



Journal of Applied Sciences

ISSN 1812-5654

science
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Homogeneous and Heterogeneous Kinetics of N-Octanol Oxidation

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Abstract: Kinetics of the oxidation of n-octanol by quaternary ammonium permanganate was investigated under homogeneous and heterogeneous (two liquid phase) conditions using the phase transfer technique. Quaternary ammonium salt, tri caprylyl methyl ammonium chloride (Aliquat 336) was used as the phase transfer catalyst. The oxidation reaction was found to follow first order with respect to each of the reactants, n-octanol and quaternary ammonium permanganate, resulting in an overall second order rate expression. The rate constants determined under homogeneous and heterogeneous conditions agreed well. Tri caprylyl methyl ammonium chloride was proved to be more effective among the different phase transfer catalysts studied in the two liquid phase reaction and gave an enhancement factor of 7.

Key words: Phase transfer catalyst, Aliquat 336, enhancement factor, potassium permanganate, purple benzene

INTRODUCTION

Phase transfer technique has received wide spread attention from preparative chemists and as well as chemical engineers. Substitution, carbene, polymerization, oxidation reactions to name a few, have been carried out using different Phase Transfer Catalysts (PTC) in two phases, organic-aqueous systems. Oxidation reactions involving permanganate and phase transfer reagents are high yielding. The oxidation reaction of piperinol gave piperonylic acid using cetyltrimethyl ammonium bromide under heterogeneous conditions (Menger *et al.*, 1975). In the permanganate oxidation of benzaldehyde, the effect of different solvents on the catalysts performance and structure activity relationship has been reported (Hanumantha and Bhagwanth, 1991). Under basic conditions in the presence of quaternary compounds as catalyst, 2 ethyl-1-hexanoic acid was synthesized from 2 ethyl-1-hexanol (Tang *et al.*, 1998). With tetraethyl ammonium hydrogen sulfate as PTC, pentafluoro pentanoic acid was prepared from pentafluoro pentanol using aqueous sodium permanganate solution (Mahmood *et al.*, 1999). Reactions of several substrates were performed under homogeneous conditions with potassium permanganate as the oxidant (Gibson and Hosking, 1965; Sam and Simmons, 1972). Employing different PTC's the permanganate ion was extracted from the aqueous phase into benzene. The resulting purple benzene was used to study the kinetics. Using hexadecyltrimethyl ammonium bromide, the enhancement of trichloroethylene degradation by aqueous permanganate solution and observed a pseudo first order reaction kinetics with respect to potassium permanganate in the presence of free trichloroethylene was demonstrated (Li, 2004). The

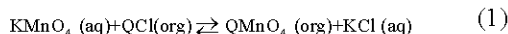
kinetics of oxidation of D-fructose by permanganate was studied in cationic miscelles of cetyltrimethyl ammonium bromide (Andrabi *et al.*, 2007). Their results indicated a very strong partitioning of the permanganate in favor of the miscellar pseudo phase. The oxidation of benzyl alcohol in benzene to benzaldehyde with solid potassium permanganate in the presence of 18-crown-6 was performed (Jose *et al.*, 2009). They observed that the initial rate was found to increase in concentration of the catalyst and benzyl alcohol and developed a homogeneous rate equation.

In this study, kinetics of the oxidation of n-octanol was investigated with the reaction carried out under both homogeneous and heterogeneous conditions. The resulting reaction rate constants were compared. Aliquat 336 (tricaprylylmethyl ammonium chloride) was employed to study the kinetics as it was found to be effective among the different PTC's. The effectiveness of these catalysts was measured by comparing the enhancement factors (ϕ). For the alkaline hydrolysis of some formate esters, it was found to be around 100 to 200 and in the hydrolysis of isobornyl acetate it was 4 (Lele *et al.*, 1983). In the reaction of diphenylchloro phosphate with sodium it was 90 (Krishnakumar and Sharma, 1985). A value of 2 to 9 with different catalysts has been reported (Sankarshana and Rao, 2003) in the case of potassium permanganate oxidation of higher alcohols.

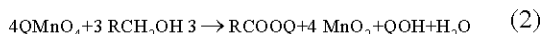
MATERIALS AND METHODS

Kinetics under homogeneous conditions: Tricaprylylmethyl ammonium permanganate, QMnO_4 (quaternary ammonium permanganate) solution (purple benzene) was prepared by mixing benzene containing

tricaprylmethyl ammonium chloride, QCl and a solution of aqueous potassium permanganate, KMnO_4 , in which the following reaction occurs.



Purple benzene was separated and diluted with benzene to get the required concentration of QMnO_4 . 0.075×10^{-3} of this solution was taken in a cylindrical borosilicate reactor with a provision for mild mixing. A temperature bath was provided to maintain the required temperature. 0.075×10^{-3} of benzene solution containing known concentration of n-octanol, RCH_2OH was added to the reactor. The reaction starts at this point and QMnO_4 gets consumed. The reaction was followed by removing samples at different time intervals. Each sample was diluted sufficiently to measure the absorbance of QMnO_4 at the wavelength of 525 nm in a uv-spectrophotometer (Schimadzu model 160). The concentration of permanganate was determined from the calibrated values of absorbance vs. concentration of QMnO_4 . RCH_2OH oxidation reaction by QMnO_4 is represented as follows.



The reaction was performed under pseudo order conditions by maintaining large RCH_2OH concentration, C_{A0} compared to QMnO_4 concentration, C_{Q0} , so that, the change in its value during the reaction can be considered to be insignificant. MnO_2 in the reaction was considered to be negligible. All the experimental runs were carried out at 307.15 K with the initial concentration of C_{Q0} ranging between 4.5 and $13.9 \times 10^{-4} \text{ kmol m}^{-3}$. C_{A0} was varied from 0.127 and $0.286 \text{ kmol m}^{-3}$. Few runs were made in the range of 301.15 K to 323.15 K to study the effect of temperature on the reaction.

Kinetics under heterogeneous conditions: The effectiveness of different phase transfer catalysts like tricaprylmethyl ammonium chloride (Aliquat 336), tetrabutyl ammonium bromide (TBAB) tetrabutyl ammonium iodide (TBAI) and triethylbenzyl ammonium chloride (TEBAC) were compared by determining the enhancement factors. The setup consisted of a 0.08 m diameter borosilicate glass reactor with four bladed stirrer and four baffles. The reactor was kept in a temperature bath. For all the experiments, $50 \times 10^{-6} \text{ m}^3$ of organic phase consisting of benzene, RCH_2OH and respective PTC in required quantities was dispersed into $50 \times 10^{-6} \text{ m}^3$ of aqueous KMnO_4 solution in the reactor at 307.15 K and 450 rpm. After 2700 s the stirring was stopped and the two layers were allowed to separate. The sample was collected from the aqueous phase to determine the permanganate

concentration. The sample was sufficiently diluted and filtered for MnO_2 before measuring the absorbance values. For these runs, the concentration of KMnO_4 , C_{K0} was $2 \times 10^{-2} \text{ kmol m}^{-3}$ in aqueous solution and that of alcohol and catalysts were $0.382 \text{ kmol m}^{-3}$ and $2.24 \times 10^{-3} \text{ kmol m}^{-3}$, respectively in the organic solution. One run was made without the catalyst under otherwise similar conditions.

The same setup was used to find the kinetics of the reaction under heterogeneous conditions using Aliquat 336 as PTC. This catalyst was found to be more effective than the other catalysts. The experimental procedure was followed as described above. The reaction was followed by collecting the samples at different time intervals to measure the KMnO_4 concentration in the aqueous solution. This was done by stopping the agitation and allowing the contents of the reactor to separate into two layers. This took a total time of 40 to 45 seconds, during which time any reaction may be neglected. The experiment was continued by restarting the agitation. The rate constant k_{ht} was determined by varying the concentration of the catalyst, concentration of alcohol and the temperature. The following conditions were maintained for experimental runs. $C_{K0} = 2 \times 10^{-2} \text{ kmol m}^{-3}$, $C_{A0} = 0.254$ - $0.508 \text{ kmol m}^{-3}$, $C_{QCl} = 1.345$ - $3.14 \times 10^{-3} \text{ kmol m}^{-3}$, $T = 307.15 \text{ K}$ to 323.15 K , speed = 450 rpm.

RESULTS AND DISCUSSION

Kinetics under homogeneous conditions: The expression for the rate of disappearance of QMnO_4 , $-r_{Qhm}$, under homogeneous conditions for the reaction in Eq. 2 can be written as :

$$-r_{Qhm} = \frac{-dC}{dt} = k_{hm} C^a C^b \quad (3)$$

k_{hm} is the rate constant and 'a' and 'b' are order of reaction. C_A can be considered constant as its value was very large with respect to C_Q and can be taken equal to C_{A0} . Eq. 3 is now represented as:

$$-r_{Qhm} = \frac{-dC}{dt} = k_{lhm} C^b \quad (4)$$

where, $k_{lhm}^1 = k_{hm} C_{A0}^a$. If 'a' is assumed to be equal to one, equation (4) after integration results in $\ln(C_{Q0}/C_Q) = k_{lhm}^1 t$. All the experimental data which include runs with different initial concentrations of PTC and RCH_2OH and different temperatures were found to follow the linear relation. These values are represented in Fig. 1, 2 and 3 and since, k_{lhm}^1 is equal to $k_{hm} C_{A0}^a$, the slope of the straight line of a log-log plot of C_{A0} vs. k_{lhm}^1 gives the value of 'b' and it was found to be around 1.0. The values $a = b = 1$ indicate that

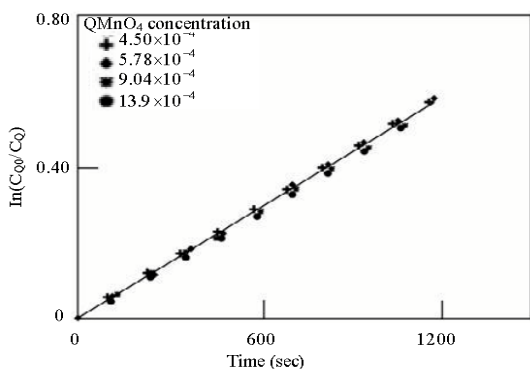


Fig. 1: Effect of different $QMnO_4$ concentration $C_{A0} = 0.223 \text{ kmol m}^{-3}$, $T = 304.15 \text{ K}$

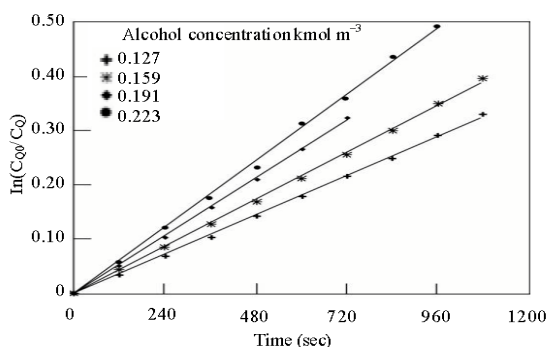


Fig. 2: Effect of RCH_2OH concentration. $C_{Q0} = 6.7 \times 10^{-3} \text{ kmol m}^{-3}$, $T = 305.15 \text{ K}$

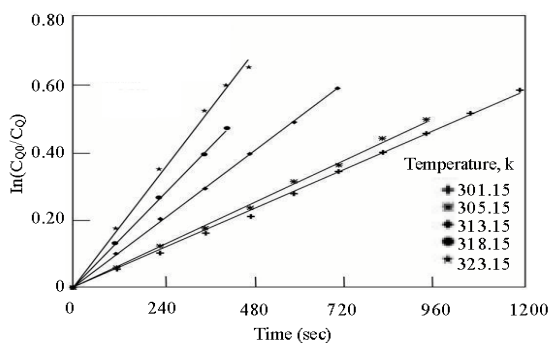


Fig. 3: Effect of Temperature. $C_{Q0} = 6.7 \times 10^{-4} \text{ kmol m}^{-3}$, $C_{A0} = 0.223 \text{ kmol m}^{-3}$

the oxidation of RCH_2OH with $QMnO_4$ is a second order reaction and first order each with respect to RCH_2OH and $QMnO_4$ concentrations. The combined average k_{im} for different C_{Q0} and C_{A0} was found to be $2.352 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$. The data with temperature were found to follow the

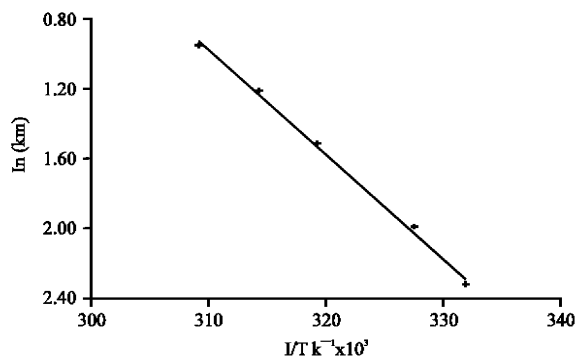
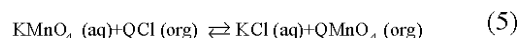


Fig. 4: Plot showing the temperature dependency of the reaction rates

Arrhenius relation as shown in Fig. 4. Activation energy, E is 11.95 kcal . The reproducibility of the results was good. The correlation coefficient obtained was above 0.97 at 95% confidence level.

Kinetics under heterogeneous conditions: The effectiveness of the different catalysts was compared by determining the enhancement factor. It is the ratio of the average rate of oxidation of using PTC to the average rate of oxidation without PTC. The oxidation occurs as follows:



The PTC, Aliquat 336 is insoluble in the aqueous phase and exchanges its anion at the interface to form $QMnO_4$ according to Eq. 5. $QMnO_4$ that formed will be equal to the initial concentration of Aliquat 336. The difference of the total permanganate ion extracted and that remaining in the form of $QMnO_4$ is the amount of permanganate reacted, based on which, the enhancement factor was determined. Catalysts TBAB, TBAI and TEBAC and their corresponding ammonium salts are soluble in both the phases and distribute themselves into two phases depending upon their distribution coefficient. However, the average rate of reaction was calculated based on the amount of permanganate ion transferred into the organic phase. The values of enhancement factors employing Aliquat 336, TBAB, TBAI and TEBAC were found to be 7 , 4.4 , 5.8 and 2.8 respectively. The effectiveness of these catalysts was found to be more or less consistent with the observations made by

Table 1: Effect of C_{QCl} and C_{A0} on $-r_{Qht}$

t, s	$-r_{Qht} \times 10^3 (kmol m^{-3})$					
	${}^a C_{QCl} \times 10^3 (kmol m^{-3})$			${}^b C_{A0} \times 10^3 (kmol m^{-3})$		
	1.35	2.24	3.14	0.254	0.382	0.508
900	1.50	2.28	3.18	1.74	2.28	3.28
1800	1.68	2.32	2.82	1.65	2.32	3.20
2700	1.50	2.32	3.13	1.70	2.32	2.87
3120	-	-	3.62	-	-	-
3600	1.52	2.80	-	1.77	2.47	-

V_{aq} : $50 \times 10^{-6} m^3$, V_{org} : $50 \times 10^{-6} m^3$, ${}^a C_{A0}$: $0.382 kmol m^{-3}$, ${}^b C_{QCl}$: $2.24 \times 10^{-3} kmol m^{-3}$, C_{Q0} : $2 \times 10^{-2} kmol m^{-3}$, Speed: 450 rpm, T: 307.15 K

Herriott and Picker (1975). To find the effect of agitation speed, experiments were performed by taking $0.1 \times 10^{-3} m^3$ volume of $3.164 \times 10^{-2} kmol m^{-3}$ of $KMnO_4$ solution, $0.05 \times 10^{-3} m^3$ volume of benzene solution containing $0.925 kmol m^{-3}$ of RCH_2OH and $2.26 \times 10^{-3} kmol m^{-3}$ of Aliquat 336 in the reactor with different values of stirrer speed i.e., from 100 to 1000 rpm. The duration of stirring was 1800 s. The conversion increased with speed but remained constant beyond 400 rpm indicating that the agitation is unimportant beyond this speed and the system can be considered to be in the kinetic regime.

As mentioned earlier, Aliquat 336 was employed as the PTC to determine the kinetic constant, k_{ht} under heterogeneous conditions. The reactions occur according to Eq. 5 and 6. The quantity of $KMnO_4$ depleted in the aqueous phase was monitored. The actual MnO_4^- participated in the reaction in the organic phase is the difference between MnO_4^- phase transferred into the organic phase minus MnO_4^- remained in the form $QMnO_4$. The rate expression for the disappearance of MnO_4^- , $-r_{Qht}$ for the reaction according to equation (2) which occurs in the organic phase can be written as

$$-r_{Qht} = -dC_Q/dt = k_{ht} C_Q C_A \quad (8)$$

k_{ht} is the rate constant under heterogeneous conditions. C_A was very large compared to C_Q and its depletion can be assumed to be negligible during the reaction. It has been observed that the reaction in Eq. 5 is considerably fast compared to Eq. 6 (Sankarshana and Rao, 2003). Hence, during the course of the reaction, the concentration C_Q remains constant and equal to its initial value, i.e. C_Q is equal to C_{Q0} ($=C_{QCl}$). Since, both C_Q and C_A in Eq. 8 are constant, the right hand side is constant and this suggests that the rate of reaction $-r_{Qht}$ is independent of C_A and C_Q . $-r_{Qht}$ values calculated using Eq. 6 are given in Table 1. It can be seen that $-r_{Qht}$ for different t, for a particular C_{QCl}/C_{A0} , is almost same. However, it increased linearly with C_{QCl}/C_{A0} as given in Fig. 5. The slopes of these lines divided by C_{A0} gives k_{ht} and were found to be

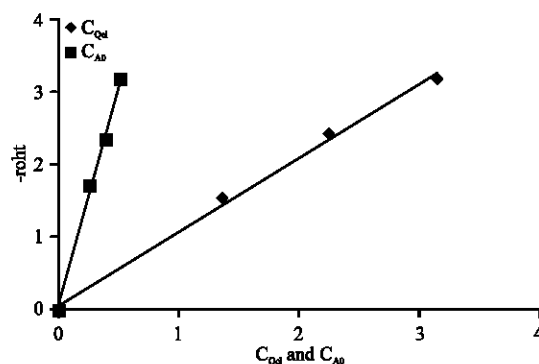


Fig. 5: Effect of C_{QCl} and C_{A0} on $-r_{Qht}$

$2.79, 2.89 m^3 kmol^{-1} s^{-1}$, respectively. The average of these values, $k_{htav} = 2.84 m^3 kmol^{-1} s^{-1}$. This is in good agreement with $k_{hm} = 2.35 m^3 kmol^{-1} s^{-1}$ obtained from homogeneous conditions. It is to be noted that the reaction is a single step in the case of homogeneous conditions, where as, under heterogeneous conditions, it involves sequence of steps.

CONCLUSIONS

The overall order for the oxidation reaction of n-octanol by tricapyryl methyl ammonium permanganate ($QMnO_4$) is two and is found to be first order with respect to each of the concentration of n-octanol and $QMnO_4$. The performance of different catalysts is found to be consistent with the observations made by Herriott and Picker, 1974 Aliquat 336 was found to be more effective among different catalysts tested and gave an enhancement factor of 7. Kinetic constants determined under both homogeneous and heterogeneous conditions agree well with each other.

NOMENCLATURE

- a, b = Constants
- C_K = Potassium permanganate concentration in aqueous phase, $kmol m^{-3}$
- C_A = n-Octanol concentration in organic phase, $kmol m^{-3}$
- C_Q = Quaternary ammonium permanganate concentration in organic phase, $kmol m^{-3}$
- C_{QCl} = Phase transfer catalyst concentration in organic phase, $kmol m^{-3}$
- E = Activation energy, kcal
- k_{hm} = Second order rate constant under homogeneous conditions, $m^3 kmol^{-1} s^{-1}$
- k'_{hm} = Pseudo first order rate constant under homogeneous conditions, s^{-1}

k_{ht} = Second order rate constant under heterogeneous conditions, $m^3 kmol^{-1} s^{-1}$
 MnO_4^- = Permanganate ion
 Q^+ = Quaternary ammonium ion
 $-r$ = Average rate of reaction, $kmol m^{-3} s^{-1}$
 T = Temperature, K
 t = Time, s
 V_{org} = Volume of organic phase, m^3
 V_{aq} = Volume of aqueous phase, m^3
 ϕ = Enhancement Factor

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