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KINETIC AND THERMODYNAMIC STUDIES FOR OXIDATION OF CARMINIC ACID BY HYDROGEN PEROXIDE

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ABSTRACT

Kinetics and thermodynamics studies for oxidation of carminic acid (CA) by hydrogen peroxide (H_2O_2) were investigated. The oxidation process was carried out under pseudo first order for both of CA and H_2O_2 at different temperatures (293, 298, 303, 308 and 313 k) and different dielectric constant by using 0, 20, 40 and 60% ethanol-water solvent. The optimum pH for oxidation was 5. Thermodynamics parameters like enthalpy, entropy, activation energy and Gibbs free energy for all temperatures and dielectric constants were calculated according to Eyring equation. Thermodynamics values found to be increased as the dielectric constant decrease. Second and pseudo first order rate constants found to be decreased as the dielectric constant increase and as the temperature increase. All thermodynamic parameters except Gibbs free energy possess negative values, which is mean the reaction is exothermic and the products is more stable than the reactants as long as the entropy for reactions have high negative values.

KEYWORDS: carminic acid, Eyring equation, oxidation by H_2O_2.

INTRODUCTION

One of the important thinks in food production is the appearance of food beside its taste therefore food producers take into account the outlook of the foods because the natural colors may be lost during processing. Currently synthesis colors are discerned to be harmful or undesirable[1-3]. These synthesis colors have been restricted to be used as food additives by European Union and United States [4]. Because of these restriction the demands for natural dyes was increased. One of these natural colorants is carminic acid (CA) (fig 1)[5]. CA, 7-b-d-glucopyranosyl-9, 10-dihydro-3, 5, 6, 8-tetrahydroxy-1-methyl- 9,10-dioxo-2-anthracenecarboxylic acid according to IUPAC, from the structure C.A is anthraquinon glycoside have a lot of acidic centers. The highest acidic site is a carboxylic group present in second carbon atom pka (2.6), the 6-hydroxyl group consider as acid base equilibrium as long as pka (5.4), while 5 and 8 hydroxyl groups have pka (8.5 and 12.2) respectively so this sites is less acidity because of its position with respect to carbonyl group which restrict the mobility of hydrogen through hydrogen bonds [6]. C.A is low toxicity red dye widely used in food and cosmetic extracted from eggs and body of insect Dactylopius coccus, or known as cochineal[7-10]. CA shows high solubility in aqueous solutions, intense redox activity [11-12]. Because of these properties in redox activity the color intensity of food can be reduced due to oxidation of hydroxyl group on CA. hydrogen peroxide H_2O_2 is one of the oxidant reagent. Which is inorganic molecular can be used as hair dyes, in medical for cleaning the wounds, and industry such as pulp and paper bleaching[13]. The oxidation by hydrogen peroxide gives water as byproduct therefore, it can consider as a unique oxidation reagent [14]. The restriction of using hydrogen peroxide in organic reactions as oxidant is inevitable of present of water as reaction product and as solvent in commercial hydrogen peroxide. A few papers were published for using of hydrogen peroxide in organic oxidation reactions [15-17]. Hydrogen peroxide was used as oxidant in this paper because of there's no byproduct can interfere with CA, and it's easy to cheek the decrease the color intensity of CA during oxidation process. Physical properties that effected by interatomic and intermolecular attraction is called dielectric constant, which is indicator for the ability of the electrolytes to separate into ions. High dielectric constants for solvents encourage complete electrolyte dissociation, while low dielectric constant, and encourage formation of ion pairing [18]. At high medium of dielectric constant the probability of formation of more polar transition state is a favorable [19]. The effect of dielectric constant on the oxidation of CA was studied in this paper by varying the concentration of ethanol in solution (0, 20, 40, and 60%).
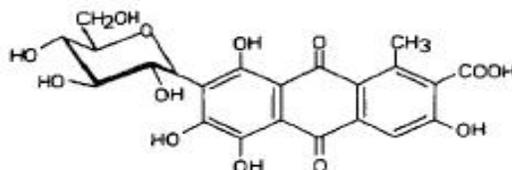

FIGURE 1: molecular structure for carminic acid.

MATERIALS & METHODS

All chemical were supported by Aldrich.

CA was dissolved in 0.02N HCl, the concentration of pure solution can be measured by using spectrophotometric technique (UV-9200) at 494nm according to lambert and beer law equation (1).

$$C \ (g.L\text{-}1) = \frac{A*f*492.39}{5800} \quad \text{......} \ (1)$$

Where A is the absorbance of sample, (f) Is dilution factor, 492.39 is the molecular weight of CA in $(g.mol^{-1})$, 5800 is extinction coefficient for CA in $(mol^{-1} \ cm^{-1})$. The experiments carried out under pseudo-first order conditions where the value for one of the reactants is excess over then the other one. The reaction with respect to hydrogen peroxide carries out by mixing equal amounts of 10^{4-} N CA and 1N H_2O_2, the absorbance was recorded for different time intervals. This experiment repeated at different dielectric constants (0, 20, 40, 60 % ethanol-water solution) and different temperature (293,298,308 and 313 k). Same procedure repeated to find kobs with respect to CA by mixing equal amounts of 10^{2-} N CA with $5* 10^{3-}$N H2O2 at (293,298,303,308 k).

RESULTS & DISCUSSION

The effect of pH on the reaction were studied at pH (2, 4, 5, 6, 8, 10) the optimum pH for oxidation found at pH 5 where is the value of (kobs) 0.2 s^{-1} at 20 °C and concentration of 1N H2O2 and 0.01N CA. the values of kobs for each reaction were calculated though the equation (2).

$$ln[A_t] = ln[A_0]\text{-}kobs \ t \quad \text{.....}(2)$$

Where $[A_t]$ the absorbance at any time, $[A_0]$ the absorbance at initial time, (kobs S^{-1}) is pseudo first order rate constant and (t) time in min. by plotting $ln[A_t]$ vs t the values of kobs can obtained through the slope. Second order rate constant k_2 can be calculated through the relation $k_2 = kobs/[H2O2]$. Thermodynamics parameters (enthalpy H and entropy S) can be calculated though Eyring equation (3).

$$ln\left(\frac{k2}{T}\right) = ln\frac{kB}{h} + \frac{\Delta S\ddagger}{R} - \frac{\Delta H\ddagger}{RT} \quad \text{.......} (3)$$

Where is k2 second order rate constant $(mol^{-1}.S^{-1})$, T temperature in (kelvin), k_B Boltzmann constant, h plank constant, $\Delta S\ddagger$ entropy in $(J \ K^{-1} \ mol^{-1})$, $H\ddagger$ enthalpy in $(KJ \ mol^{-1})$, and R is gases constant $(8.314 \ J \ K^{-1} \ mol^{-1})$. The value of $ln\frac{kB}{h} = 23.76$ hence equation (3) become.

$$ln\left(\frac{k2}{T}\right) = 23.76 + \frac{\Delta S\ddagger}{R} - \frac{\Delta H\ddagger}{RT} \quad \text{.....} (4)$$

By plotting ln(k2/T) vs 1/T the enthalpy can be calculated from the slope, while the entropy can be calculated from the intercept. The activation energy of the reaction can calculated from the equation (Ea = H‡ + RT) (19, 20). Gibbs free energy G in (KJ) calculated from the equation (G = H - T S). the data in table 1 and 2 reveals the values of k2 decrease by increase the temperature for booth of the reactions (with respect to CA and H2O2). This decrease can explain according to Le Chatelier's principle (any stress like changing in concentration, pressure or temperature is inflicted on the reaction equilibrium; the reaction will shift to restore the equilibrium). As long as the enthalpy H of the reaction have negative values then the reaction is exothermic. Therefore, The elevation in temperature of the system by external source this will add more stress on the reaction besides the other parameters that affect the reaction (concentration) remind unchanged hence the rate constant will decreased for both kobs and k2. Similarly the values of kobs and k2 decrease as the percentage of ethanol increase (decrease in dielectric constant). This decrease can attributed to the fact, as the dielectric constant increase the ability of electrolyte to separate into ions increase therefore, the rate constant of the reaction increase as the concentration of ethanol in solvent decrease.

TABLE 1: values of pseudo first order (kobs) and second order (K2) rete constants at o.oo5 N of H_2O_2 and 0.01 C.A for different temperatures.

	293 K		298 K		303 K		308 K	
Ethanol %	Kobs	K2	Kobs	K2	Kobs	K2	Kobs	K2
0%	0.0253	5.08	0.0213	4.26	0.0128	2.56	0.00325	0.65
20%	0.0235	4.7	0.01395	2.79	0.0041	0.82	3	0.6
40%	0.0144	2.88	0.006	1.2	0.00184	0.368	0.00154	0.308
60%	0.00879	1.75	0.00445	0.89	0.0016	0.32	0.0015	0.3

TABLE 2: the values of ln(k2/T) for different dielectric constants and different temperatures at 0.01N C.A and 0.005 N H_2O_2.

Ethanol%	293 k	298 k	303 k	308 k
0%	-4.05	-4.24	-4.77	-6.16
20%	-4.13	-4.67	-5.91	-6.24
40%	-4.62	-5.5	-6.71	-6.8
60%	-5	-5.8	-6.85	-7.3

TABLE 3: values of pseudo first order (kobs) and second order (k2) rete constants at H2O2 (1 N) and o.oo5 N of C.A and for different temperature.

	293 K		298 K		308 K		313 K	
	Kobs	K2	Kobs	K2	Kobs	K2	Kobs	K2
0%	0.0638	12.6	0.045	9	0.0365	7.3	0.002	4
20%	0.0381	7.62	0.0331	6.62	0.0255	5.1	0.0186	3.72
40%	0.0337	6.74	0.0326	6.52	0.023	4.6	0.0144	2.82
60%	0.0303	6.06	0.022	4.4	0.018	3.6	0.01158	2.31

TABLE 4: the values of $\ln(k2/T)$ for different dielectric constants and different temperatures at 1N H_2O_2 and 0.005N C.A.

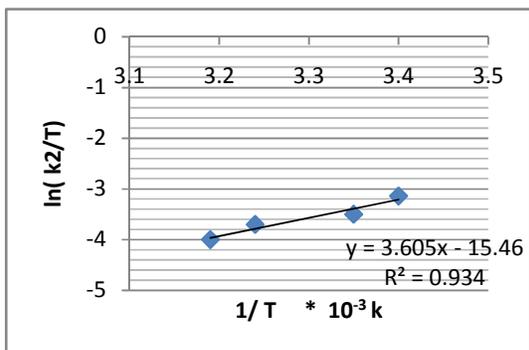| Ethanol %	293 k	298 k	308 k	313 k
0%	-3.14	-3.5	-3.7	-4
20%	-3.64	-3.8	-4.1	-4.56
40%	-3.77	-3.98	-4.2	-4.7
60%	-3.87	-4.21	-4.45	-4.86

FIGURE 2: Erying plot for % 0 ethanol at 0.005N CA.
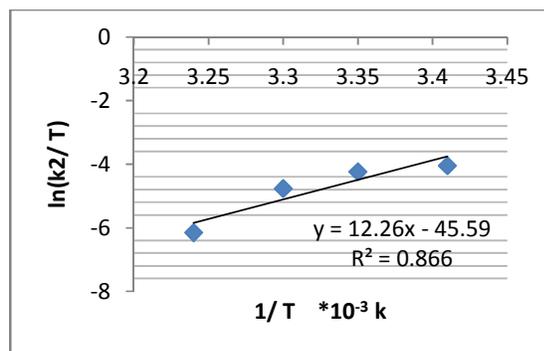

FIGURE 3: Erying plot for % 0 ethanol at 0.005N H_2O_2.
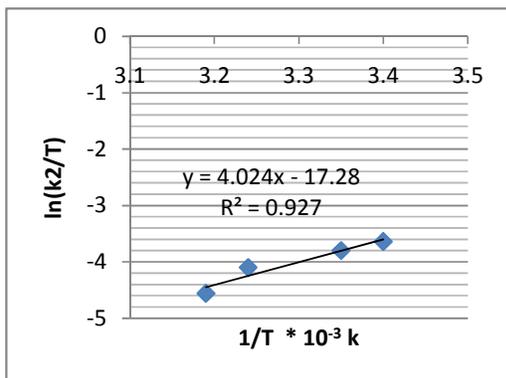

FIGURE 4: Erying plot for % 20 ethanol at 0.005N CA.
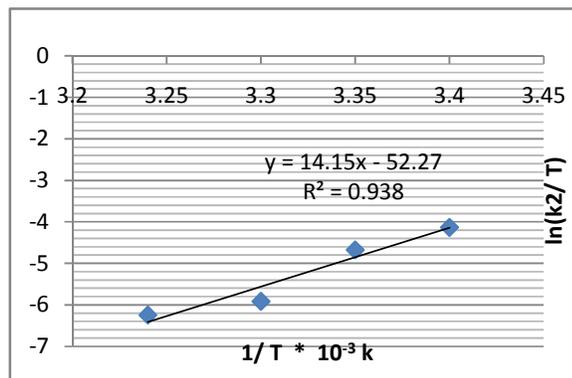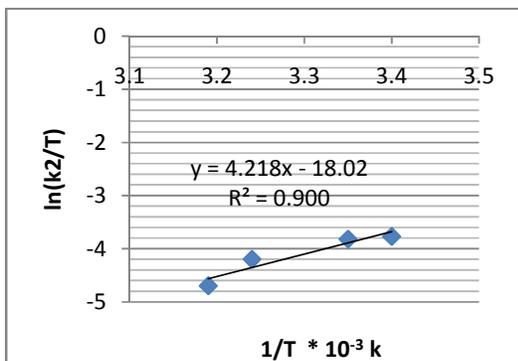

FIGURE 5: Erying plot for %20 ethanol at 0.005N H_2O_2.

FIGURE 6: Erying plot for % 40 ethanol at 0.005N CA.
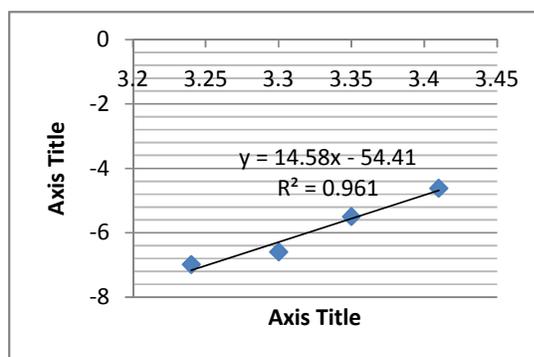

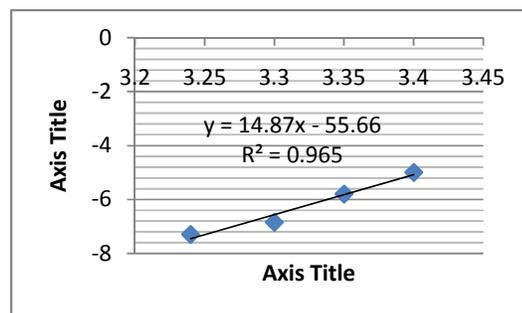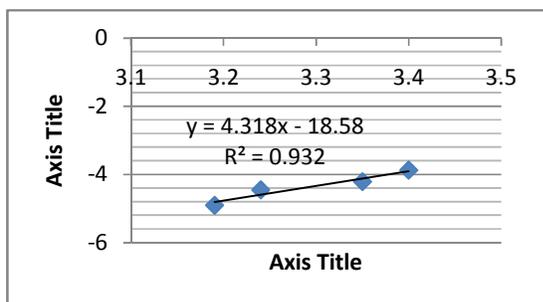**FIGURE 7**: Erying plot for % 40 ethanol at 0.005N H_2O_2.

FIGURE 8: Erying plot for % 60 ethanol at 0.005 N CA.

FIGURE 9: Erying plot for %60 ethanol at 0.005N H_2O_2.

TABLE 5: thermodynamic parameters for oxidation at mean temperature 303k, CA 0.005 N   and H_2O_2 1N

Ethanol %	H kJ. mol^{-1}	S $J.K^{-1}.mol^{-1}$	G kJ. mol^{-1}	Ea kJ. mol^{-1}
0%	-29.97	-326	68.8	-27.45
20%	-33.42	-341.26	69.97	-30.91
40%	-35.06	-347.39	70.199	-32.55
60%	-35.9	-352	70.756	-33.39

TABLE 6: thermodynamic parameters for oxidation at mean temperature 300.1 k, CA 0.01 N and H_2O_2 0.005 N

Ethanol %	H kJ. mol^{-1}	S $J.K^{-1}.mol^{-1}$	G kJ. mol^{-1}	Ea kJ. mol^{-1}
0%	-101.99	-576.57	71.26	-99.49
20%	-117.7	-632.17	72.26	-115.2
40%	-121.21	-649.94	74.1	-118.71
60%	-123.67	-660.3	74.75	-121.17

From the data of table 5 and 6 we can note that. The high values for negative entropy it's refers to the ability of compounds to convert from less stability reactant to more stability products. This may be due to tendency of tow molecules of reactants to convert to product of one molecule. Similarly the activation energy Ea has negative values this can be explained according to Arrhenius equation $\mathbf{k = A} e^{\frac{-Ea}{RT}}$, as long as the rate constants decreased by increase the temperature in this experiments and the exponential for previous equation where taken as $\mathbf{Ea = - RT\ ln(k/A)}$ then the activation energy will have negative values. Gibbs free energy   G has positive values which are meaning the reaction is spontaneous.

CONCLUSION

The reaction between carminic acid CA and hydrogen peroxide is second order reaction but it can consider as pseudo first order with respect both of reactants. The kinetics and thermodynamics for the reactions were studied under different conditions of varying pH, temperatures and dielectric constants. The optimum pH for oxidation was found to be 5. The values of kobs and k2 were decrease as the concentration of ethanol in water increase (decrease dielectric constant) also the values decreased as the temperature increase this can also confirm by the values of negative activation energy Ea which mean the rate of reaction decrease by increase temperature. Thermodynamic parameter shows negative values of enthalpy which is mean the reaction is exothermic. The negative entropy of reaction attributed to increase the stability of the product. All the thermodynamics parameters were increased by increase the concentration of ethanol in water (decrease dielectric constant).

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