

## STUDIES ON THE CATALYTIC HYDROLYSIS OF BENZAMIDE BY Bi-Mo-O CATALYSTS

M.A. WASSEL and R.A. SABER\*

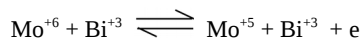
*Chemistry Department, Faculty Of Science , Al-Azhar University, Nasr City , Cairo , Egypt.*

\* National Organization for Drug Control and Research ,  
P.O. 29 , Cairo , Egypt.

### Abstract

The catalytic hydrolysis of benzamide over mixed oxides  $\text{Bi}_2\text{O}_3\text{-MoO}_3$  ,  $\text{Bi}_2\text{O}_3\text{-2MoO}_3$  and  $\text{Bi}_2\text{O}_3 - 3\text{MoO}_3$  , was carried out at initial concentrations of benzamide (0.03 and 0.07M), using variable amounts of catalyst 0.25, 0.50 and 1.0 gm/200 ml solution. The kinetic study was carried out at (25,35 and 45C°) and the effect of calcination time (30, 60, 90 and 120hr) was investigated, Such study revealed that the reaction is kinetically of first order type, and that the percent conversion increased with reaction temperature, quantity of catalyst, and also with increasing the ratio of  $\text{MoO}_3$  present in the catalyst, with the calcinations time .

In all steps of study the reaction rate is characterized by the presence of an induction period, in which the reaction velocity is slow, after which it is accelerated appreciably, is proposed that this period is sequence of the formation of some active sites on the surface of the catalyst. These active sites resemble themselves as ions ( $\text{Mo}^{+5}$  ) resulting form side reaction between ( $\text{Bi}^{+3}$ ) ions and ( $\text{Mo}^{+6}$ ) ions according to the following equation :



where the increase in formed ( $\text{Mo}^{+5}$ ) ions leads to the increase of the active sites, and consequently an increase in the reaction velocity. The activity in the catalytic hydrolysis of benzamide found to follow the following sequence of the prepared catalysts:  $\text{Bi}_2\text{O}_3 - \text{MoO}_3 < \text{Bi}_2\text{O}_3 - 2\text{MoO}_3 < \text{Bi}_2\text{O}_3 - 3\text{MoO}_3 < \text{Bi}_2\text{O}_3 - 3\text{MoO}_3$  (30hrs)  $< \text{Bi}_2\text{O}_3 - 3\text{MoO}_3$  (60hrs)  $< \text{Bi}_2\text{O}_3 - 3\text{MoO}_3$  (90hrs)  $< \text{Bi}_2\text{O}_3 - 3\text{MoO}_3$  (120hrs).

### Introduction

Mixed oxides have been usually prepared either by mechanical mixing of the oxides with good results, or by co-precipitation of the hydroxides or acetates of the metals followed by calcinations<sup>(1)</sup> . If the two oxides are merely mechanically mixed, the adsorption of the mixture should be equal to the sum of the adsorptions by the individual components . This is certainly true if the mixture is coarse, but if the mixing is intimate, approaching molecular or colloidal dimensions , the resulting mixture may have very different properties from the individual components<sup>(2)</sup> .

Mixed oxides have been employed successfully in many industrial catalytic processes since many decades , of the most familiar catalysts of these used is the

process of activation (e.g., molybdena-chromia or molybdena-cobalt oxide<sup>(1)</sup>, in cracking (e.g. silica-alumina<sup>(2)</sup> zinc oxide-chromia<sup>(3)</sup>, or manganous oxide-chromia<sup>(4)</sup>, in dehydration and aromatization (e.g., aluminaferric oxide-alumina). The rate of hydrolysis at 25°C of the following amides reaches a maximum in approximately the acid strengths shown<sup>(5)</sup>: benzamide, in 4-5 M hydrochloric acid or 3-5M sulphuric acid, p-methoxybenzamide, in 3M-sulphuric acid, p nitrobenzamide in 4-5 M-sulphuric acid. The rates of the acid-catalyzed hydrolysis of several amides go through a maximum as the concentration of acid is increased.

Acid-catalyzed amide hydrolysis<sup>(6)</sup> is generally considered to proceed by pathways involving irreversibly formed tetrahedral intermediates. Numerous <sup>18</sup>O-exchange studies with labeled benzamides and one occurs is recovered starting material during the course of hydrolysis in strongly acidic media. However, Slebocka<sup>(6)</sup> observed that 90% <sup>18</sup>O-enriched benzamide exhibited 0.2% exchange per  $t_{1/2}$  hydrolysis in 5.9% H<sub>2</sub>SO<sub>4</sub> at 85°C. Apparently, further increases in [H<sub>3</sub>O<sup>+</sup>] do not lead to additional <sup>18</sup>O exchange, at least for benzamides.

Wassel and Amira<sup>(7)</sup> studied the effect of sodium salts on the catalytic properties of Co-Mo oxide catalysts in the hydrolysis of acetamide by introduction of Na<sub>2</sub>-MoO<sub>4</sub>, NaCl and NaNO<sub>3</sub> in amounts containing more than 0.4 wt.% Na into Co-Mo oxide catalysts with a Co:Mo atom ratio of 2.5 and 1.55 decreases the activity of the initial samples by a factor of about 9. The selectivity remains unchanged. The introduction of sodium into supported catalysts leads also to a decrease in selectivity. An explanation of the observed effects is proposed by Paryjczak and co-workers<sup>(8)</sup> studied the influence of preparative conditions on specific area and porosity of supported Co and Mo catalysts, thus temperature, pH of precipitation, roasting temperature, the initial solution concentration and percentage contents of Co-Mo were studied. Roasting temperature (400°C) and pH of precipitation (4-5.5) were found to have an essential influence on the properties of the catalyst.

## Experimental

### Kinetic Measurements :

The catalytic activity, of the prepared catalyst towards hydrolysis of benzamide was evaluated in the liquid phase. Accurate weights of catalyst samples (0.25, 0.5 and 1.0 gm) were added to a stirred thermostated vessel containing 200 ml of benzamide of known concentration (0.05 and 0.07 M). The temperature of the reaction mixture was kept constant at the desired temperature within  $\pm 0.2^\circ\text{C}$  by

means of an ultra-thermostat and a double-jacketed cell. The kinetic measurements were carried out at different temperature ranges between 25 and 45°C. The route of the reaction was followed up by periodic withdrawing aliquots (5 ml) from the reaction mixture at definite periods of time (5 min) and the concentration of the resulting benzamide acid was determined by titration against sodium hydroxide solution (0.1 N).

### Results And Discussions

Surface Area of Prepared Catalysts :

The  $S_{\text{BET}}$  <sup>(9,10)</sup> values were calculated and given in Table (1) . The general trends of variation of  $S_{\text{BET}}$  with temperature of calcinations indicate that the surface area increases with the increasing of the calcination times of the catalysts from 15 hrs to 120 hrs . The highest surface area is obtained in case of 120 hrs calcinations , and lower values of  $S_{\text{BET}}$  is obtained in case of unclacinated  $\text{Bi}_2\text{O}_3\text{-MoO}_3$  catalyst . Hence , we could expect a mild increase in  $S_{\text{BET}}$  value by rising the calcination time to 120 hrs , and the sintering effect is no doubt in action . Calcination time for 15 hrs lead to drop in  $S_{\text{BET}}$  value , whereby we do have a stabilized crystal structure suffering to a great extent from sintering .

**Table (1) : Specific surface area of prepared catalysts .**

Catalyst	$S_{\text{BET}}$ ( m <sup>2</sup> /g )
$\text{Bi}_2\text{O}_3 - \text{MoO}_3$	1.23
$\text{Bi}_2\text{O}_3 - 2\text{MoO}_3$	1.64
$\text{Bi}_2\text{O}_3 - 3\text{MoO}_3$	1.97

### Kinetic Studies of Benzamide Hydrolysis in Presence of the Mixed Oxides $\text{Bi}_2\text{O}_3\text{-MoO}_3$ , $\text{Bi}_2\text{O}_3\text{-2MoO}_3$ and $\text{Bi}_2\text{O}_3\text{-3MoO}_3$ Catalysts :

The catalytic hydrolysis of benzamide over the mixed oxides  $\text{Bi}_2\text{O}_3\text{-MoO}_3$ ,  $\text{Bi}_2\text{O}_3\text{-2MoO}_3$  and  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$ , was carried out at different initial concentrations of benzamide (0.03 and 0.07 M), using variable amounts of catalyst ranged between 0.25 and 1.0 gm/200 ml solution In most cases the kinetic study was carried out at different temperatures (25, 35 and 45°C) .and the effect of calcination time (30, 60, 90 and 120 hr) was studied as in Table (2).

**(a) Kinetic studies of benzamide hydrolysis in presence of mixed oxide  $\text{Bi}_2\text{O}_3\text{-MoO}_3$ , catalyst at initial concentration of benzamide = 0.05 M :**

The catalytic hydrolysis of benzamide over  $\text{Bi}_2\text{O}_3\text{-MoO}_3$  catalyst was investigated at constant initial concentration of benzamide (0.05 M.) in presence of variable amounts of catalyst (0.25, 0.50 and 1.0 gm) at three different reaction temperatures of (25,35 and 45°C). Table (3) represent the degree of hydrolysis . It is clear from these amounts that the degree of hydrolysis increases with time as well as with increasing the amount of catalyst. In general, increasing the

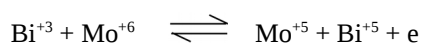
**Table ( 2 ) : Conditions of the kinetic studies on the catalytic hydrolysis of benzamide.**

1	Initial concentration of benzamide	0.05 M and 0.07 M
2	Temperature of the catalytic hydrolysis reactions C°	25°C, 35°C and 45°C
3	Amount of catalyst, gm/200 ml solution	0.25 gm, 0.5 gm and 1.0 gm
4	Types of catalyst.	$\text{Bi}_2\text{O}_3\text{-MoO}_3$ , $\text{Bi}_2\text{O}_3\text{-2MoO}_3$ and $\text{Bi}_2\text{O}_3\text{-3MoO}_3$ (uncalcinated)
5	Time of calcination (hrs)	$\text{Bi}_2\text{O}_3\text{-3MoO}_3$ (30 hrs) $\text{Bi}_2\text{O}_3\text{-3MoO}_3$ (60 hrs) $\text{Bi}_2\text{O}_3\text{-3MoO}_3$ (90 hrs) $\text{Bi}_2\text{O}_3\text{-3MoO}_3$ (120 hrs)

**Table ( 3 ) : Effects of Temperature and amount of  $\text{Bi}_2\text{O}_3\text{-MoO}_3$  catalyst on the degree of hydrolysis% of benzamide (initial concentration = 0.05 M.).**

Experimental	Temperature °C	Degree of Hydrolysis %
$\text{Bi}_2\text{O}_3\text{-MoO}_3$ (0.25 gm)/200 ml solution Benzamide (0.05 M)	25	53.0%
	35	56.4%
	45	59.2%
$\text{Bi}_2\text{O}_3\text{-MoO}_3$ (0.50 gm)/200 ml solution Benzamide (0.05 M)	25	61.5%
	35	65.6%
	45	69.4%
$\text{Bi}_2\text{O}_3\text{-MoO}_3$ (1.0 gm)/200 ml solution Benzamide (0.05 M)	25	71.6%
	35	74.8%
	45	78.0%

temperature of the hydrolysis reaction leads to an increase of the reaction rate. The slow rate of benzamide hydrolysis observed at the initial stage of the reaction indicated the presence of an induction period at the beginning of the reaction due to the formation of some active centers which will be accumulated on the surface of the catalyst. These active centers may be  $\text{Mo}^{5+}$  ions formed as a result of side reaction involving the interaction of  $\text{Mo}^{+6}$  ions with  $\text{Bi}^{+3}$  ions leading to the formation of  $\text{Mo}^{5+}$ . This can be illustrated as follows ;



Since, after a certain period (induction period), the number of active centers on the catalyst surface increased, the rate of benzamide hydrolysis after this period would take place more faster. These results are in accordance with the work of Wassel <sup>(11)</sup> for the catalytic hydrolysis of benzamide over the mixed oxide (NiO-CdO). On the other hand the induction period observed in the present study was found to decrease by increasing both the amount of catalyst and the temperature of the reaction. These results can be explained to be due to an increase in active centers resulting from increasing of the amount of catalyst, accompanied by increase in the number of active centers and that increasing the temperature may activate the side reactions involved.

**(b) Kinetic studies of benzamide hydrolysis in presence of mixed oxide  $\text{Bi}_2\text{O}_3$ - $\text{MoO}_3$  catalyst at initial concentration of benzamide = 0.07 M :**

The heterogeneous hydrolysis of benzamide in presence of  $\text{Bi}_2\text{O}_3$ - $\text{MoO}_3$  catalyst was carried out at constant concentration of 0.07 M, using constant amount of catalyst = 1.0 gm/200 ml solution at different temperatures (25, 35 and 45°C). The obtained results in table ( 4 ) which illustrate the degree of catalytic hydrolysis, with deferent temperatures It is clear that the degree of catalytic hydrolysis, % of benzamide increases with time and with increasing the amount of catalyst. The rate of catalytic hydrolysis of benzamide increased markedly with increasing temperature.

As mentioned before, the slow rate of benzamide hydrolysis observed at the initial stage of the reaction indicates the presence of an induction period at the start of reaction due to the formation of some active centers on the surface of the catalyst. The induction period decreases by increasing both the amount of catalyst and temperature. The first order plots ( $\log a/a-x$ ) vs (t) at different temperatures in

presence of different amounts of catalyst. These results are similar to those obtained previously at initial concentration of benzamide equal to 0.05 M. These results showed also that the values of degree of hydrolysis% and rate constant of benzamide hydrolysis increase with increasing both the amount of catalyst and the temperature of the reaction.

**Table (4) :** Effects of Temperature and amount of **Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>** catalyst on the degree of hydrolysis% of benzamide (initial concentration = **0.07 M**).

Experimental	Temperature °C	Degree of Hydrolysis %
Bi <sub>2</sub> O <sub>3</sub> -MoO <sub>3</sub> (1.0 gm)/200 ml solution Benzamide (0.07 M)	25°C	85%
Bi <sub>2</sub> O <sub>3</sub> -MoO <sub>3</sub> (1.0 gm) /200 ml solution Benzamide (0.07 M)	35°C	85.5%
Bi <sub>2</sub> O <sub>3</sub> -MoO <sub>3</sub> (1.0 gm)/200 ml solution Benzamide (0.07 M)	45°C	86%

The results of the catalytic hydrolysis of benzamide in presence of Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> at initial concentration of benzamide equal to 0.07 M, are higher as compared with the previous concentration of benzamide = 0.05 M.

**(c) Kinetic studies of benzamide hydrolysis in presence of mixed oxide Bi<sub>2</sub>O<sub>3</sub>-2MoO<sub>3</sub> catalyst at initial concentration of benzamide equal to 0.07 M :**

The third series of experiments in this study was carried out at constant concentration of benzamide of 0.07 M, using constant amount of catalyst (1.0 gm)/200 ml solution at different temperatures (25, 35 and 45°C). The degree of hydrolysis, % vs time curves obtained under these experimental conditions are presented in Table (5).

Similar to the results obtained previously, the rate of benzamide hydrolysis is slow at the initial period of the reaction indicating the presence of an induction period at the beginning of the reaction. Furthermore, the induction period was found

to be decreased by increasing both the amount of catalyst and the temperature of the reaction .

The first order plots  $\log (a/a-x)$  vs ( t ) under the aforementioned condition are show that the reaction of benzamide hydrolysis over  $\text{Bi}_2\text{O}_3\text{-}2\text{MoO}_3$  catalyst obeys first order kinetics. It seems that the values of the degree of hydrolysis%, are higher as compared with those for  $\text{Bi}_2\text{O}_3\text{-MoO}_3$ . This could be due to the chemical composition <sup>(12)</sup> , activation temperature of the catalyst <sup>(13,14)</sup>, the method of activation<sup>(15)</sup> and the temperature of catalytic hydrolysis <sup>(13,14)</sup>. Other important factors that contribute to the activity and selectivity are the texture and structure of the catalyst <sup>(16)</sup>

**Table ( 5 )** Effects of Temperature and amount of  **$\text{Bi}_2\text{O}_3\text{-}2\text{MoO}_3$**  catalyst on the degree of hydrolysis% of benzamide (initial concentration = **0.07 M**).

Experimental	Temperature °C	Degree of Hydrolysis %
$\text{Bi}_2\text{O}_3\text{-}2\text{MoO}_3$ (1.0 gm)/200 ml solution Benzamide (0.07 M)	25°C	86%
$\text{Bi}_2\text{O}_3\text{-}2\text{MoO}_3$ (1.0 gm)/200 ml solution Benzamide (0.07 M)	35°C	87%
$\text{Bi}_2\text{O}_3\text{-}2\text{MoO}_3$ (1.0 gm)/200 ml solution Benzamide (0.07 M)	45°C	88.5%

**(d) Kinetic studies of benzamide hydrolysis in presence of mixed oxide  $\text{Bi}_2\text{O}_3\text{-}3\text{MoO}_3$  catalyst :**

In this series of experiments the study was carried out at constant concentration of benzamide equal to 0.07 M, using constant amount of catalyst (1.0 gm)/200 ml solution and also at constant temperature (45°C). The degree of hydrolysis, % obtained in table ( 6 ) . Similar to the results obtained previously, the

rate of benzamide hydrolysis is low at the initial period of the reaction . The first order plots  $\log (a/a-x)$  vs (t) under the aforementioned conditions illustrate that the catalytic hydrolysis of benzamide over uncalcinated  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$  catalyst obeys first order kinetics. It seems that the values of the degree of hydrolysis is higher than that in case of  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$  .

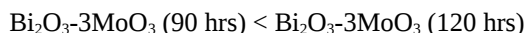
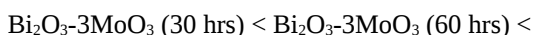
**Table ( 6 )** Effect of calcination time of  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$  catalyst (1.0 gm)/ 200 ml solution used in catalytic hydrolysis of benzamide (0.07 M) at 45°C on the degree of hydrolysis%.

Catalyst	Time of calcination hrs	Degree of hydrolysis, %
$\text{Bi}_2\text{O}_3\text{-3MoO}_3$	Uncalcinated (15 hrs)	91%
	30 hrs	92%
	60 hrs	93%
	90 hrs	95.02%
	120 hrs	96%

**(e) Effect of calcination time of  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$  catalysts on the catalytic hydrolysis of benzamide (Kinetic study):**

In this series of experiments, the study was carried out at constant concentration of benzamide = 0.07 M, using constant amount of catalyst (1.0 gm)/200 ml solution and at constant temperature (45°C), the catalysts being calcinated for different times (30, 60, 90 and 120 hrs) . The effect of the over all calcinations time in the  $\text{Bi}_2\text{O}_3 - 3\text{MoO}_3$  catalyst ( 1.0 gm ) / 200 ml solution used in catalytic hydrolysis of benzamide ( 0.07 M ) at 45 °C . On the degree of hydrolysis % . showed in Table (6)

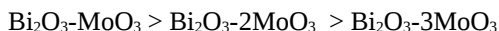
The kinetic studies of catalytic hydrolysis of benzamide over calcinated  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$  illustrate that the degree of hydrolysis in the increasing order :



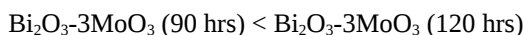
i.e. the degree of hydrolysis, % increased with increasing the time of calcination. It is probable that increasing the time of calcination lead to the growth of the  $\text{Bi}_2\text{O}_3\text{-3MoO}_3$



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 3MoO<sub>3</sub> crystals. The degrees, % of hydrolysis over uncalcinated Bi-Mo oxides decrease in the folloing order:



The degrees of catalytic hydrolysis of benzamide over all prepared catalysts under study (calcinated and uncalcinated) as in Table (7) the proceed according to the following sequence.



**(f) Mechanism of catalytic hydrolysis of benzamide :**

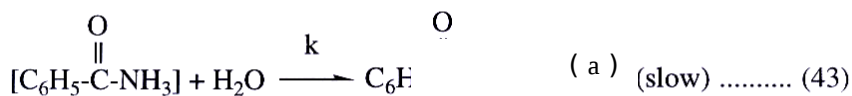
From the kinetic study it can be concluded that the Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> (2:1) catalyst showed relatively lower activity towards the benzamide hydrolysis which was generally intensified by using the mixed oxides Bi<sub>2</sub>O<sub>3</sub>-2MoO<sub>3</sub> (1:1) and Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (2:3) catalyst, (uncalcinated) or calcinated Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> catalyst. These results suggested that benzamide hydrolysis is promoted by a composite oxide of both components and the catalytic activity increases by increasing the amount of MoO<sub>3</sub> in the catalyst used. The mutual interaction between Bi<sup>+3</sup> and Mo<sup>+6</sup> ions leads to the accumulation of active centers consisting of Mo<sup>+5</sup> ions on the surface of the catalyst, and these active centers may increase with increasing the amount of MoO<sub>3</sub> in the catalyst. This concept is indirectly supported by the existence of Mo<sup>5+</sup> ions<sup>(17)</sup>, which serve as catalytic centers in the dehydrogenation of ethanol<sup>(18)</sup>.

**Table No. (37) :**

**Table (7)** Effect of catalyst structure used in the catalytic hydrolysis of benzamide on the degree of hydrolysis%. **(1.0 gm) catalyst / 200 ml solution initial benzamide concentration = 0.07 M and reaction temperature = (45°C).**

Catalyst	Degree of catalytic hydrolysis, %
<b>A) Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub></b>	86.00
<b>B) Bi<sub>2</sub>O<sub>3</sub>-2MoO<sub>3</sub></b>	88.50
<b>C) Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (15 hrs)</b>	91.00
<b>D) Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (30 hrs)</b>	92.00
<b>E) Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (60 hrs)</b>	93.00
<b>F) Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (90 hrs)</b>	95.02
<b>G) Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (120 hrs)</b>	96.00

Similarly in the hydrogenation of ethylene, the catalytic activity of MoO<sub>3</sub> has been found to increase with the progressive reduction of Mo<sup>+6</sup> to Mo<sup>+4</sup>. These two ionic species may interact to give Mo<sup>+5</sup> ions<sup>(18)</sup>. A modified mechanism in presence of heterogeneous uncalcinated catalysts [Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>-2MoO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub>, calcinated Bi<sub>2</sub>O<sub>3</sub>-2MoO<sub>3</sub> (30 hrs), Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (60 hrs), Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (90 hrs) and Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> (120 hrs). could be suggested as follows :



Under the condition where mechanistic paths in equations ( rate law as :

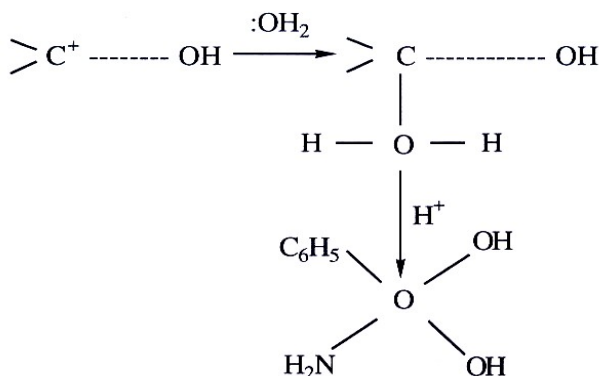
(b)  $2] \gg [H^+]$ , the could lead to the

$$\frac{-d [H^+]}{dt} = \frac{kK [H^+] [C_6H_5 - CO - NH_2]}{1 + K (C_6H_5 - CO - NH_2)}$$

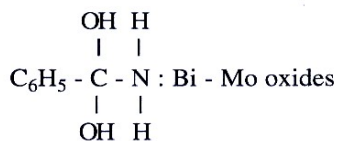
$$\text{Rate} = \frac{1}{(a)} [C_6H_5 - \overset{\overset{O}{\parallel}}{C} - NH_2] [H^+].$$

In acid medium, oxygen of the carbonyl group of benzamide catches proton to give  $(\overset{\overset{O}{\parallel}}{C} - NH_2)^+$ . This facilitates complete

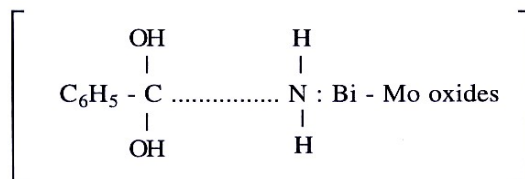
In acid medium, oxygen of the carbonyl group of benzamide catches proton to give ( $>C=^+O\text{H}$ ). This facilitates complete polarization of the double bond towards oxygen which creates positive charge on the carbon atom  $>C^+ \text{---} O\text{---}H \rightarrow C^+ \text{---} O\text{---}H$ . The positive carbon can react with water ( nucleophilic reagent ) to give:



It is suggested that the role of the catalyst is to make coordination bond with the lone pair of nitrogen electrons :



This coordination will weaken the C-N bond and consequently weaken the O-H bond ( $C \text{---} H$  and  $O \text{---} H$ ) and creates a partial P bond between oxygen and carbon ( $C \text{---} O$ ) to give the activated complex :



This activated complex will decompose to the benzoic acid, ammonia and the catalyst.

Possible scheme of benzamide hydrolysis on different types of the prepared mixed oxide catalysts could be represented as in following equations

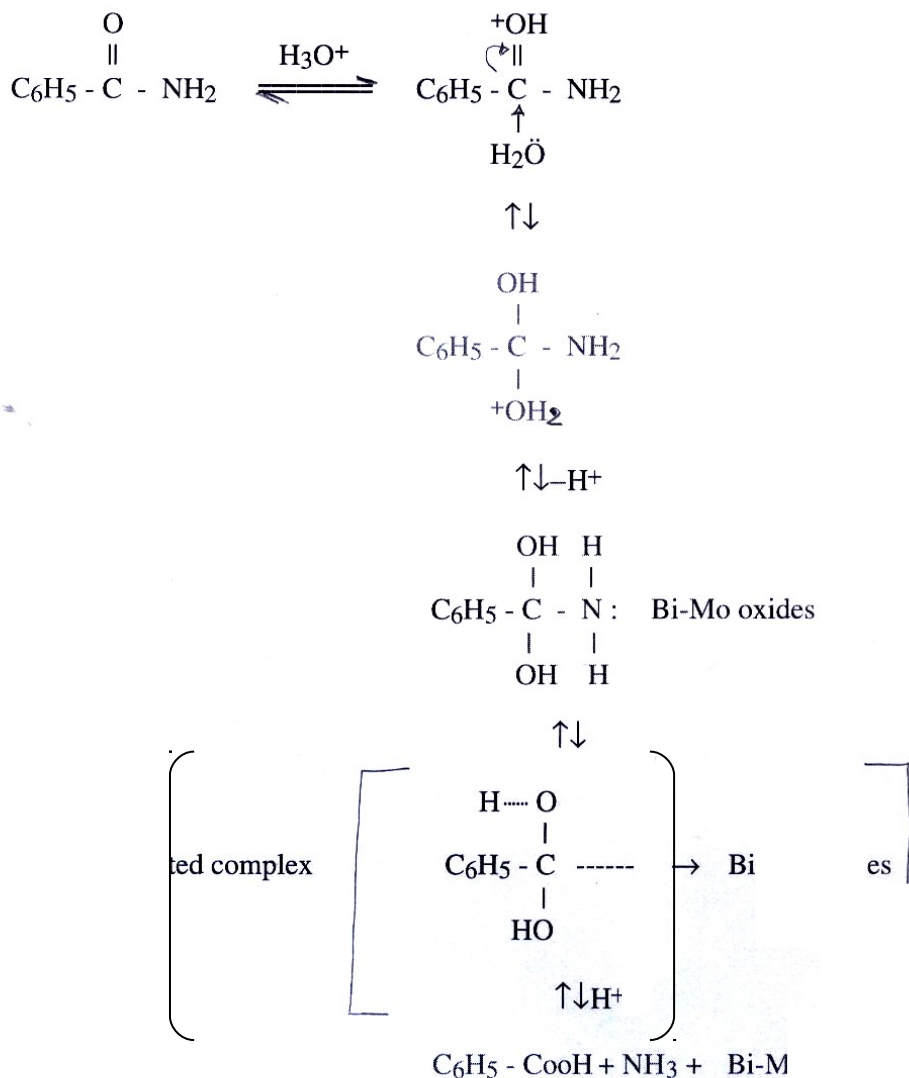


Fig ( 10)

Fig. (62) :

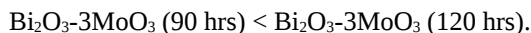
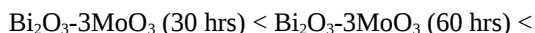
Possible mechanism of catalytic hydrolysis of benzamide over the prepared catalysts.

**Conclusion :-**

2. 1. The study of the chemical kinetics of the hydrolysis of benzamide using these seven catalysts include the determination of the effect of reaction temperature (25, 35 and 45°C), the effect of benzamide concentration (0.05, 0.07 molar solution), and also the amount of each catalyst (0.25 & 0.5 & 1.0 gm) / 200 ml solution.
3. Such study revealed that the reaction is first order, and that the percent conversion for the hydrolysis of benzamide increases with reaction temperature, quantity of catalyst, and also with increasing the ratio of molybdenum oxide (MoO<sub>3</sub>) present in the catalyst, as well as the calcination time.
4. In all steps of study it became obvious that the curve of the reaction rate is characterized by the presence of an induction period, in which the reaction velocity is slow, after which it is accelerated appreciably, it's proposed that this period is due to of the formation of some active sites on the surface of the catalyst. These active sites resemble themselves as ions (Mo<sup>+5</sup>) resulting form side reactions between (Bi<sup>+3</sup>) ions and (Mo<sup>+6</sup>) ions according to the following equation : 
$$\text{Mo}^{+6} + \text{Bi}^{+3} \rightleftharpoons \text{Mo}^{+5} + \text{Bi}^{+5} + e$$
5. where the increase in formed (Mo<sup>+5</sup>) ions leads to an increase in the active sites, and consequently an increase in the reaction velocity.
6. In all studied cases its formed that the induction period is largely affected by the following factors :(a) Quantity of used catalyst . (b) reaction temperature. (c) calcination time. where the induction period decreases with increasing each of the above mentioned factors.
7. These results could be explained on the basis that increasing the quantity of catalyst increases the number of active sites and that the increasing the reaction temperature and calcination time lead to an increasing the in the side reactions which promote the formation of active sites.
8. It's found that the percent conversion of the hydrolysis of benzamide over the mixed oxides (Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>) reaches (86%) at 45°C, in presence of 1.0 g catalyst/ 200 ml solution. It reaches about (88.6%) in presence of Bi<sub>2</sub>O<sub>3</sub>-2MoO<sub>3</sub> under the same conditions. On the other hand in presence of Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> it reached (91%); while in presence of Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> calcinated for (30 hrs) it reached (92%). Calcination for (60 hrs) results in percent conversion

of (93%) whereas it is reached (95%), and (96%) in case of Bi<sub>2</sub>O<sub>3</sub>-3MoO<sub>3</sub> calcinated for (90 hrs), and (120 hrs) respectively.

9. At the same conditions it was found that calcinated mixed, oxides are more active in the hydrolytic catalytic reaction of benzamide according to the following sequence of the prepared catalysts:



10. The mechanism for the hydrolysis reaction of benzamide over the prepared catalysts is also suggested.

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