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KINETIC AND ACTIVATION PARAMETERS FOR THE REDUCTION OF DIPHENYLBENZIDINE WITH ASCORBIC ACID

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In order to get an insight into the activation parameters, rate of the reaction between ascorbic acid (ASC) and diphenylbenzidine (DPBD) was studied. The reactants were mixed in four different ratios (1:10, 1:15, 1:20 and 1:25) and the rate was determined at temperatures of 15°C, 20°C, 25°C and 30°C by measuring absorbance of the violet solution (DPBD) at λ_{max} = 570 nm. Diphenylbenzidine (DPBD) was prepared by mixing diphenylamine and cerium (IV) sulfate tetrahydrate solutions in a ratio of 1:2. The pseudo first order rate constants, k_{obs} , thus obtained was used to calculate the second order rate constant, $k' = k_{obs}$ / [DPBD] . The activation energy of the reaction was determined using Arrhenius equation and was found to be 30.00 ± 0.56 kJ mol^{-1}. Other activation parameters, $\Delta S^{\neq}$ and $\Delta H^{\neq}$, were calculated from the slope and intercept of Eyring equation obtained from a plot of ln (k´/T) against inverse temperature, (1/T). Entropy of activation $\Delta S^{\neq}$ has been found to be – 99±0.05 J mol^{-1} K^{-1} and that $\Delta H^{\neq}$ was 28.00±0.34 kJ mol^{-1}.

Keywords: Diphenylbenzidine (DPBD), Ascorbic acid, UV/Visible spectrophotometer, Rate constants, Thermodynamics parameters.

1. Introduction

Thermodynamics describes the behaviour of macroscopic systems characterized by temperature, volume, number and the type of particles. The state of such systems is further explained by total energy and other parameters like entropy. The pivotal status of thermodynamics was well recognized by G. N. Lewis and Marle Randall [1]. They described the two different uses of the thermodynamic parameters, (E_a , $\Delta S^{\neq}$ and $\Delta H^{\neq}$) which are in vogue: (1) the use of the Arrhenius equation as a guide for extrapolation of rate constant (2) its employment as criterion for mechanistic interpretation [2]. Bernasconi, Ali and Gunter have already studied and discussed the kinetics and thermodynamic acidities of substituted 1-benzyl-1-methoxy-2- nitroethylenes in terms of proton transfer behavior [3].

Kinetics and activation parameters of Mn (III) to Mn (II) by SO_3^{-2} ion in $(MnSiW_{11}O_{40}H_2)_5$-hetropoly ion had been investigated by Ali and Ashiq who established the outer and inner sphere mechanisms [4]. The compensation or phantom phenomenon related to the enthalpy and entropy has been delved by Bowden. He recognized the extent to which the two variables could vary largely and that the same variable may be looked at in two different ways [5]. The kinetics and thermodynamics of intermolecular saturated Amine Excimers was studied by Halpern et al. [6]. Khan and Rafique have extensively worked on the effect of temperature, pH, hydrindantin, of ascorbic acid and other organic solvents in the calorimetric estimation of α-amino acid with ninhydrin [7]. Several other investigations have been reported which involve the kinetics and activation parameter [8-12].

The amine derivatives play an important role in the electron transfer reaction due to the presence of a lone pair of electron. Study of diphenylbenzidine (DPBD) derivative of diphenylamine (DPA) is undertaken to evaluate the effect of activation parameters on the secondary amines.

2. Experimental

All chemicals were of Analar grade. Kinetic measurement was carried out on Shimadzu UV-160 spectrophotometer using quartz cells. A thermostat (HAAKE KT33) was used to maintain the desired temperature. Sodium hydroxide solution of 0.5 mol dm^{-3} was employed to maintain pH 4.0 of the reaction mixture and was monitored using a pH meter of combined glass Ag/AgCl electrode (HI-1332). Ionic strength of the reaction

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mixture consisting of diphenylbenzidine and ascorbic acid was maintained with 0.4 mol dm^{-3} stock solution of sodium sulfate. An appropriate aliquot of this solution was added to the reaction mixture and its ionic strength was calculated using equation $I=1/2C_iZ_i^2$.

The stock solution of diphenylamine of concentration (0.1mol dm^{-3}) was prepared by dissolving an appropriate amount in 99% methanol. An appropriate volume of 0.5 mol dm^{-3} solution of sodium hydroxide was added to maintain pH 4.0. A 0.1 mol dm^{-3} cerium (IV) sulfate tetrahydrate stock solution was prepared in 0.5 mol dm^{-3} H_2SO_4. pH of the cerium (IV) sulfate tetrahydrate solution was maintained to a required value with sodium hydroxide (0.5 mol dm^{-3}). Diphenylbenzidine was prepared by mixing diphenylamine and cerium (IV) sulfate tetrahydrate solution in the ratio of 1:2. Oxidation of diphenylbenzidine yielded a violet solution due to the following reactions.

$$2\left[C_6H_5-NH-C_6\ H_5\right]\leftrightarrow$$

$$\left[C_6H_5-NH-C_6H_4-C_6H_4-NH-C_6H_5\right]+2e^-+2H^+$$

$$\left[C_6H_5-NH-C_6H_4-C_6H_4-NH-C_6H_5\right]\xrightarrow{Ce(IV)}$$

$$\left[C_6H_5-N=C_6H_4=C_6H_4=N-C_6H_5\right]\ \text{(Violet)}$$

Mole ratio between diphenylamine and cerium (IV) sulfate tetrahydrate was established by measuring absorbance of the violet colour solution at λ_{max} = 570 nm. For this purpose reaction mixture was taken in a 3 ml cuvet. The concentration of diphenylamine was kept constant (5×10^{-5} mol dm^{-3}) and that of cerium (IV) sulfate tetrahydrate was varied to obtain concentration ratios of 1:1, 1:2 and 1:3. The 1:2 concentrations produced the peak of diphenylbenzidine at 570 nm.

3. Results and Discussion

3.1. Kinetic measurements

The plots of ln $[(A_\infty-A_o)/(A_\infty-A_t)]$ against time at different temperatures are shown in Figs. 1 to 4. In each case a straight line is obtained indicating first order kinetics with respect to ASC. A_o and A_∞ are the absorbance values measured at t = 0 and t = ∞ respectively, whereas A_t values correspond to different times. The pseudo first order rate constants (k_{obs}) were determined from the slope of the linear plots. In all, measurements were made at four different concentrations of DPBD at each temperature and k_{obs} were calculated in each case. In order to determine activation energy, measurements for each concentration of DPBD were made at four different temperatures. The k_{obs} and k´ values are reported in Tables 1 and 2 (Fig. 5).

The reaction involving ASC as a reducing agent has been studied and the mechanism established.

$$C_{12}H_{10}N_2C_{12}H_{10}H^+ + C_6H_8O_6 \longrightarrow C_6H_6O_6^{2-} + \text{Product} \quad (1)$$

The second order rate law for the reaction is

$$-d\left[ASC\right]/dt = k\left[DPBD\right]\left[ASC\right] \quad (2)$$

Concentration of DPBD was taken in excess with respect to ASC. The pseudo first order rate constant is related to second order rate constant as

$$k_{obs} = k'\left[DPBD\right] \quad (3)$$

3.2. Determination of thermodynamic parameters

Energy of activation for the reaction between DPBD and ASC was determined by plotting a graph between ln k´ vs. 1/T using Arrehenius equation (Fig. 6).

$$k = A\,e^{-Ea/RT}$$

and was found to be 30.00 ± 0.56 kJ mol-1. Eyring equation was applied to determine the enthalpy and entropy of activation. For this ln k´/T was plotted against inverse temperature.

$$\ln k' = \ln(kT/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT$$

These plots produced $\Delta S^{\neq}$ = – 99 ± 0.05 J mol^{-1} K^{-1} and $\Delta H^{\neq}$ = 28.00 ± 0.34 kJ mol^{-1} (Table 3, Fig. 7). The rate constant of electron transfer reaction can be explained by considering the parameter of entropy of activation $\Delta S^{\neq}$, which is independent of the standard state, from the transition state theory

$$k = (\kappa T/h)\, e^{\Delta S^{\neq}/R}.\, e^{-\Delta H^{\neq}/RT}$$

Since kT / h ≅ 10^{13} s^{-1} and if 10^{13} $e^{-\Delta H^{\neq}/RT}$ is taken as normal value i.e. at standard conditions,

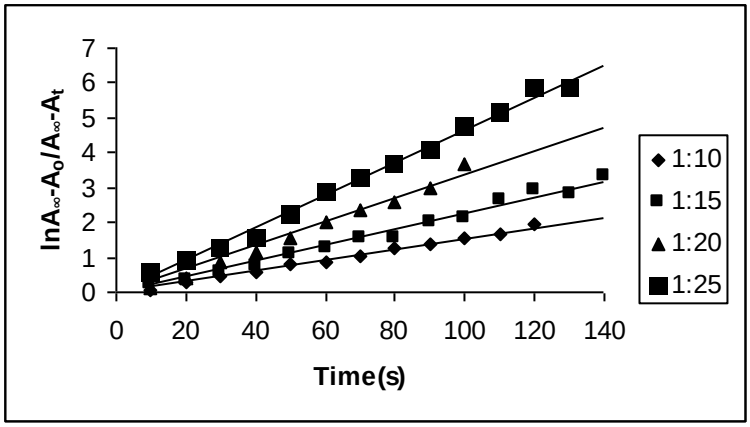

Figure 1. Plot of ln $(A_\infty-A_o)/(A_\infty-A_t)$ vs. time for various ascorbic acid diphenylbenzidine ratios at 15ºC.

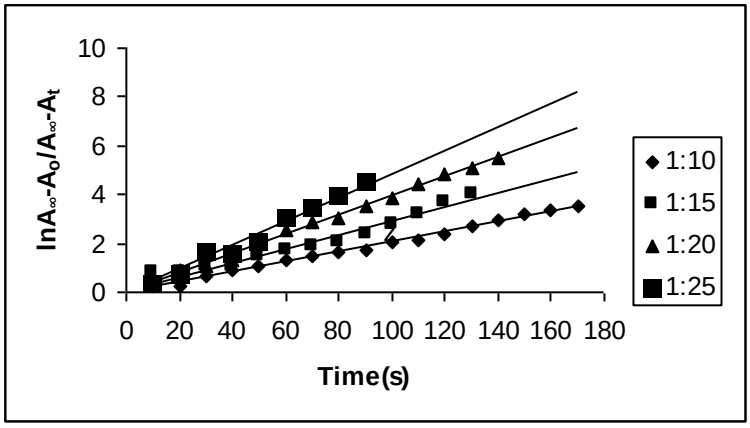

Figure 2. Plot of ln $(A_\infty-A_o)/(A_\infty-A_t)$ vs. time for various ascorbic acid diphenylbenzidine ratios at 20ºC.

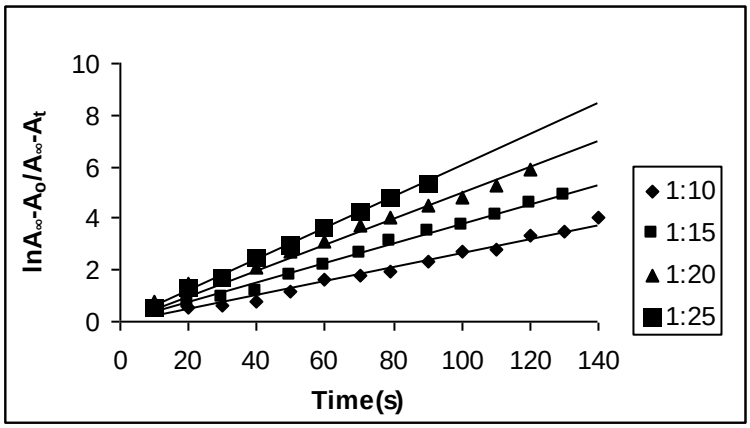

Figure 3. Plot of ln $(A_\infty-A_o)/(A_\infty-A_t)$ vs. time for various ascorbic acid diphenylbenzidine ratios at 25ºC.

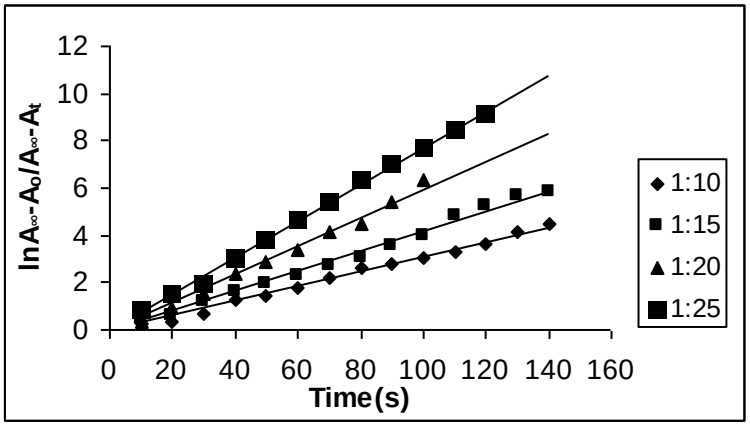

Figure 4. Plot of ln $(A_\infty - A_o) / (A_\infty - A_t)$ vs. time for various ascorbic acid diphenylbenzidine ratios at 30°C.

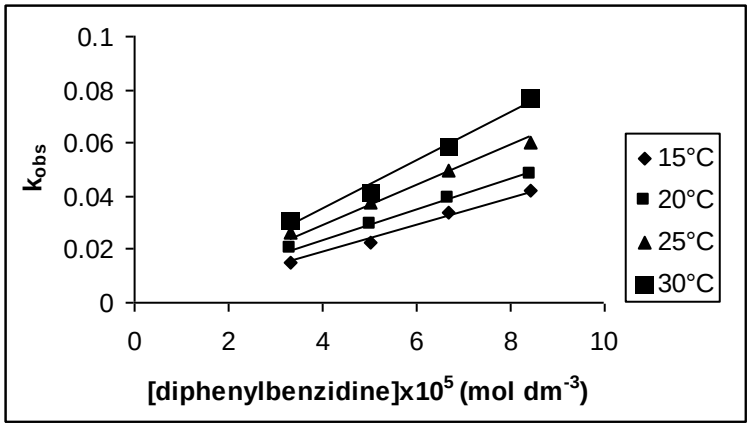

Figure 5. Determination the second order rate constant with respect to diphenylbenzidine at various temperatures.

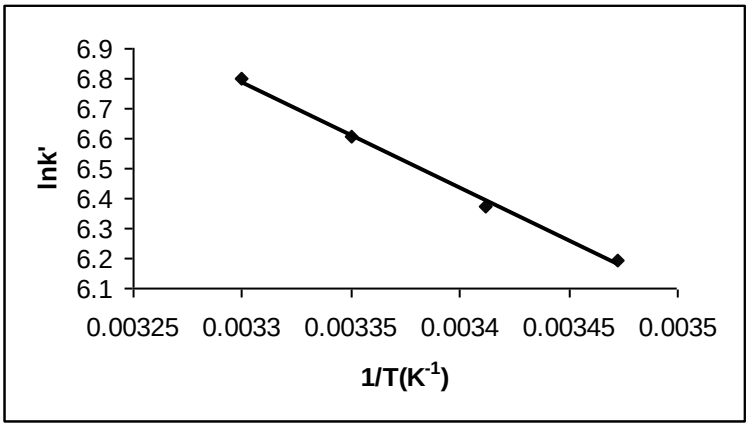

Figure 6: Plot of ln k´ vs. 1/T for determination of the energy of activation of the reaction between diphenylbenzidine and ascorbic acid

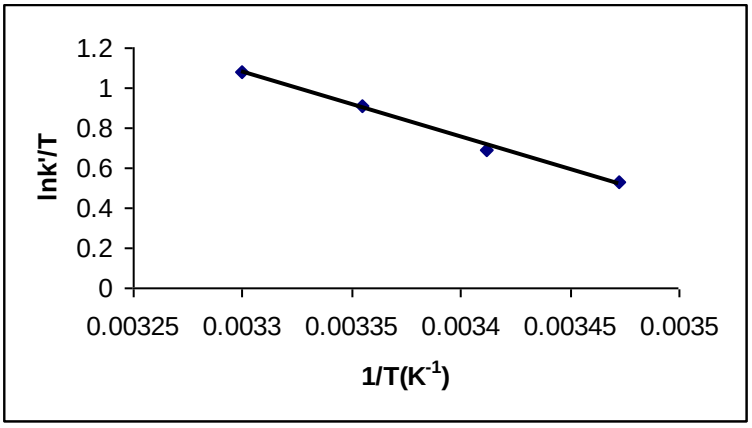

Figure 7. Plot of ln k´/T vs. 1/T for the determination of energy of activation of the reaction between diphenylbenzidine and ascorbic acid.

Table 1. Pseudo first order rate constant, k_{obs} , measured at four different concentrations of DPBD as a function of temperature. [ASC] = 3.33×10^{-6} mol dm^{-3}, λ_{max} = 570 nm, ε = 4920 dm^3 $mol^{-1}cm^{-1}$.

T (K)	[DPBD] 3.3×10^{-5} mol dm^{-3} k_{obs} $s^{-1}\times10^3 \pm$ S. D $\times10^2$	[DPBD] 5.0×10^{-5} mol dm^{-3} k_{obs} $s^{1}\times10^3 \pm$ S. D $\times10^2$	[DPBD] 6.6×0^{-5} mol dm^{-3} k_{obs} $s^{-1}\times10^3 \pm$ S. D $\times10^2$	[DPBD] 8.3×10^{-5} mol dm^{-3} k_{obs} $s^{-1}\times10^3 \pm$ S. D $\times10^2$
288	15.33 ± 1.00	22.50 0.20	33.53 ± 0.50	42.10± 0.30
293	20.62 ± 0.20	29.18 ± 0.20	39.34 ± 0.50	48.42 ± 0.01
298	26.60 ± 0.07	37.50 ± 0.50	49.90 ± 0.70	60.02 ± 0.07
303	31.00 ± 0.01	41.40 ± 4.00	59.00 ± 0.20	76.80 ± 1.0

Table 2. Second order rate constant obtained by plotting k_{obs} vs. [DPBD] .(pH = 4.0, [ASC] = 3.3×10^{-6} mol dm^{-3}.

Temperature	15 °C	20 °C	25 °C	30 °C
k′ (dm^3 $mole^{-1}$ s^{-1}) $\times10^{-2}$	4.91 ± 3.30	5.86 ± 0.19	7.40 ± 0.21	8.95 ± 0.7

Table 3. Thermodynamic parameters for the reaction of DPBD with ascorbic acid.

E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
30.00 ± 0.56	28.00 ± 0.34	-99.21± 0.05

then $e^{\Delta S^{\neq}/R}$ is the sole factor which determines whether the reaction goes faster or slower than normal. Negative value of $\Delta S^{\neq}$ means that the activated complex in the transition state has a more ordered or rigid structure than the reactants in the ground state. This is generally the case if on going from the ground state to the transition state degree of freedom of translation, rotation or vibration is frozen. For organic molecules it agrees with contemporary views of the SN^2 transition state according to which two independent reactant molecules combine to form a single transition complex.

With the help of the entropy of activation values, it can be proposed that the ordering of solvent molecules around the activated complex is less as compared to its value around the individual reactants.

Changes in the entropy of activation resulting from electrostatic interactions between neutral molecules are generally small. However, substantial changes can arise if a reactant molecule or the activated complex has high dipole moment. As a result the complex tends to bind solvent molecules much more strongly than do the reactants molecules. This effect results in considerable negative entropy of activation and correspondingly low frequency factor.

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