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Kinetic study of unsaturated ketones epoxidation with hydrogen peroxide through the inverse phase transfer catalysis and effect of ultrasonic waves in this epoxidation

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Abstract

Kinetic study of epoxidation of unsaturated ketone of mesityl oxide was studied by using Hydrogen peroxide in the presence of dodecyltrimethyl ammonium bromide (DTAB) as an inverse phase transfer catalyst. The reaction was carried out in the two-phase media of water-heptane with 1:1 ratio in 25 °C. It was found that the order of reaction for mesityl oxide for ketone concentration in the range of 0.03- 0.1 mol L^{-1} are 0.8906. And also with regard to catalyst concentrations in the range of 0.07- 0.2 mol L^{-1}, the order of reaction for catalyst is 0.1205. The order of reaction of Hydrogen peroxide in the range o of 1.5-4 mol L^{-1} concentration for mesityl oxide is –0.1411. The activation energy of the reaction is 27.51 kJ mol^{-1} in the restricted temperature between 10-25 °C and it was observed that reaction rate enhances by temperature increase. As the phase transfer catalyst depends strongly on mass transfer between two phases, it is well understood that ultrasonic waves have a greater efficiency of interface mixing than conventional agitation. So, in this research the effect of ultrasonic waves in comparison with magnetic stirrer was studied. The results showed that an ultrasonic wave accelerates on the reaction.

***Keywords**:* Kinetic study; Epoxidation; Ultrasonic waves; Inverse phase transfer catalyst.

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1. Introduction

The epoxidation reaction is an important one is organic chemistry because the epoxide functional group is a very useful intermediate in organic synthesis: indeed, epoxides are versatile products that easily undergo ring- opening reactions to form bifunctional compounds, and in asymmetric molecules two new chiral centers are created in one step. Therefore, in recent years a great deal of effort has been directed towards the promotion of this reaction and several synthetic procedures have been reported for the epoxidation of unfunctionalized olefins. These methods involve matalloporphyrin catalysts [1-4], manganese (III)-salen type complexes [5-7], peroxometalate [8], and more recently hydrotalacites [9], dimethyldioxiran [10-11], and titanium silicalites [12-13]. It is noteworthy that the oxidation of organic substrates with aqueous hydrogen peroxide is very attractive from the viewpoint of industrial technology and synthetic

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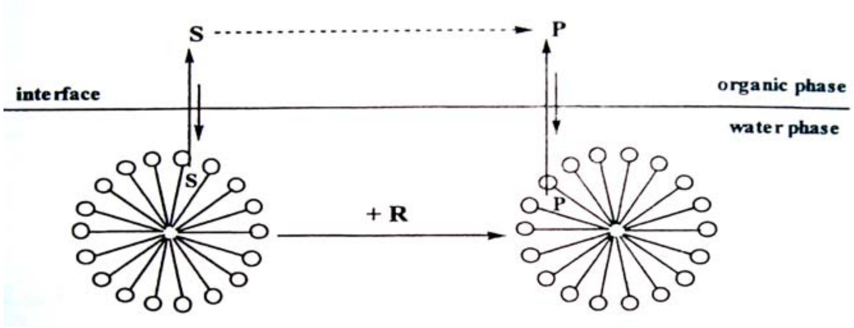
organic chemistry. Nevertheless, the epoxidation of α, β – unsaturated ketones has received much less attention because they do not react under the conditions described above. *α*, *β* – unsaturated ketones and esters are difficult to epoxidize by peracid or metal-catalyzed methods. The epoxidation of *α*, *β* – unsaturated ketones is usually performd by using dimethyldioxirane or hydrogen peroxide under alkaline conditions [14-15]. Recently a new method is used for epoxidation of *α*, *β* – unsaturated ketones, which are called inverse phase transfer catalysis (IPTC). For the first time this method was presented by Mathias and Vaidya [16]. IPTC method involves the conversion of a reactant in the organic phase by a phase transfer catalyst to anionic intermediate, which is transported into the water phase for reaction. The IPTC technique provides one of the most attractive methods for synthesizing acid anhydrides [17-20], which being less reactive than acylchlorides are very important intermediates for the synthesis of esters, amides and peptides.

The other type of IPTC is based upon the fact that any lipophilic substrate could be transferred into the aqueous phase by means of hydrosoluble surfactants. Indeed, it is well known that micelles formed in the aqueous phase, are able to solubilize a fraction of the substrate in equilibrium with the organic phase. Reaction takes place at the surface of the micelles in the water phase [21]. That can be represented by Scheme 1.



Scheme 1

As the IPTC strongly depend on mass transfer, it seems to that the application of ultrasound on these kinds of systems could be very effective. There is some research reported in the literature, which used a combination of sonocation and phase transfer catalysis [22-25]. One of these is the reaction of benzaldehyde with dichlorocarben generated in situ from chloroform and solid sodium hydroxide in the presence of a phase transfer catalyst under an ultrasonic wave [26]. One of the interesting results from these kinds of reactions is to shorten the time of the reaction. Here, we would like to report our observations on the epoxidation reaction of α, β – unsaturated ketone by hydrogen peroxide under ultrasonic waves. In this work the kinetic of epoxidation of unsaturated ketones was studied by using hydrogen peroxide and an inverse phase transfer catalyst and effect of ultrasonic waves in this reaction.

2. Experimental

2.1. Materials

Mesityl oxide (Aldrich), heptane (Merck), dodecyltrimethyl ammonium bromide (DTAB) (Merck), cetyltrimethyl ammonium bromide (CTAB) (Merck), sodium hydroxide and 30% hydrogen peroxide were used in this work.

2.2. Apparatus and procedure

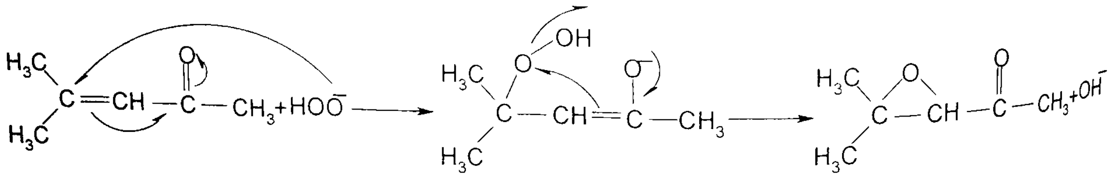
Reactions in two-phase media were studied according to the following protocol. 5 mL of organic phase (0.1 mol L^{-1} *α*, *β* – unsaturated ketone in heptane) were added to 5 mL of aqueous phase. The aqueous phase was prepared just before the beginning of the reaction by mixing together 2.5 mL of 1.5 mol L^{-1} hydrogen peroxide in the case of Mesityl oxide, 1.25 mL of 2.0 mol L^{-1} NaOH and 1.25 mL of 0.1 mol L^{-1} DTAB or CTAB. The mixture was placed in a jacket flask, and its temperature was controlled by a circulating bath at 25 °C.

An ultrasonic generator (Dr. Hielscher UP200 H ultrasonic processor) with an H3 sonotrode (Ø = 3 mm) was used in this experiment. The frequency of the ultrasound was 24 kHz, and the outputs were set at 40 and 100 W. In the case of magnetic stirrer, the rate of stirrer was controlled in 1200 rpm. At a given time, 20 μL of the emulsion were withdrawn and placed in a tube containing 2.4 mL heptane and 20 mg solid sodium tiosulphate to block the reaction. The tube was shaken vigorously and then allowed to stand for 5 minute to separate the two phases. The UV absorbance of the organic phase was measured by a Shimadzu-UV-120-02 spectrophotometer. The absorbance of the unsaturated ketone reactant was monitored as a function of time.

3. Results and discussion

The reaction mechanism can be represented by Scheme 2.

$$H_2O_2 + OH^- \rightleftharpoons HOO^- + H_2O$$



Scheme 2

The progress of the reaction was monitored by measuring the absorbance of the reaction mixture at 231 nm ($\lambda_{\max}$ of mesityl oxide) versus time (Fig. 1).

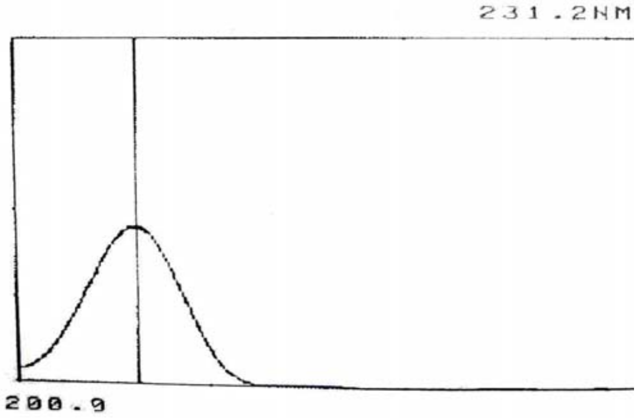


Fig. 1. UV spectra of mesityl oxide

Fig. 2 and 3 presented the FT-IR spectra of mesityl oxide before and after epoxidation reaction, respectively. As shown in Fig. 2, the absorbance at 1689 cm^{-1} assigned to C=O stretching vibrations. Two bands at 2914 and 2977 cm^{-1} are due to aliphatic C-H stretching vibrations. Two new absorbance bands at 872 and 1242 cm^{-1} in Fig. 3, appears in the spectrum after the reaction, which is assigned to epoxide ring characteristic vibration. These results manifest the successful epoxidation of mesityl oxide.

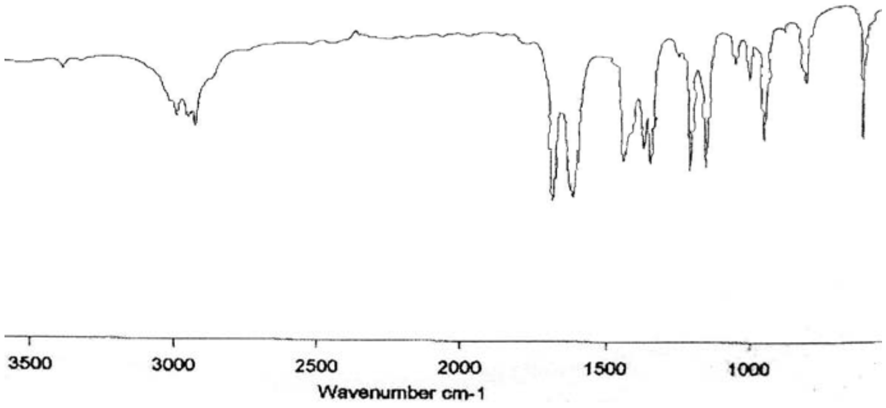


Fig. 2. The spectra of FT-IR before epoxidation reaction of mesityl oxide.

3.1. Kinetic method treatment

Van't Hoff differential method has been used for reaction kinetics study, such that sampling of reaction mixture was made in different times and ketone concentration decrease versus the time was followed by UV- spectroscopy method. Initial rates values were obtained from absorbance curves versus time in the linear region of the curve, then partial reaction orders were calculated using initial rates logarithms diagram vs. concentrations logarithms for each reactants.

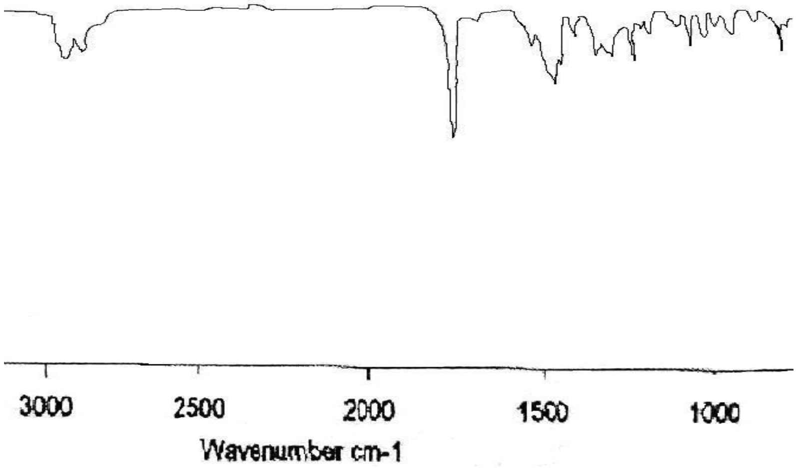


Fig. 3. The spectra of FT-IR after epoxidation reaction of mesityl oxide.

3.2. Effect of hydrogen peroxide concentration

Epoxidation reaction was studied changing the concentration of hydrogen peroxide between 1.5-4 mol L^{-1} in constant concentrations of ketone and inverse phase transfer catalyst. The effect of hydrogen peroxide concentration on the epoxidation reaction of mesityl oxide is shown in Fig. 4.

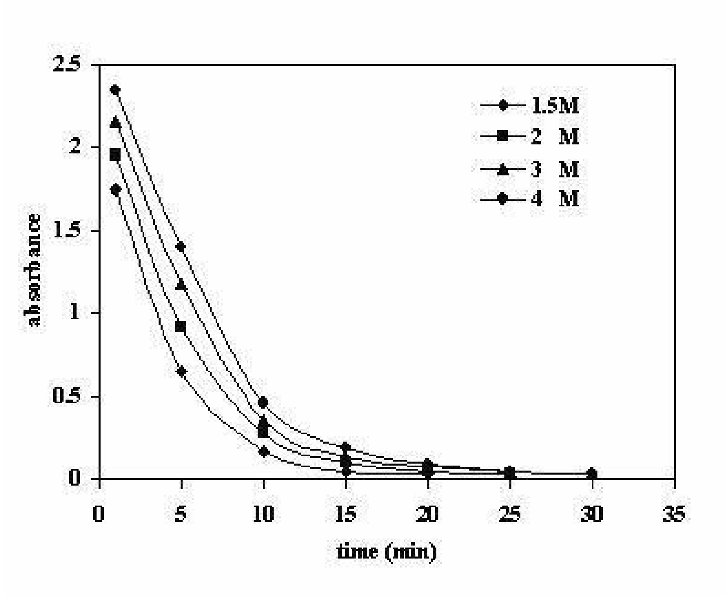


Fig. 4. Plot of absorbance versus time for mesityl oxide epoxidation at variations of [H_2O_2] and constants [NaOH]= 2 mol L^{-1}, [DTAB]= 0.1 mol L^{-1}, [mesityl oxide]= 0.1 mol L^{-1} and T=25 °C.

It indicates that the rates of reactions decrease with increasing of concentration hydrogen peroxide. The decrease of reaction rate with increasing of hydrogen peroxide concentration may be related to ring-opening in acidic media. The curves of absorbance vs. time showed an approximately linear relationship at the initial 5 min, which allows estimating the initial rate. The rate of reaction can be expressed by the following equation [27]:

$$R = K^{/} [H_2 O_2]^{\gamma} \qquad (1)$$

$$K^{/} = K\,[\text{ketone}]^{\alpha}_{\text{constant}}\ [\text{DTAB}]^{\beta}_{\text{constant}} \qquad (2)$$

and integrating equation (1) gives equation (3):

$$\text{Log } R = \log K^{/} + \gamma \log [H_2 O_2] \qquad (3)$$

Thus with plot of log V_0 vs. Log [H_2 O_2], the order of reaction for hydrogen peroxide (γ) is defined as the gradient of the curve (Fig. 5). The plot of log V_0 vs. log C (initial concentrations of hydrogen peroxide) is linear. The reaction order for hydrogen peroxide in the range of 1.5-4 mol L^{-1} concentration of hydrogen peroxide is (-0.1411), it indicates that the rate of reactions decrease with increasing of hydrogen peroxide concentration.

3.3. Effect of catalyst concentration

The dependence of epoxidation reactions on the amount of DTAB concentration were studied in the range of 0.07-0.2 mol L^{-1} at constant concentrations of hydrogen peroxide and ketone. The effect of DTAB concentration on the epoxidation reaction is shown in Fig. 6. The rate of reaction can be expressed by the following equation:

$$R = K^{/} [\text{DTAB}]^{\beta} \qquad (1)$$

$$K^{/} = K\,[\text{ketone}]^{\alpha}_{\text{constant}}\,[H_2 O_2]^{\gamma}_{\text{constant}} \qquad (2)$$

and integrating equation (1) gives equation (3):

$$\text{Log } R = \log K' + \beta \log [\text{DTAB}] \qquad (3)$$

Thus with plot of log V_0 vs. Log [DTAB], the order of reaction for DTAB (β) is defined as the gradient of the curve (Fig. 7). The plot of log V_0 vs. log C (initial concentrations of DTAB) is linear. The reaction order for DTAB in the range of 0.07-0.2 mol L^{-1} concentration of DTAB is 0.1205. It indicates that the rates of reactions increase with increasing of DTAB concentration. As expected, the increase of the surfactant concentration markedly increases the reaction rate. Indeed, the higher its concentration, the higher its micellar catalysis efficiency.

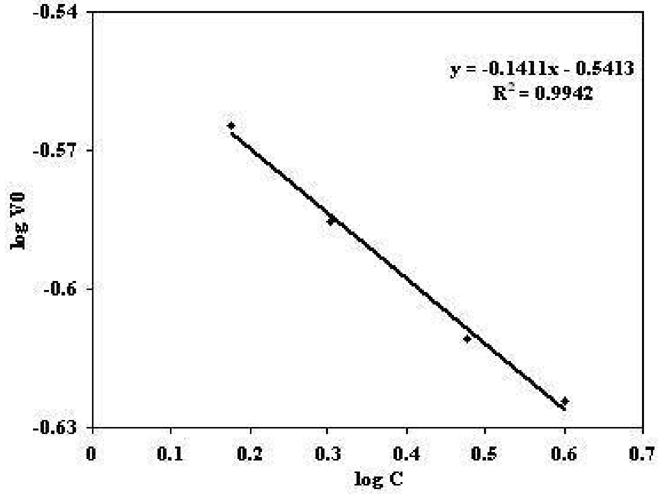


Fig. 5. Plot of log V_0 versus log C with other conditions as in Fig. 4.

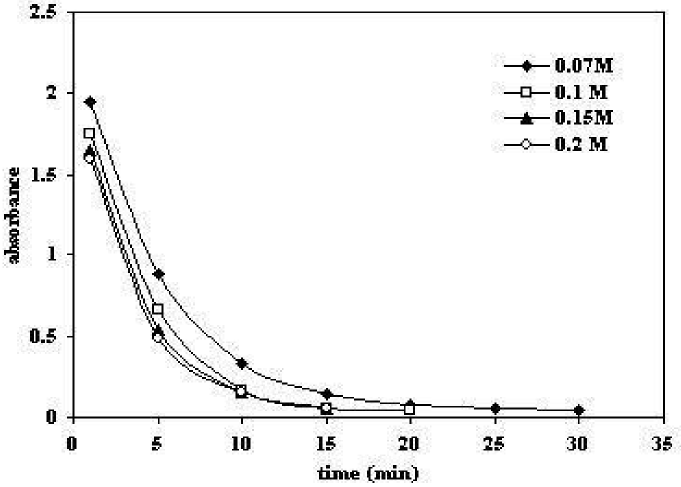


Fig. 6. Plot of absorbance vs. time for mesityl oxide epoxidation at variations of [DTAB] and constants [NaOH] = 2 mol L^{-1}, [mesityl oxide] = 0.1 mol L^{-1}, [H_2O_2] = 1 mol L^{-1} and T= 25 °C.

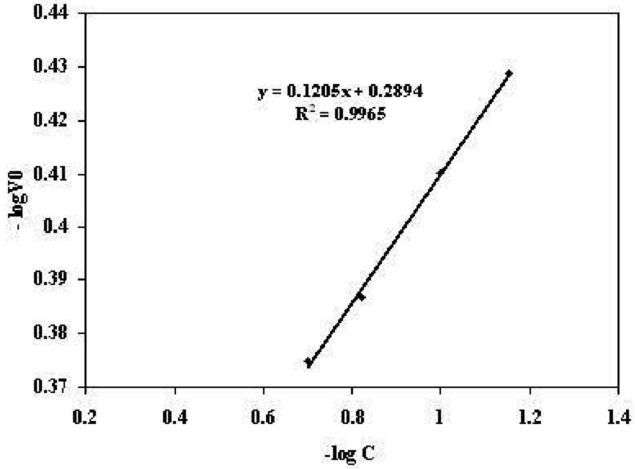


Fig. 7. Plot of -log V_0 versus -log C with other conditions as in Fig. 7.

3.4. Effect of ketone concentration

The dependence of epoxidation reactions on the amount of ketones concentration were studied in the range of 0.03-0.1 mol L^{-1} for mesityl oxide at constant concentrations of hydrogen peroxide and DTAB. The effect of ketone concentration on the epoxidation reaction is shown in Fig. 8. The rate of reaction can be expressed by the following equation:

$$R = K^{/} [\text{ketone}]^{\alpha} \qquad (1)$$

$$K^{/} = K\,[\text{DTAB}]^{\beta}{}_{\text{constant}}\,[H_2O_2]^{\gamma}{}_{\text{constant}} \qquad (2)$$

and integrating equation (1) gives equation (3):

$$\text{Log } R = \log K^{/} + \alpha \log [\text{ketone}] \qquad (3)$$

Thus with plot of log V_0 vs. Log [ketone], the order of reaction for ketone (α) is defined as the gradient of the curve (Fig. 9). The plot of log V_0 vs. log C (initial concentrations of ketone) is linear. It was found that the order of reaction for mesityl oxide for ketone concentration in the range of 0.03- 0.1 mol L^{-1} is 0.8906.

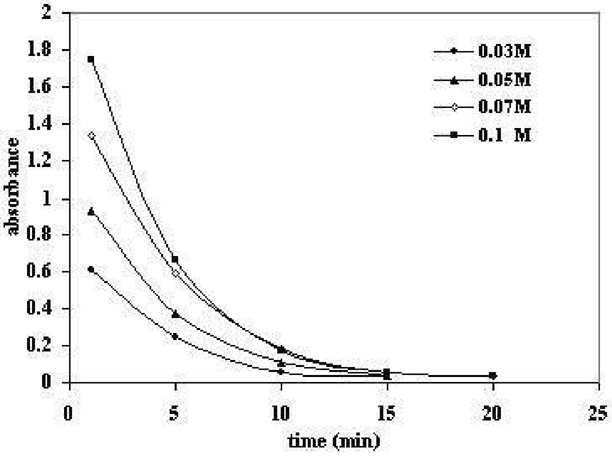


Fig. 8. Plot of absorbance versus time for mesityl oxide epoxidation at variations of [mesityl oxide] and constants [NaOH]= 2 mol L^{-1}, [DTAB]= 0.1 mol L^{-1}, [H_2O_2]= 1 mol L^{-1} and T= 25°C.

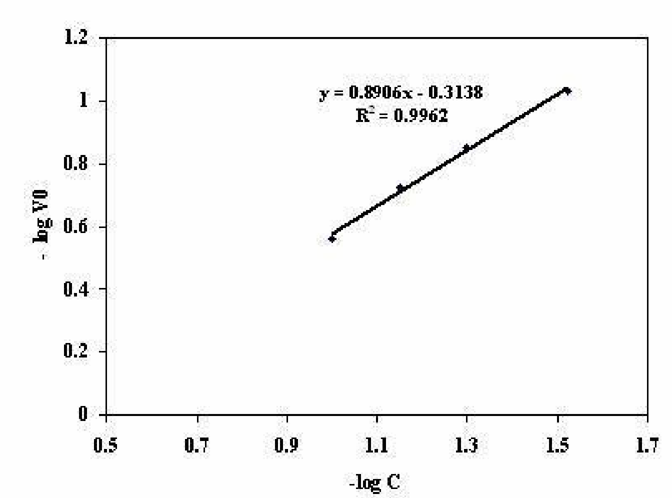


Fig. 9. Plot of -log V_0 versus -log C with other conditions as in Fig. 8.

3.5. Effect of temperature

The epoxidation reactions were carried out at different temperatures from 10-25 °C in constant conditions. The effect of temperature on the epoxidation reactions are shown in Fig. 10. It indicates that the rates of reactions increase with increasing of temperature. The dependence of reaction rate constant in relation of to temperature is expressed by Arrhenius equation:

$K = A\, e^{-Ea/RT}$
$R = K\,[\text{ketone}]^{\alpha}\,[\text{DTAB}]^{\beta}\,[H_2O_2]^{\gamma}$
$R = A\,[\text{ketone}]^{\alpha}\,[\text{DTAB}]^{\beta}\,[H_2O_2]^{\gamma}\, e^{-Ea/RT}$

and by a logarithmic form:
$\text{Log } R = \text{Log } \{A\,[\text{ketone}]^{\alpha}\,[\text{DTAB}]^{\beta}\,[H_2O_2]^{\gamma}\} - Ea / 2.303\, R \times 1/T$

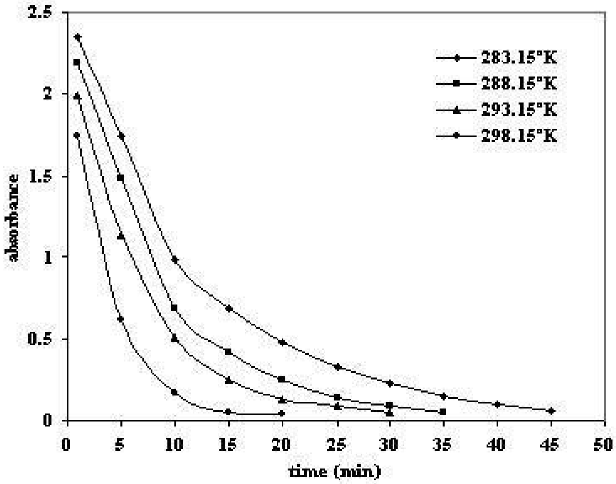


Fig. 10. Plot of absorbance vs. time for mesityl oxide epoxidation at variations of temperature at constants [NaOH]= 2 mol L^{-1}, [mesityl oxide]= 0.1 mol L^{-1}, $[H_2O_2]$= 1 mol L^{-1}, [DTAB] = 0.1 mol L^{-1} and T= 25 °C.

The curves of absorbance vs. time show an approximately linear relationship at the initial 5 min, which allows estimating the initial rate. The plots of log V_0 vs. 1/T are liner (Fig. 11). According to the Arrhenius equation, the overall activation energy for reaction is 27.51 kJ mol^{-1}.

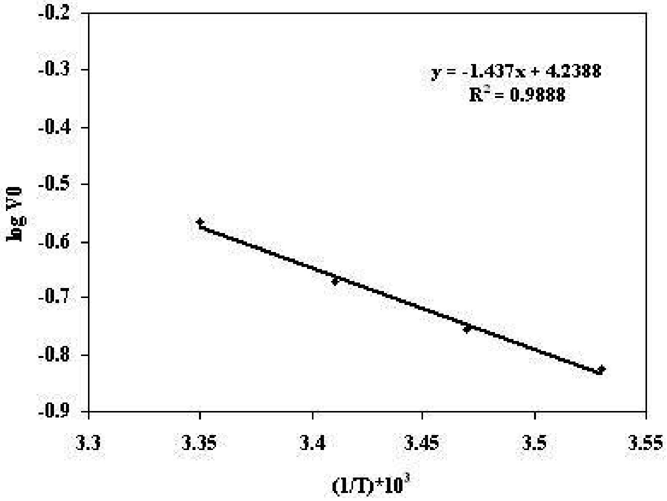


Fig. 11. Plot of log V_0 versus 1/T with other conditions as in Fig. 10.

3.5. Effect type of catalyst

The effect of inverse phase transfer catalysts DTAB and CTAB (cetyltrimethyl ammonium bromide) was studied on the epoxidation reactions. As it is seen in Fig. 12, CTAB is better than the DTAB. CTAB has a long alkyl group (cteyl) in comparison with DTAB. Therefore, CTAB could more accumulate at the interface of organic phase and water phase and this produces a lower interfacial tension.

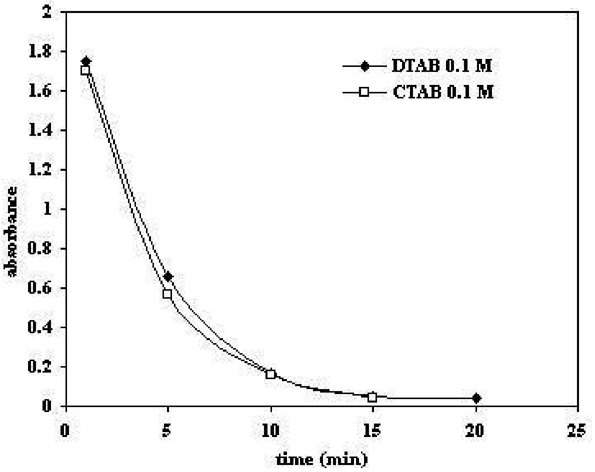


Fig. 12. Plot of absorbance vs. time for mesityl oxide epoxidation at variations type of surfactant at constants [NaOH]= 2 mol L^{-1}, [H_2O_2]= 1 mol L^{-1}, [mesityl oxide]= 0.1 mol L^{-1}, [surfactant]= 0.1 mol L^{-1} and T= 25 °C.

3.6. Effect of ultrasonic wave

Fig. 13 and 14 shows the plots of the absorbance variations of mesityl oxide reaction with DTAB and CTAB versus the reaction time under sonication at 40 and 100 W and magnetic stirrer (1200 rpm) respectively.

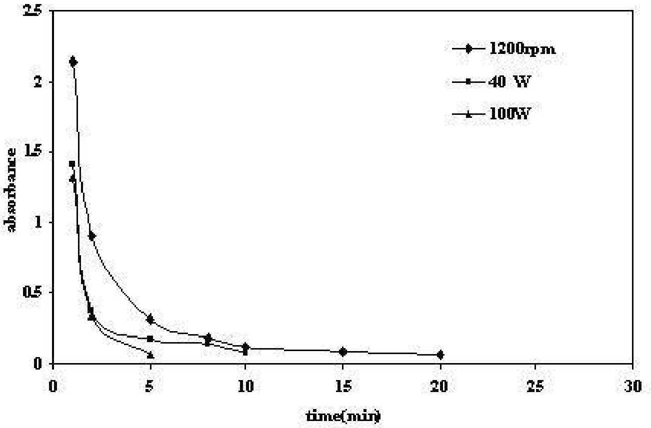


Fig. 13. Plot of epoxidation of mesityl oxide in the presence of DTAB in different condition in 25 °C.

As it is seen, the slope of the curve for 100 W is higher than two others. This could be explained by the intense turbulence generated by cavitation, which produces emulsion with a high contact surface area of ketones and water phases. As it is seen in the curve, CTAB is better than the DTAB. Table 1 shows the percent yield and time of epoxidation reactions of mesityl oxide in different conditions and it shows the time of reactions were very shorten by using of ultrasonic waves in comparison with magnetic stirrer.

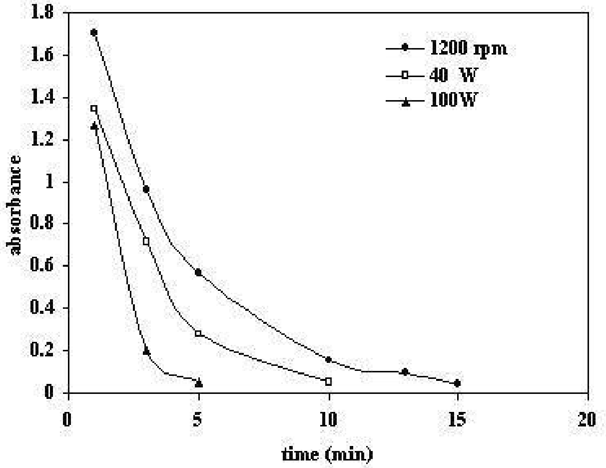


Fig. 14. Plot of epoxidation of mesityl oxide in the presence of CTAB in different condition in 25 °C.

Table 1
Reaction yield (%) and time for mesityl oxide epoxidation in three cases: sonication with 40 and 100 W intensity and 1200 rpm stirring rate.

Catalyst	**1200 rpm (%)**	**40 W (%)**	**100 W (%)**
DTAB	68 (20 min)	68 (15 min)	72 (10min)
CTAB	70 (15 min)	70 (10 min)	73 (5 min)

4. Conclusion

From the present results, it can be concluded that rate of epoxidation reactions in two phase system more effectively dependence catalyst and ketone and hydrogen peroxide concentration. The main role played by the surfactant is transfer of the ketone to the water phase. Surfactant with long alkyl group is more reactive than surfactant with small alkyl group. Under the experimental condition suitable rate equations were proposed follows:

$$R_p = K\,[\text{Mesityl oxide}]^{0.8906}\,[\text{DTAB}]^{0.1205}\,[H_2O_2]^{-0.1411}$$

The above equation is for epoxidation reaction of mesityl oxide. The overall activation energy was 27.51 kJ mol^{-1}. The most important factor for biphasic reaction is the extent of dispersion of one phase into another one. This extension is a function of catalysis and ultrasonic wave. By using a combination of inverse phase transfer catalysis and ultrasonic waves the rate of reaction increases in comparison with magnetic stirrer.

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