Effect of Temperature and Evaluation of Thermodynamic Parameters for Ag(I) Catalyzed Oxidation of Tris (2, 2´-bipyridine)Fe(II)complex ion by peroxodisulfate

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ABSTRACT

Ag(I) catalyzed oxidation of tris(2,2'-bipyridine)Fe(II) complex ion by peroxodisulfate has been undertaken at different temperatures (20°C-40°C). Redox reaction was investigated at different temperatures to evaluate the thermodynamic parameters of activation $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$. The value of energy of activation (E_a) of the redox reaction was estimated from Arrhenius plot and found to be 18.316±0.21 kJ/mol. The values of thermodynamic parameters of activation such as enthalpy of activation ($\Delta H^\#$) and entropy of activation ($\Delta S^\#$) were consequently evaluated from Eyring plot. The Gibbs energy of activation ($\Delta G^\#$) was calculated by employing equation, $\Delta G^\# = \Delta H^\# - T\Delta S^\#$. These values have been estimated with standard deviation to be as $\Delta H^\#$=15.92±0.42 kJ/mol, and $\Delta S^\#$ = -73.85±1.97 J/mol.K and $\Delta G^\#$ = 37.93± 0.78 kJ/mol at 298K. The positive values of $\Delta H^\#$ and $\Delta G^\#$ recommend the redox reaction to be an endothermic reaction.

Key Words: catalysis, peroxodisulfate, tris(2,2'-bipyridine)Fe(II), activation parameters

1. INTRODUCTION

Peroxodisulphate anion ($S_2O_8^{2-}$), commonly referred as persulfate is an oxyanion[1]. The standard reduction potential of peroxodisulphate anion +2.1V show it a powerful oxidizing agent[2,3]. Regardless of a very high reduction potential value its reaction kineticswas found to be extremely slow. However, in thepresence of some catalysts like Ag(I), Mn(II), Cu(II), Cr(III) etc., the rate of $S_2O_8^{2-}$ reduction gets significantly enhanced due to the formation of SO_4^{-2} radicals. Since nineteenth century researchers have been extensively focused on the kinetics of reactions involving peroxodisulphate as an oxidizing agent and the role of Ag(I) ion as catalyst to enhance its oxidation power. Investigations pertaining to Ag(I) catalyzed oxidation of different reducing agents,i.e., oxalate, thiosulphate, Ce(IV), ammonia, ammonium ion, arsenious acid and hydrogen peroxide by peroxodisulphate have also been done and it was found that the   reaction order is first for both $S_2O_8^{2-}$ and Ag^+ but zero in reductant[4,5]. Naqviet al. studied decomposition kinetics of peroxodisulphate inpresence of silver nitrate[6]. Their results showed that Ag(I) ion positively catalyzed the rate of decomposition of $S_2O_8^{2-}$. The authors also found that the reaction is first order dependent on the concentrations of $S_2O_8^{2-}$ and Ag^+. Several other Ag^+catalyzed oxidations by $S_2O_8^{2-}$ have also been investigated and found to follow the same kinetic behavior[7,8].

Oxidation kinetics of metal complexes have also been a subject of great interest. The oxidations by peroxodisulfate and the role of Ag^+ in this regard have been the matter of many investigations[9,10]. Both of these pieces of research have shown that the oxidation reactions are independent of concentration of metal complexes. Previously we have published a research work showing kinetics of Ag^+ catalyzed oxidation of $[Fe(2,2´-bipyridine)_3]^{2+}$ by peroxodisulphate ($S_2O_8^{2-}$) and studied the influence of various factors such as concentration of reagents, pH and ionic strength of the medium[11].

Temperature is a vibrant factor that affects the rate of a chemical reaction. It is a source of energy in order to have a chemical reaction occurs. But usually this factor is not discussed in detail in most of the research articles. In the current research attention was paid on the influence of temperature on the electron transfer kinetics of the aforementioned redox reaction.

2. EXPERIMENTAL

Potassium peroxodisulphate ($K_2S_2O_8$), silver nitrate ($AgNO_3$), sodium acetate (CH_3COONa), acetic acid (CH_3COOH), and sodium sulphate (Na_2SO_4), were of BDH (AnalaR) grade. Double distilled and deionized water was used where required. Standard solutions of 0.1 mol.dm^{-3} acetic acid and 0.1 mol.dm^{-3} sodium acetate were prepared and mixed with different combinations to prepare buffer solutions of required pH from 3.8 to 4.8[12]. $[Fe(2,2´-bipyridine)_3]SO_4$ complex was prepared[13] and characterized[11,14]. The Wavelength of maximum absorption of complex (522 nm) and the molar extinction coefficient (7876.8 dm^3/mol.cm)[11,14] were used for recording kinetic data. These values match very close to the available values of literature[15].

The kinetic runs for aforesaid redox reactions were carried out under the conditions at different temperatures(20° - 40 °C). The temperature of the reaction mixture was controlled by using Techno TE-8J, thermostat bath[11].

3. RESULTS AND DISCUSSION

Kinetic data was collected by recording change in optical density of complex (at 522 nm) as a function of time. The rate constants were evaluated by following integrated rate equation for pseudo first order reaction. A plot of $\ln A_t$ versus time (t) yields a slope equivalent to pseudo-first order rate constant (k_{obs}) (Table-1).

Table-1:   Dependence of pseudo first order rate constant (k_{obs}) on Temperature

S. No.	T (K)	$1/T \times 10^3$ (K^{-1})	k_{obs} / 10^{-5} (s^{-1})	ln k$_{obs}$	ln (k_{obs}/ T)
1	293	3.41	6.35	-9.66	-15.34
2	298	3.36	7.24	-9.53	-15.23
3	303	3.30	8.27	-9.40	-15.11
4	308	3.25	9.05	-9.31	-15.04
5	313	3.20	10.4	-9.17	-14.92

[Fe (2, 2′-bipy)$_3$]$^{2+}$ =5×10^{-5} mol dm^{-3} [S$_2$O$_8$$^{-2}$]=4.16×10^{-4} mol dm^{-3} [Ag$^+$]=4.16×10^{-5} mol dm^{-3}
pH = 4.2   μ=0. 5mol dm^{-3} λ$_{max}$=522 nm

All the plots were found to bestraight line with intercept $\ln A_0$. The temperature of the reaction mixture was controlled at different values by using Techno TE-8J, thermostat bath. It was observed that the values of pseudo-first order rate constant get improved with increasing temperature. Kinetic datawas used to quantify thermodynamic properties of reaction system by employing Arrhenius and Eyring equations respectively.

$$lnk_{obs} = lnA - (E_a/RT)$$
$$k = (k_BT/h) . e^{(\Delta S^\#/R)} . e^{-(\Delta H^\#/RT)}$$

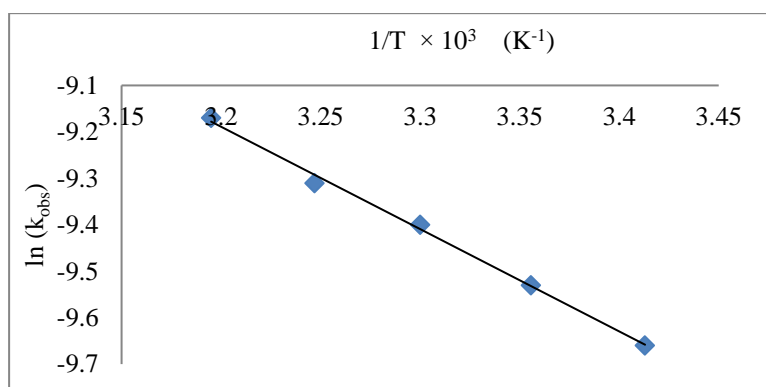Arrhenius equation was graphically employed as ln(k_{obs}) versus 1/T plot(Fig-1).

Fig-1: Plot of log k$_{obs}$ versus 1/T (Arrhenius Plot), in order to determine the influence of temperature on pseudo-first order rate constant (k$_{obs}$)

E$_a$ (energy of activation) and A (pre-exponential factor), were evaluated from slope and intercept of the plot respectively. Whereas, Eyring equation was implimented in order to getln (k$_{obs}$ /T) versus 1/T plot (Fig-2).
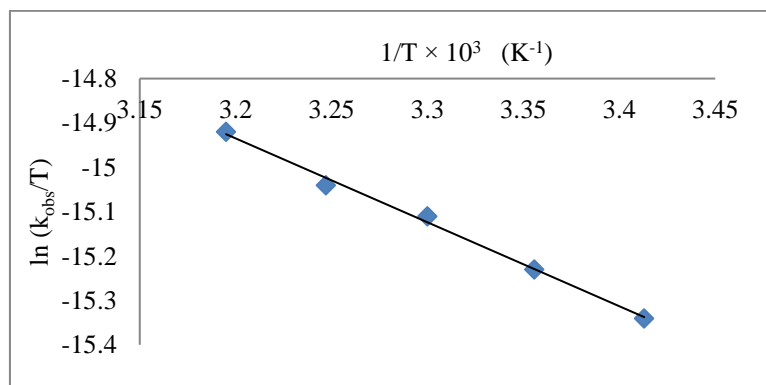

Fig-2: Plot of log (k$_{obs}$/ T) versus 1/T (Eyring Plot), in order to determine the influence of temperature on pseudo-first order rate constant (k$_{obs}$)

Enthalpy of activation ($\Delta H^\#$) was calculated fromtheslope,whileentropy of activation ($\Delta S^\#$) was evaluated from intercept. The Gibb's free energy of activation ($\Delta G^\#$) was calculated by using equation, $\Delta G^\# = \Delta H^\# - T\Delta S^\#$. Calculated values of E$_a$, $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$ are shown in (Table-2).

Table-2 Thermodynamic parameters for Ag^+ Catalyzed redox reaction between $[Fe(2, 2'-bipy)_3]^{2+}$ and $[S_2O_8^{-2}]$

Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
18.316	15.92	-73.85	37.93 at 298 K

When kinetic investigation of a reaction is carried outand influence of temperature on reaction rate constant is analyzed by employing Eyring equation, two activation parameters i.e., enthalpy of activation andentropy of activationare obtained. These two parameters provide useful information regarding the transition state. The first parameter specifies the required energy for the reaction while the second one shows how this energy is redistributed within the molecule so that reaction can take place[17]. The value of $\Delta S^{\#}$ provides hints about the molecularity of the rate determining step in a reaction[16], Positive values suggest a dissociative mechanism which is due to an increasein entropy upon attaining the transition state i.e., transition state is less organized as compared to the initial state.Whereas, negative values for $\Delta S^{\#}$ showadecrease inentropy on attaining the transition state, which indicates an associative mechanism in which two participating species form a single activated complex.

For current reaction system, the positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ recommend the redox reaction to be an endothermic reaction. Whereas,the positive value of $\Delta H^{\#}$ with a gain in entropy ($\Delta S^{\#}$) is an indication that reaction is occurring between species with unlike charges, which also reinforce the suggested rate equation for redox reaction between tris(2,2'-bipyridine)Fe(II) complex and peroxodisulfate ion in presence of Ag(I) as catalyst[11].

Rate = $k'[Ag^+][S_2O_8^{2-}]$

4. CONCLUSION

The study of effect of temperature on redox reaction between tris(2,2'-bipyridine)Fe(II) complex ion and peroxodisulfate ion in presence of Ag(I) as catalyst and consequently evaluated activation parameters suggest that reaction is endothermic and transition state is more organized as compared to initial state which validates that reaction is occurring between two oppositely charged species.

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CONFLICTS OF INTEREST

This is to certify that all Authors have seen and approved the manuscript being submitted. We assure that the article is the Authors' original work and that the article has not received prior publication and is not under consideration for publication elsewhere. All authors agree the author list content and order.Moreover, authors have no conflict of interest either financial or non-financial in the subject matter or materials discussed in this manuscript.

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