

## Enhancement of Carbon Dioxide Absorption in Caustic Soda by Organic Solutes Addition

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### ABSTRACT

Absorption of carbon dioxide in a bubble column by 0.5M Sodium Hydroxide aqueous solution with and without various organic compound concentrations of glucose, fructose and saccharose "0.05 , 0.2 , 0.4M" and various superficial gas velocities "0.008 , 0.012 , 0.016 m/s" were studied in the present work.

The experiments were conducted under conditions in which the reaction of carbon dioxide was of Pseudo-first order. The results show that the absorption rate enhances with organic solute additive and increasing solute concentration.

### تحسين عملية امتصاص غاز ثاني اوكسيد الكربون بواسطة الصود الكاوية باضافة المركبات العضوية المذابة

#### الخلاصة

يتضمن البحث عملية الامتصاص لغاز ثاني اوكسيد الكربون من خليط غازي مكون من غاز ثاني اوكسيد الكربون -هواء في العمود الفقاعي "Bubble Column" باستخدام محلول هيدروكسيد الصوديوم بتركيز 0.5M .

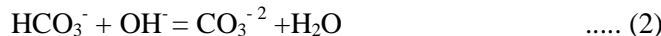
تم في هذا البحث دراسة تأثير اضافة كل من المركبات العضوية التاليه الكلوكوز , فركتوز , والسكروز على عملية الامتصاص وبتركيز مختلفة "0.05 , 0.2 , 0.4 M" ومعدلات جريان للغاز يتراوح بين "0.008-0.016 m/s" . وقد اوضحت النتائج وجود تحسن ملحوظ عن اضافة المركبات العضويه على معدل الامتصاص لغاز ثاني اوكسد الكربون ومعامل انتقال الكتلة.

## INTRODUCTION

The separation of carbon dioxide from gas mixtures with other gases is process of substantial industrial importance . In the manufacture of ammonia from hydrocarbons or coal feeds , the removal of carbon dioxide from the synthesis gas is a vital process step . Large volumes of natural gas are also treated for carbon dioxide removal . Several processes are in use for carbon dioxide removal but process selection must be based on economic and clean up ability . Among the processes , the absorption with chemical reaction provides an economic and efficient way for removing large quantities of carbon dioxide from synthesis gases <sup>(1)</sup> .

The theory of gas-liquid absorption with chemical reaction is sufficiently established and known. In the present work the Penetration theory with random surface –renewal was used and this theory assumed that each element of surface would not be exposed for the same time, but that a random distribution of ages would exist and assumed that the probability of any element of surface becoming destroyed and mixed with the bulk of the fluid was independent of the age of the element<sup>(2)</sup> .

When carbon dioxide is absorbed into alkaline solutions, the dissolved carbon dioxide reacts with the hydroxyl ions<sup>(2)</sup> :



and the overall reaction is:



The chemical absorption can be enhanced by addition of homogeneous catalysts (solute) such as arsenite<sup>(3)</sup> , hypochlorite<sup>(4)</sup> , or carbonic anhydrase<sup>(5)</sup> . These species or their hydration or dissociation products , act as catalysts whose reaction with carbon dioxide is followed by a process in which  $\text{HCO}_3^-$  is released as the catalyst is regenerated <sup>(5,6)</sup> .

Another class of additives employed in absorption comprises the organic solutes used to control the viscosity of the liquid phase <sup>(7,8,9)</sup> .

Vazquez et al <sup>(7,10)</sup> observed that certain solute such as glycerin and commercial sugar had increased the absorption rate of carbon dioxide in a wetted wall column .This increase in the absorption rate is related to the structural similarities and the inorganic and enzymatic solutes . <sup>(8,9)</sup>

Vazque G. etal <sup>(10)</sup> studied absorption of carbon dioxide in alkaline .5M sodium carbonate/.5M bicarbonate buffers containing two enhancers. The used enhancers are either saccharose and sodium arsenite or saccharose and formaldehyde. They found the joint action of the two enhancers were always less than the sum of their individual effects.

Gomez-Diaz et al <sup>(11)</sup> ,studied the gas-liquid mass transfer process of carbon dioxide in aqueous solutions of glucose and glucoseamine. They found that the liquid phase composition influences the value of the mass transfer coefficient due to the variation of solution viscosity. The absorption rate of carbon dioxide will be higher when the glucoseamine concentration in the liquid phase increases.

Garcia-Abuin et al <sup>(12)</sup> indicated from their study that the glucose amine reagent has similar behavior to other common amines( i.e. monoethanolamine ) , as regarding the capture rate of carbon dioxide.

The present work aimed to study the absorption rate of carbon dioxide in caustic soda ( 0.5 M NaOH) solution in various superficial gas velocities(homogenous flow regime) “0.008 , 0.012 , 0.016 m/s” with and without various concentration of glucose, fructose and saccharose”0.05 , 0.2 , 0.4M” , at constant temperature (25 °C), operating pressure (1atm) and carbon dioxide concentrations (10 % vol.).

## **EXPERIMENTAL WORK**

### **Experimental Apparatus**

Experiments of absorption of carbon dioxide from gaseous mixture (10% carbon dioxide - air) have been carried out by aqueous solution of (0.5 M) NaOH. These have been performed in a bubble column (7.5 cm inside diameter \* 100 cm height, glass cylindrical tube) over a wide range of gas flow rate (0.75, 1, 1.5 m<sup>3</sup>/h (0.008-0.016 m/sec), homogeneous flow regime), with and without various concentration of glucose, fructose and saccharose”0.05 , 0.2 , 0.4M” to study the effect of these parameters on the absorption rate of carbon dioxide. Schematic diagram of experimental set up was shown in Figure (1).

Perforated plate sparger was used as gas distributor (26 hole of 1mm diameter) and placed between the column and distributor chamber which having a drain at the bottom and gas inlet at the side. Gas (carbon dioxide - air) flow rate was measured by using two calibrated rotameters. In all experiments the volume of liquid has been constant and equal to (1.5 liter, 30 cm height above the sparger). The temperature was measured each 1 minute until the end of the absorption run, the temperature remain constant. All experiments were perforated at ambient temperature and atmospheric pressure.

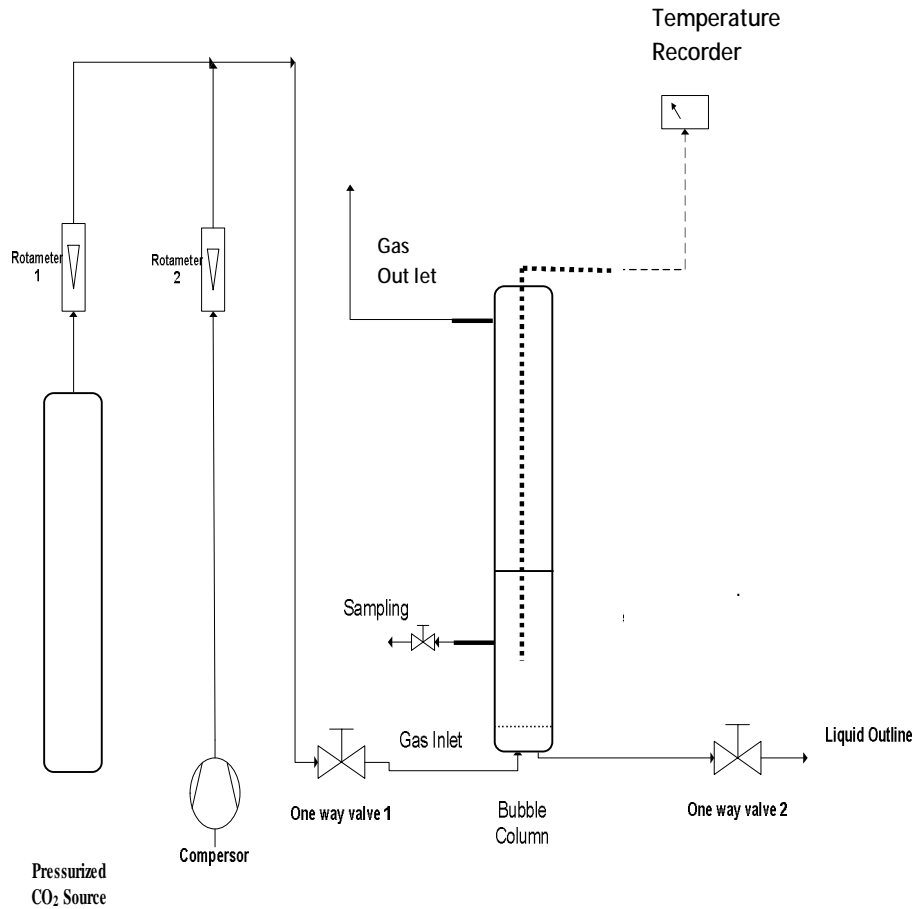


Figure (1) Schematic diagram of experimental apparatus.

**PHYSICO - CHEMICAL PROPERTIES**

Diffusivity ( $D_{CO_2-NaOH}$ ) of carbon dioxide in aqueous sodium caustic soda solution was estimated as follows<sup>(13)</sup>:-

$$\frac{D_{CO_2-NaOH}}{D_{CO_2,w}} = \frac{D_{N_2O}}{D_{N_2O,w}} \quad \dots(4)$$

The diffusion coefficient ( $D_{CO_2,w}$ ,  $D_{N_2O,w}$ ) of  $CO_2$  and  $N_2O$  in water was obtained as follows<sup>(13)</sup>:-

$$D_{CO_2,w} = 2.35 \times 10^{-6} \exp\left(\frac{-2119}{T}\right) \quad \dots (5)$$

$$D_{N_2O,w} = 5.07 \times 10^{-6} \exp\left(\frac{-2371}{T}\right) \quad \dots (6)$$

The diffusion coefficient of ( $D_{N_2O}$ )  $N_2O$  in aqueous caustic soda solution with and without organic solute “glucose, fructose and saccharose” was obtained using Stoenstein equation<sup>(13)</sup>:-

$$D_{N_2O,w} m_w^g = D_{N_2O} m^g \quad \dots (7)$$

Where  $\gamma = 0.6$

The viscosity of water and aqueous solution were measured in the laboratory by pignometer.

Reaction rate constant ( $k_2$ ). In the reaction of carbon dioxide with caustic soda, the reaction rate constant was estimated as follows<sup>(14)</sup> :-

$$\log k_2 = 11.985 - \frac{2895}{T} + 0.221I_c - 0.016I_c^2 \quad \dots (8)$$

Where  $I_c$  is the ionic strength were estimated as follows<sup>(15)</sup>:

$$I_c = \frac{1}{2} \sum Z_i^2 C_i \quad \dots (9a)$$

$$I_c = \frac{1}{2} [1 * OH^- + 2 * CO_3^{2-}] \quad \dots (9b)$$

$$m = b_1 + 2b_2$$

$$\text{where : } b_1 = OH^- \quad , \quad b_2 = CO_3^{2-} = my$$

$$\therefore I_c = \frac{1}{2}m \quad \dots\dots (9c)$$

Solubility of carbon dioxide in the liquid phase was calculated using the Henry's law . Henry's law constant for CO<sub>2</sub>-NaOH system was determined as follows<sup>(15,16):-</sup>

$$\log \frac{H}{H^o} = -\sum I_c h_i \quad \dots\dots (10)$$

Where  $h_i = h_- + h_+ + h_g$

Where H<sup>o</sup> is Henry's law constant for CO<sub>2</sub> in water and can be obtained as follows<sup>(17):-</sup>

$$\log[H^o]^{-1} = -4.3856 + \frac{867.4932}{T} \quad \dots\dots (11)$$

$$\text{Caustic soda conversion\%} = \frac{[NaOH] \text{ reacted}}{[NaOH] \text{ input}} \quad \dots\dots (12)$$

Liquid side mass transfer coefficient can be obtained as follows<sup>(18):-</sup>

$$k_L^o = 0.5 \frac{D_i}{d_{vs}} \left( \frac{v_L}{D_i} \right)^{0.5} \left( \frac{gd_{vs}^3}{v_L^2} \right)^{0.25} \left( \frac{gd_{vs}^2 r_L}{s} \right)^{3/8} \quad \dots\dots (13)$$

$$d_{vs} = 26 \left( \frac{D_i^2 g r_L}{s} \right)^{-0.5} \left( \frac{g D_c^3}{v_L^2} \right)^{-0.21} \left( \frac{u_g}{\sqrt{g D_c}} \right)^{-0.2} D_c \quad \dots\dots (14)$$

**Reaction Kinetic Type and Regime**

Carbone dioxide undergoes a second-order reaction with hydroxyl ions, OH<sup>-</sup>, and the absorption of carbon dioxide in to caustic soda solution conforms to the model just described ; in this case  $k_2=k_{OH^-}$  and C<sub>B<sub>0</sub></sub> is the bulk concentration of caustic soda ,so the absorption rate is given by<sup>(16)</sup>

$$N = C_{CO_2}^* a \sqrt{D_{AB} k_2 C_{B_0} + k_L^o{}^2} \quad \dots\dots (15)$$

If the carbon dioxide absorption into a thin film is occurring according to a pseudo first-order regime in which the concentration of caustic soda is not depleted across the film, so that the absorption rate can be described as follows :

$$N = C_{CO_2}^* a \sqrt{D_{AB} k_2 C_{B_0}} \quad \dots (16)$$

## RESULTS AND DISCUSSION

### Reaction Kinetic Type

In the present work, the reaction kinetics of carbon dioxide with carbonate solution undergoes a pseudo first order reaction (i.e. where the concentration of the reactant in the neighborhood of the surface is very little different from that in the bulk of the liquid, and the dissolved gas undergoes as a pseudo first order reaction). Furthermore, the following conditions are also satisfied<sup>(16)</sup> (Table (1)):-

$$\sqrt{D_{AB} k_2 C_{B_0}} \geq 5 * k_L^0 \quad \dots(17)$$

### Influence of Superficial Gas velocity

Figure (2) shows the effect of volumetric gas flow rate on absorption rate. It can be noticed that the absorption rate increased with increasing volumetric gas flow rate. This is attributed to the fact that higher superficial gas velocity gives smaller bubbles. The smaller bubble of lower rising velocity this leads to form large residence time and consequently higher gas – liquid interfacial and absorption rate<sup>(19)</sup>.

### Influence of Organic Solute Additive

Figure (3) shows the effect of organic solute additive on absorption rate at a given volumetric gas flow rate. It can be noticed that the absorption rate increases with organic solute additive and increasing solute concentration. These results are in agreement with the previous finding of Va'zquez et al 1997<sup>(8 and 10)</sup>. This effect was to be related to the presence of OH<sup>-</sup> groups and the tetrahedral nature of their carbon atoms. It is generally accepted that in aqueous solution these species act as catalysts whose reaction with CO<sub>2</sub> is followed by a process in which HCO<sub>3</sub><sup>-</sup> is released as the catalyst is regenerated. All of these species feature O<sup>-</sup> or OH<sup>-</sup> groups, all can act as Lewis bases for CO<sub>2</sub> as Lewis acid (some through atoms with electron lone pairs), and all have tetrahedral carbon units facilitating the approach of the CO<sub>2</sub> molecule to the basic site<sup>(8)</sup>. Figure(4) shows the catalytic reaction for an active species OX<sup>-</sup><sup>(8)</sup>.

Table (2) show the molecular mass, number of OH<sup>-</sup> groups and chemical structure of each solute. From this table it can be seen that saccharous has 8 groups of OH<sup>-</sup> ions, while it gives less absorption rate than the fructose and glucose. This is attributed to the fact that the viscosity of the absorbent when used saccharose is higher as compared when used glucose and fructose as it can be seen in Table (1). Also the

OH<sup>-</sup> density of the solute molecule ( $\beta$ )<sup>(8)</sup> for saccharose is less than for glucose and fructose. It can be concluded from that, the physical properties (i.e. viscosity) has great importance for the enhancement of carbon dioxide capture by addition a series of organic solutes and it controlled not only with the number of OH<sup>-</sup> ion groups.

### CONCLUSIONS

The following points are concluded from the present work:-

- § The absorption rate increased with increasing volumetric gas flow rate .
- § The absorption rate increases with organic solute additive and increasing solute concentration. The enhancement of carbon dioxide absorption was to be related to the presence of OH groups and the tetrahedral nature of their carbon atoms.

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**NOMENCLATURE**

<b>Symbol</b>	<b>Definition</b>	<b>Unit</b>
A	Interfacial area	m <sup>2</sup> /m <sup>3</sup>
C <sub>Bo</sub>	Concentration of liquid reactant (B) in the bulk	kmol/m <sup>3</sup>
C <sub>CO<sub>2</sub></sub> <sup>*</sup>	Concentration of carbon dioxide at equilibrium	kmol/m <sup>3</sup>
C <sub>i</sub>	Concentration of ions	kmol/m <sup>3</sup>
D <sub>AB</sub>	Diffusivity of carbon dioxide in caustic soda solution	m <sup>2</sup> /s
H	Henry's constant	atm.m <sup>3</sup> /kmol
H <sup>o</sup>	Henry's constant in pure water	atm.m <sup>3</sup> /kmol
H <sub>i</sub>	Parameters of equation 7 of cation h <sub>+</sub> , anion h <sub>-</sub> and gas h <sub>g</sub> respectively	( - )
I <sub>c</sub>	Ionic strength	m <sup>3</sup> /Kmol
k <sub>L</sub> <sup>o</sup>	Liquid side mass transfer coefficient	m/s
k <sub>2</sub>	Reaction rate constant	m <sup>3</sup> /kmol.s
N	Absorption concentration	Kmol/m <sup>3</sup>
M	Molarity	kmol/m <sup>3</sup>
T	Temperature	K
Y	Fractional conversion	( - )
Z <sub>i</sub>	Valance of ion	( - )
<b>Greek Symbols</b>		
v <sub>L</sub>	Kinematic vescosity	m <sup>2</sup> /s
μ	Viscosity	Kg/m.s
P	Density	Kg/m <sup>3</sup>

Table(1) Physicochemical properties.

Organic solute concentration (m)	Viscosity (Kg/m.s)	$D_{CO_2-NaOH}$ with organic solute	$k_2$	$\sqrt{D_{AB}k_2C_{B_0}}$	$5k_L^o$
Volumetric gas flow rate 0.75 m <sup>3</sup> /h					
0.05 Glucose	1.28E-03	1.44E-09	11044.57	0.00282	0.000131
0.05Fructose					
0.2 Glucose	1.48E-03	1.32E-09	11044.57	0.0027	0.000125
0.2Fructose					
0.4 Glucose	1.61E-03	1.25E-09	11044.57	0.002627	0.000122
0.4Fructose					
0.05 Saccharose	1.36E-03	1.39E-09	11044.57	0.002771	0.000128
0.2 Saccharose	1.64E-03	1.24E-09	11044.57	0.002617	0.000121
0.4 Saccharose	1.96E-03	1.11E-09	11044.57	0.002476	0.000115
Volumetric gas flow rate 1 m <sup>3</sup> /h					
0.05 Glucose	1.28E-03	1.44E-09	11044.57	0.00282	0.000125
0.05Fructose					
0.2 Glucose	1.48E-03	1.32E-09	11044.57	0.0027	0.00012
0.2Fructose					
0.4 Glucose	1.61E-03	1.25E-09	11044.57	0.002627	0.000117
0.4Fructose					
0.05 Saccharose	1.36E-03	1.39E-09	11044.57	0.002771	0.000123
0.2 Saccharose	1.64E-03	1.24E-09	11044.57	0.002617	0.000116
0.4 Saccharose	1.96E-03	1.11E-09	11044.57	0.002476	0.00011
Volumetric gas flow rate 1.5 m <sup>3</sup> /h					
0.05 Glucose	1.28E-03	1.44E-09	11044.57	0.00282	0.000122
0.05Fructose					
0.2 Glucose	1.48E-03	1.32E-09	11044.57	0.0027	0.000117
0.2Fructose					
0.4 Glucose	1.61E-03	1.25E-09	11044.57	0.002627	0.000114
0.4Fructose					
0.05 Saccharose	1.36E-03	1.39E-09	11044.57	0.002771	0.00012
0.2 Saccharose	1.64E-03	1.24E-09	11044.57	0.002617	0.000113
0.4 Saccharose	1.96E-03	1.11E-09	11044.57	0.002476	0.000107

Table (2) : Molecular Mass, Number of OH Groups and  
Chemical Structure for each Organic Solutes.

Organic Solute	M kg/kmole	N <sub>OH</sub> (number of hydroxyl ion)	$\beta = N_{OH^-}$	Structure
Saccharose	342	8	0.39	
Glucose	180	5	0.47	
Fructose	180	5	0.47	

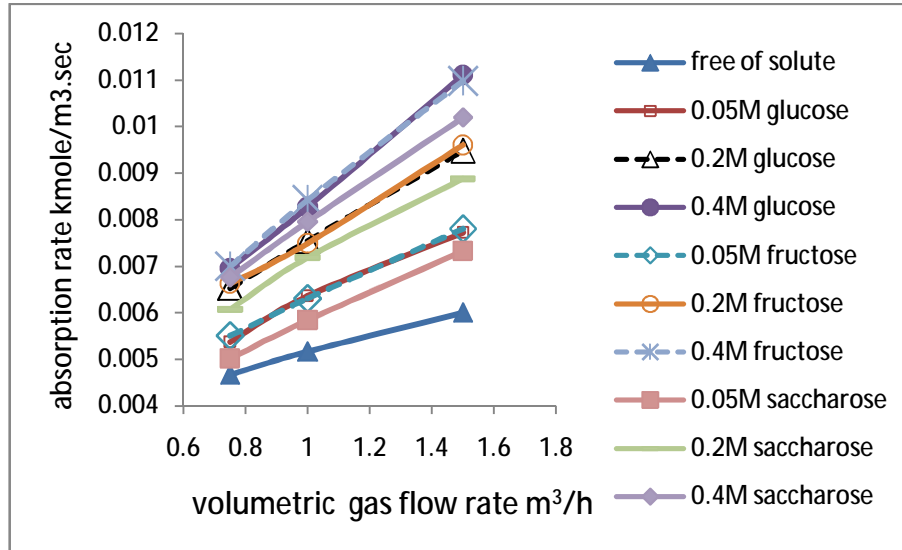


Figure (2) absorption rate vs. volumetric flow rate as a function of organic solute concentration.

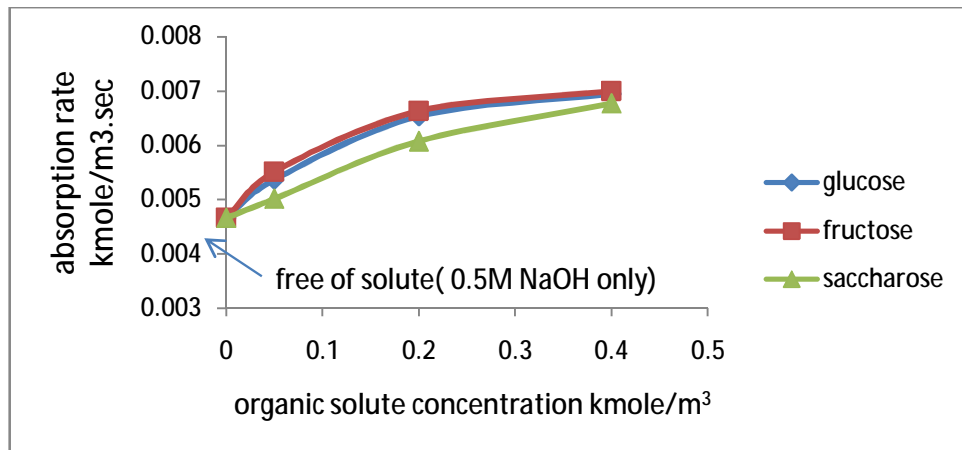


Figure (3) absorption rate vs. organic solute concentration.

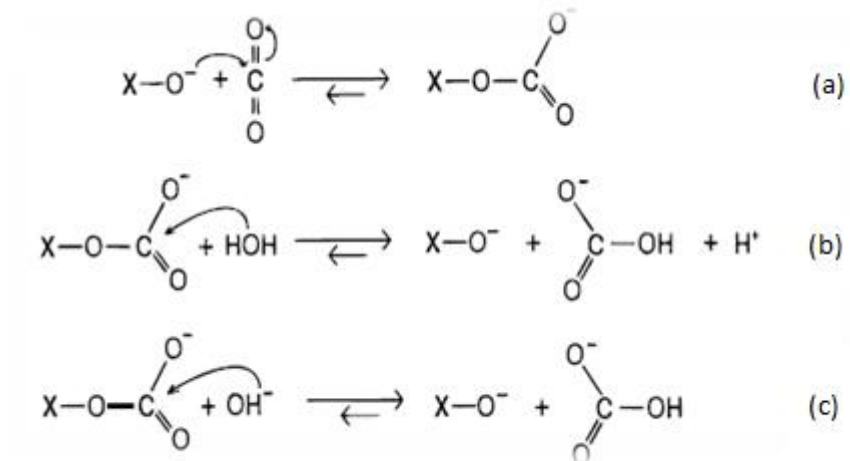


Figure (4) The catalytic reaction for an active species  $\text{OX}^{(8)}$ .