed a stoichiometry of 1:2. The order of one was observed with respect to both theobromine and permanganate ion. The rate of the reaction was enhanced by added NO_3^-,$HCOO^-$, Mg^{2+} and Ca^{2+}. The Michaelis-Mentens plot of $1/k_{obs}$ versus 1/[TB] showed no intercept on the $1/k_{obs}$ axis, suggesting the absence of an intermediate complex formation. From the above reasoning it can be inferred that the kinetic and spectroscopic evidences are in support of the occurrence of outer-sphere mechanism in the theobromine–permanganate reaction.

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