KINETICS OF THE HYDROLYSIS OF AMIDES HAVING ARLY GROUP CATALYSED BY EXCHANGE RESIN OR AN ACIDIC SOUTION IN 1, 4-DIOXANE %30-WATER MEDIA

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Abstract

The mechanism of the n-benzoyl benzamide hydrolysis was studied in hetero and homogenous 30%(V/V) 1, 4-dioxane–water mixture within the temperature range between 60ºC and 100ºC.The reaction mechanisms was carried using a batch reactor method limited technique. The variation of the rate constant was found 2nd –order type with temperature in presence of a bulk solution consists of 30%, 40% and 50% 1, 4-dioxane .The efficiency ratio of an acid resin and acid solution has been measured and compared at a number of temperatures. Specific solvent effects on the reaction rate and mechanism have been investigated. The equilibrium in 10% and 20% 1, 4-dioxane has no determined because that the-amide did not soluble in water solution .The equilibrium conversion of the benzoyl benzamide was found to increase with an increase of reaction temperature and with the catalytic loading. Energy of activation (E_a) and the thermodynamics parameters such as: ΔG^*, ΔH^* and ΔS^* were calculated by applying the Arrhenius and van’s Hoff equation in the range of temperature mentioned before.

Key words: Amide hydrolysis, Ion exchange catalysis, Hydrolysis of organic materials.

General abstract;

Primarily the hydrolysis of amides is a reaction with water. Amides are hydrolysed in presence of cation exchanger or hydrochloric acid. The acids of both are act as a catalyst for the reaction between the amide and water. The final products would contain ammonium form of exchanger and of chloride and bi-products of carboxylic acid.

$$C_6H_5CONHCH_2C_6H_5 + H_2O + H^+ \rightarrow C_6H_5COOH + C_6H_5CH_2OH + NH^+_4$$

Introduction

Few or no studies however have ever focused on how the solid acid or acid solution affects on the hydrolysis of amide likes benzoyl benzoate. In spite of the long history of hydrolysis of esters [1-2] or a few literatures has been carried out on aliphatic amide or aryl amide in the presence of salts or acid [3-6]. They concluded that the reactions include two water molecules as reactants to obtain tetrahedral intermediate in ester hydrolysis, while in amide mechanisms there is a further one step in the medium needed for produced the final products ,acid and ammonium ion for complete of hydrolysis as the following mechanisms;

$CH_3\text{-}CO\text{-}NH_2 + H^+ \leftarrow\rightarrow CH_3\text{-}CO^+HNH_2 \leftarrow\rightarrow H_2O \rightarrow CH_3 - C\ \text{-}OH\ O^+H_2$
$\text{-}NH_2 \leftarrow\rightarrow H_2O \leftarrow\rightarrow CH_3\text{-}\ C\ (OH)_2\ NH_2 \rightarrow H^+ \rightarrow CH_3\ \text{-}HC\ (OH)\ \text{-}NH_2 \leftarrow\rightarrow CH_3C$
$(OH)_2\ N^+H_3 \leftarrow\rightarrow CH_3\text{-}CO^+H\text{-}(OH) + NH_3 \leftarrow\rightarrow CH_3\text{–}COOH + NH_4^+$ [4]

Other attempt was made to determine the number of water molecules needed from ground state to transition state in acid catalysed hydrolysis of amide using relative first order rate constants with activity coefficient term independent expression of acid amide hydrolysis [7]

In many reactions of ion exchange resins have been found to offer better selectivity towards the desired products [8].The use of ion–exchange resins as solid catalysts have many advantages over homogenous acid catalysts. They can be separated from liquid reaction mixture by filtration or decantation and have high selectivity [8].However the hydrolysis of amide or ester in the presence of ion exchange resins as catalyst has received much less attention than the reaction in homogenous medium. Therefore the resin catalysed hydrolysis of amides is controlled by (a) film diffusion, (b) chemical reaction within the catalyst beads and (c) chemical reaction at the particle surface. From (a) and (c) the rate is inversely proportional to the particle size for a given amount of catalyst. Whereas (b) is established when the overall rate is independent of the particle size with a given amount of the catalysts .Often the overall rate is a combination of inter-particle reaction and intra-particle diffusion. The latter factor was found affects the rate but it can never be the sole rate determining step [9].

Therefore the focus of the present study was to provide a fundamental insight into the similarities and differences existing between acid in solution and a solution containing a solid acid catalyst Purolite C-100 cation exchange resin in H-form in the hydrolysis of the amide. The resin exchanger is strongly acidic in behaviour and with stand temperature up to slightly not than 105^{0}C [9]. Determination of reaction kinetic parameter together with the derivation of the analytical kinetic model able to satisfactorily explain our experimental observation led to some important why resin used. Activation energy (Ea) and thermodynamic parameter of free energy ΔG*, enthalpy ΔH* and entropy ΔS* of activations were calculated from the acid hydrolysis of benzoyl benzoate in 30% 1, 4-dioxane, and compare the results with those in HCl –medium-30% 1, 4-dioxane The other objective was to study the catalytic efficiency of the resin in 30% isopropyl alcohol and acetone -water media

Experimental:

The reactor consists of a three necked Pyrex flask of 500ml capacity fitted with a spiral reflux condenser 100cm long at one side –arm, the middle fitted with thermometer equipped with magnetic stirrer. The temperature was controlled within ±0.1C by circulating water from a thermo-state into the cylindrical water-jacket of the reactor. The reaction mixture was magnetically stirred at about 600 rpm.

Materials; N-benzoyl benzamide (M.wt.211.26) (ACROS) immiscible in pure water, hydrochloric acid (PRS), 1,4-dioxane, phenolphthalein (GPR) ,paraffin wax (BDH), Methyl orange(PA-ACS) and Purolite C-100 strong cation exchange resin 3.816 m.eq, supported from Co-Red-word city Calif. USA. The reaction was realized in solution consist of 1, 4-dioxane 30 %(V/V) and 70% water (V/V). All aqueous solutions used in the analysis are prepared with bi- distilled water. One millitres of liquid sample was withdrawn from the flask reactor are a regular intervals for analysis.

Procedure; In a typical procedure 30%(V/V) 1,4-dioxane and the reactants N-benzoyl benzamide were placed in the reactor to obtain of 250 ml volume .The steady state value of the desired temperature bath was attained at such of temperature reach taken the zero time for run.

Analysis; The converted of benzoic acid was determined by standardized 0.1M NaOH. By that analysis it was found that the concentration of species of acid is therefore determined the remaining unconverted ester. From the titration the reaction consider to be determined completely. The reaction rate is determined with batch operation at 60°C, 80°C, and 100°C with an equivalent amount of ion exchange resin in H-form 0.05M and 0.01M, 0.02M and 0.05M of amide were employed. The rate constants in the presence of exchange resin 0.01M, 0.02M and 0.05M were compared with those of a volume containing an equivalent amount of hydrogen ions of liquid solutions from HCl.

Establishment of the rate determining step; the all cases under investigation the order of the chemical reaction in the presence of solid catalyst was found to be the same at in liquid catalyst. This emphasized that the reaction mechanism was the same in both cases.

The equation of the first order in the same of an equal concentration is:

$$K_r=2.303/T.w \log a/ (a - x)] \qquad -1$$

While in case of unequal concentration of both acid and amide the equation taken is;

$$K_r = 2.303 /T.w (a - b) [\log b (a - x)/ a (b - x)] \qquad -2$$

$$K_r = 2.303 /T.w (b - a) [\log a (b - x)/ b (a - x)] \qquad -3$$

Those are employed in case of solid exchanger catalyst hydrolysis of amide (benzoyl benzamide), where K_r- is the specific rate constant of the reaction, w- weight of the dry resin, T- is absolute temperature and a, x- are the concentrations of final acid concentration at equilibrium and of the acid librated at interval of time of hydrolysis respectively.

Net reaction energy and pseudo-thermodynamic parameters of the hydrolysis of amide were calculated. From absolute rate theory, the rate constant is related to free energy of activation ΔG*by equation (4).

$$K_r = k T /h \exp (- \Delta G^* /RT) \qquad -4$$

Where k- is the Boltzmann constant, h- is the Plank's constant, R and T have their usual meanings. The entropy of activation (ΔS*) can be calculated from the rate constant equation (5) using Eyeing rate theory

Ladler or from its relation with (ΔG*) equation (6)

$$K_r = k T / h \exp \Delta S^* / R \exp (-\Delta G^* / RT \qquad -5$$

$$\Delta G^* = \Delta H^* - \Delta T \Delta S \qquad -6$$

Where ΔH* is the enthalpy of activation calculated from its relationship with activation energy of reaction hydrolysis Ea equation (7) or from (6)

$\Delta H^* = Ea - RT$ -7

Activation energy Ea was calculated by equation (8) given by Adamson.

$\mathrm{Log}\ k_2 / k_1 = Ea / 2.303R \{1/T_1 - 1/T_2\}$ -8

Where k_1 and k_2 are the specific rate constants at T_1 and T_2 respectively.

Results and discussion

The hydrolysis reaction of benzoyl benzamide ($C_6H_5CONHCH_2C_6H_5$) was studied in a batch reactor in presence of acidic ion exchange resin Purolite C-100 as a catalyst. A pseudo – homogenous model has been used to describe the hydrolysis reaction catalyzed by ion exchange resin. The effect of temperature, catalyst load, amide concentration, organic solvents (1, 4-dioxane in different proportions), isopropyl alcohol and acetone at 30% V/V with water were studied. Unfortunately benzoyl benzamide has obtained a limited range of miscibility with pure aqueous within 0.0 to 25% V/V organic solvents. Therefore the hydrolysis of amide was used in this media to complete of reaction. On this bases the infinity values obtained water 70%-30%1, 4-dioxane and in different mixtures above of these composition. This assured the complete hydrolysis even in the presence of 30%V/V 1, 4-dioxane.This proves that 1, 4-dioxane alters the reaction rate without influencing the mechanism. Second-order rate constant in litre/mole/sec. were measure in the various reactions during the study of the hydrolysis of amide in the 1, 4-dioxance, acetone and isopropyl alcohol –water mixtures.

Catalyst performance:

In Table (1) a comparison of the behaviour of the Purolite C100 strongly cation exchange resin and HCl solution as catalyst is shown. Catalysts were used to assess their efficiency in the hydrolysis reaction of amide. Purolite C-100 is shown to be higher effective catalyst for hydrolysis of amide than of hydrochloric acid in the same of H^+-concentration in this range of concentrations. It is an expected result due to that of the ion exchange resin has higher volume surface area and high adsorption.

The effect of catalytic loading on the hydrolysis of benzoyl benzamide or the initial reaction rates and represented in Table (1) and Fig (1). Catalyst loading was varied from 2.6205, 3.275 and 3.930 g of dry resin at total of molar ion concentration 0.04M, 0.05M and 0.06M and amide concentration 0.05M in presence of 30%V/V 1,4-dioxane with total volume 250ml. It was seen that the conversion of hydrolysis of amide increased with an increase in the catalyst loading. Thus the time required to reach to the increase in the total number or molar of ion exchange resin sites available. Also the catalyst loading has an effect on the percent conversion. It show that from the figure (1) that the higher catalyst loading due to the greater hydrolysis of benzoyl benzamide. In this case it was found also that the specific of rate constant is proportion directly with the catalyst Fig (1). In a further addition of solid catalyst the rate of acid hydrolysis did not influenced with H^+-ion concentration at higher amount of resin. On other hand the velocity of homogenous catalytic reaction was found is greatest with further the addition of hydrochloric acid to convert amide into acids. When the acid increased beyond this point the acid may be combines with the anion to form an un-dissociated salt which does not reacting water and hence the velocity may constant. The mechanism of the reaction of benzoyl benzamide under acidic condition in presence follows the following reaction

$$\mathrm{C_6H_5CONHCH_2C_6H_5{+}HR^*\leftarrow\rightarrow C_6H_5C{=}OHR^*NHCHR^*C_6H_5\rightarrow{+}H_2O\leftarrow\rightarrow C_6H_5COH}$$
$$\mathrm{R^*O^+H_2NHCH_2C_6H_5\rightarrow{-}R^*\leftarrow\rightarrow C_6H_5C\ (OH)_2NHCH_2C_6H_5\leftarrow\rightarrow}$$
$$\mathrm{{+}HR^*\leftarrow\rightarrow C_6H_5C(OH)_2N^+H_2R^*CH_2C_6H_5\leftarrow\rightarrow C_6H_5COOH{+}R^*HNH_2H_5}$$

Where R^*H is the cation exchanger in the present salt of benzoyl amide-form. This is converted to H^+–form easy with the use of hydrochloric acid to produce the exchanger and exchanger benzoyl ammonium

Effect of 1, 4-dioxane percent

The effect of the 1, 4-dioxane percent on the initial reaction rate and conversion was carried out at three different proportions 30%, 40% and 50% V/V to examine the influence of an the dielectric constant and the results obtained were shown in Table (2) .It clear that there was vary little effect of the percent in the 1, 4-dioxane 40% and 50%V/V,while a large difference of influences in between 30% and 40%V/V on the overall initial rate of the reaction. This implies that there was no resistance to mass transfer of amide to the external surface of the dielectric constant of phase solution and of the catalyst.

It is evident from the results in Fig (2) that the values of specific rate constant (k) for the hydrolysis of benzoyl benzamide decrease noticeably in the range of 30% to 40%V/V 1, 4-dioxane and then slightly on further successive addition of organic solvent in the range between 40% and 50%V/V. Primarily we note that the amide which was employed in this reaction immiscible in pure aqueous medium initially. But it soluble in

30% V/V: 70 % V/V water, and therefore it was considered that is the blank media for the reaction hydrolysis. The rate of acid hydrolysis of amide in 30%-1, 4-dioxane-water mixture on further addition of organic solvent decrease with increase of organic component in solvent mixture because (i)-water concentration decreases on successive addition of 1, 4-dioxane, (ii) - A water molecule involved in hydrogen bond formation with amide molecules is less nucleophelic than that involved on hydrogen bond formation with another molecule of water. Thus will appear in the expected bi-molecules mechanism (iii)-The proton donating tendency of the medium falls on successive addition of 1, 4-dioxane to the aqueous external medium up to 50% V/V .This, when the 1, 4-dioxane concentration in the external medium increases the H_2O^+ ions were replaced by the organic solvated, and the acidity decreases with decreasing water constant through this range of solvent concentration. This has been explained in terms of gradual breakdown of quasi-crystalline tetrahedral structure of water [7]; (IV) - Addition of 1, 4-dioxane to water lowers the dielectric constant of the medium [8]. Thus from an electrostatic view point, a rate decrease might be expected because of destabilisation of polar transition state when the bulk of dielectric constant is lowered by successive addition of organic solvent. Since highly polar transition state is more strongly solvated relative to the less polar ground state. It is expected that as the solvent polarity decreases the reaction rate decrease.

Effect of amide concentration:

The results are presented in amide concentration was varied from 0.01M to 0.05M at 100°C and 30% V/V 1, 4-dioxane. It is found that the hydrolysis of benzoyl benzamide decreased with an increase in amide concentration. Therefore the time of attainment reach to equilibrium and the half life period increase with an increase of amide concentration. This can be explained in terms of the fact that due to conversion of H^+ form of the exchanger to NH_4^+ –form. When the amide increased that the total ionic strength of acidity a gradual decreases observed Table (3) and Fig (3).

Effect of the dielectric constant of the medium

The rates of the acid hydrolysis of amide increase with increase in dielectric constant of the medium. This can explained in terms of the fact the activated complexes are much more polar than the reactants. The acidity is appreciably reduced by further addition of solvents. The tetrahedron structure of water has been broken by successive addition of solvents in spite the soluble of amide it is dependant on solvent addition and so the proportion of free water molecules decrease as the water activity decreases, since the highly polar transition state is more strongly solvated relative to less polar ground state. In the light of these effects the variation of the rate constant with solvent composition can be understood. The values of the dielectric constant of 1, 4-dioxane –water mixture were obtained by calculation and interpolation from [12] (c.f. Table 4)

Effect of organic solvents:

The estimated rate and the percent conversion along with the organic solvents (isopropyl alcohol and acetone) were investigated. The concentration of the reactants of amide and of solid catalyst at the same molar concentration of 0.05M and at 100°C water addition experiments used in presence of isopropyl alcohol and acetone 30%V/V to keep the total reaction volume constant at 250ml .Fig (4), shows that amide conversion on solid cation exchange resin (H^+-form) versus time (1,4-dioxane, acetone and isopropyl alcohol). The rate of conversion was significant inhibited with of high dielectric constant in the reaction mixture. [13] Have show when hydrolysis of amide is carried using a solvent as alcoholic solvents in presence of initial percent of amide hydrolysis decreases after alcohol solutions addition. The estimated rate is found second order for both isopropyl alcohol and 1, 4-dioxane as well as presented in Table (4),

Activation energies and pseudo-thermodynamic parameters:

The influence of temperature on the hydrolysis of benzoyl benzamide has been carried out and the data are presented in Table (5). It was seen that the conversion increases with temperature indicating an absence of mass transfer effects. It was observed that a plot of ln k_r versus 1/T Arrhenius plots Fig (4) to get the activation energy as 27.69KJ/mole which is a typical value of adsorbing controlled reaction. ΔS^* becomes negative. The $\Delta G^*$is a measure of the change in free energy in changing from reactant to activation complex was found 96.572, 100.802 and 105.115KJ/ mole suggesting that a further increase of amide conversion with temperature. Similarly the ΔH^* an index of heat energy and positive in sign Table (6) indicates an endothermic hydrolysis.

Conclusion:

The experimental work showed that the hydrolysis of benzoylbenzamide can successfully being carried out over of Purolite C100 cation exchange resin and HCl solution as heterogeneous and homogenous catalysts respectively. The reaction rate was higher over the heterogeneous that that over homogenous catalyst. The reactions of hydrolysis also were carried out in presence of different proportion of dioxane and at of 30 %(V/V) isopropyl alcohol and acetone solutions. At the same conditions the rate of reaction of hydrolysis was found are affected by organic solvents. A mathematical expression of kinetic equation was applicable for heterogeneous reaction catalysis as well as in homogenous one.

Table (1) Specific rate constant and percent conversion of benzoyl benzamide as function of resin loading inthe H^+-form at 100°C.

concentration of H^+ ion	Percent conv;%	k_r X10^3	K^* X10^{16}	time at equilibrium (min)
0.04M	70.00	11.284	14.525	280
0.05M	90.00	14.220	19.019	240
0.06M	92.00	14.498	18.663	240

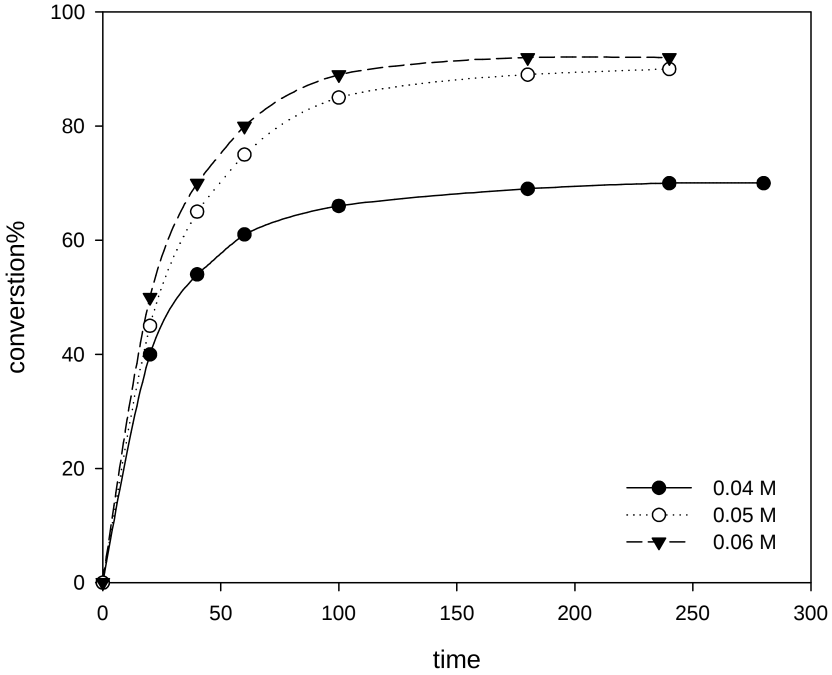

Fig (1): Plots of percent conversion against time/ min at different resin in the H^+-form concentration for amide

Table (2): Specific rate constant and percent conversion as a function of 1, 4-dioxane proportions for 0.05M amide hydrolysis at 100ºCinpresence of 0.05MH+-form of resin.

Concentration of amide ;M	Percent conv;%	$kx10^3$	K^*x10^{16}	time at equilibrium (min)
0.01M	98.00	22.227	28.612	100
0.02M	95.00	17.500	22.527	240
0.05M	90.00	14.220	19.019	240

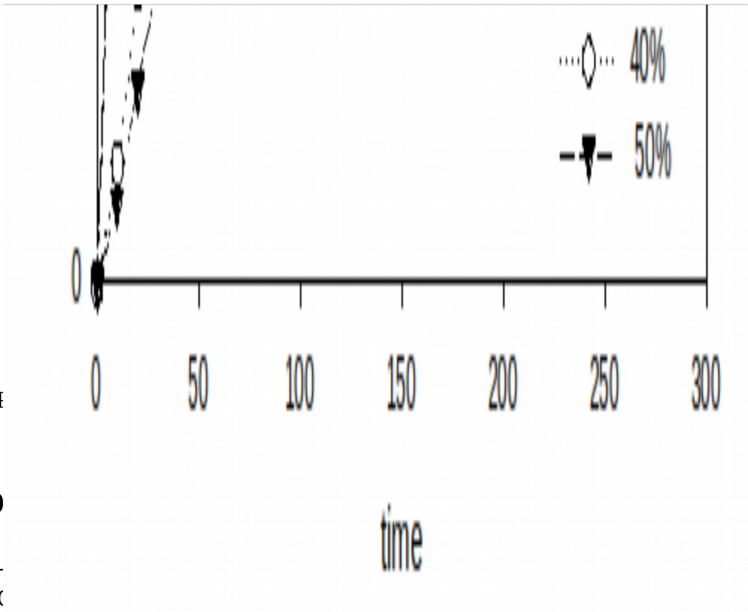

Fig (2): I **esence**

Table (3) **f amid**

(tion of amide ; M	conv;%			t um (min)
0.01M	98.00	22.227	28.612	100
0.02M	95.00	17.500	22.527	240
0.05M	90.00	14.220	19.019	240

Fig (3): Plots of percent conversion against time/min for amide hydrolysis at different concentrations of amide in presence of 0.05M H^+– form.

Table (4): Values of the specific rate constant and percent conversion as function of 30% V/V organic solvents for the hydrolysis of amide 0.05M at 100oC in presence of 0.05M cation exchange resin.

Percent of solvent (30 %,V/V)	Percent conv;%	$k_r X10^3$	$K^* x10^{16}$	time at equilibrium	$t_{1/2}$
1,4-dioxane	90.00	14.220	19.019	240	22.56
Acetone	84.00	14.180	19.438	180	22.07
Isopropyl alcohol	85.00	18.289	23.543	100	15.94

Table (5) Values of the specific rate constant and percent conversion as a function of different temperatures for the hydrolysis of amide at 0.05M H+- resin.

Temperature	Percent conv;%	$k_r X10^3$	$K^* x10^{16}$	time at equilibrium	$t_{1/2}$
60°C	68.00	4.9184	7.092	300	67.77
80°C	86.00	8.9089	12.118	300	37.41
100°C	90.00	14.220	19.019	240	22.56

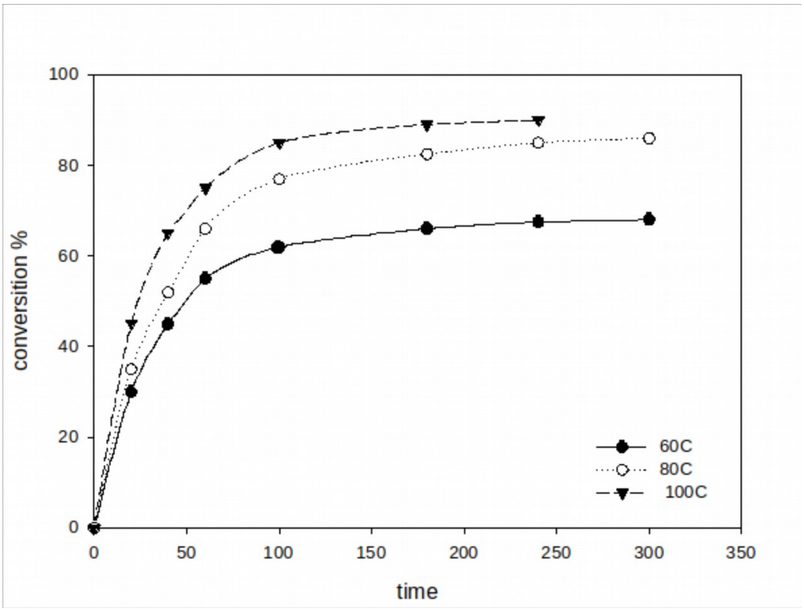

Fig (4): Percent conversion as a function of temperature for the hydrolysis of amide in presence of 30%V/V 1, 4-dioxane.

Table (6): Values of the thermodynamic functions for the hydrolysis of benzoyl benzamide in presence of 0.05MH+ of cation exchanger and 0.05M amide concentration

Tamp, K	$krx10^3$	K^*x10^{16}	Δ E* KJ/mole	Δ G* KJ/mole	Δ H* KJ/mole	Δ S* KJ/mole/ deg.	ln kr
333	4.918	7.091		96.572	24.921	-0.215	-5.314
353	8.908	12.118	27.690	100.802	24.755	-0.215	-4.720
373	14.220	19.019		105.115	24.588	-0.215	-4.214

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