



Catalysis, Kinetics and Reaction Engineering

Phase Transfer Catalysis: Oxidation of 2-Methyl-1-butanol



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ABSTRACT

In liquid–liquid systems, the substrates in the liquids are inaccessible to each other for the reaction. By adding a small quantity of phase transfer catalyst, the reaction can be made accessible and accelerated. The present study involves the phase transfer catalyzed oxidation of 2-methyl-1-butanol by quaternary ammonium permanganate (tricaprylyl methyl ammonium permanganate). The attempt was to compare the kinetics under homogeneous and heterogeneous conditions. Experiments were conducted in a batch reactor to determine the kinetics under homogeneous conditions. A baffled borosilicate agitated reactor was used to find the enhancement factor and the kinetics under heterogeneous conditions. The rate constants determined under both homogeneous and heterogeneous conditions agreed very well. The oxidation was found to be first order with respect to each of the reactants, quaternary ammonium permanganate and the alcohol, resulting in an overall second order rate expression. Aliquat336 (tricaprylylmethylammonium chloride) was found to be the best compared with the other catalysts tested (triethylbenzylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium iodide and tetrabutylammonium hydrogen sulfate) and it gave an enhancement factor of 9.8.

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1. Introduction

Phase transfer catalysis provides many good benefits primarily related to reducing the cost of manufacture of organic chemicals. For the past four decades, extensive work has been reported using this technique. It accelerates the reaction between the compounds present separately in two immiscible liquid phases. Many reactions like substitution, dichlorocarbene reaction, oxidation, and polymerization involving aqueous–organic systems have been carried out using phase transfer catalysts (PTCs). Oxidation reaction of various organic compounds by extracting permanganate ion into the organic phase from an aqueous reservoir of potassium permanganate has been reported by many investigators using various PTCs like triethylbenzylammonium chloride (TEBAC), tetrabutylammonium bromide (TBAB), cetyltrimethylammonium bromide (CTMAB) and tricaprylylmethylammonium chloride (Aliquat336). Herriott and Picker [1] studied the extractability of permanganate ion from aqueous solution into benzene. Gibson and Hosking [2] reported the phase transfer catalytic oxidation of various organic compounds by extracting permanganate ion from an aqueous reservoir of potassium permanganate. Sam and Simmons [3] found that PTC, dicyclohexyl-18-crown-6, could solubilize solid potassium permanganate in benzene to the extent of about $0.6 \text{ mol} \cdot \text{L}^{-1}$. The resulting purple benzene solution was used to oxidize a number of organic substrates in good to excellent yields. The two phase permanganate oxidation of piperonyl to piperonylic acid was reported by Menger *et al.* [4]. The effect of different solvents on

the catalyst performance and structure–activity relationship of catalyst was investigated by carrying out oxidation reactions of benzaldehyde and benzyl cyanide by potassium permanganate using different phase transfer catalysts [5]. Sankarshana *et al.* [6] investigated the kinetics of the oxidation of 2-ethyl-1-hexanol, *n*-heptanol and *n*-hexanol under homogeneous conditions. Pentafluoro-pentanol was converted to pentafluoro-pentanoic acid using aqueous sodium permanganate solution employing tetraethylammonium hydrogen sulfate as the PTC by Arshad Mohamood *et al.* [7]. Tang *et al.* [8] synthesized 2-ethyl-1-hexanoic acid from 2-ethyl-1-hexanol using potassium permanganate in aqueous solution under basic conditions in the presence of quaternary ammonium compounds as PTC. Li demonstrated the enhancement of trichloroethylene degradation by aqueous permanganate solution in the presence of hexadecyl-trimethyl-ammonium bromide and observed a pseudo first order reaction kinetics with respect to potassium permanganate in the presence of free trichloroethylene [9]. The kinetics of oxidation of D-fructose by permanganate was studied in cationic micelles of cetyltrimethyl ammonium bromide by Andrabi *et al.* [10]. Their results indicated a very strong partitioning of the permanganate in favor of the micellar pseudo phase. The oxidation of benzyl alcohol in benzene to benzaldehyde with solid potassium permanganate using the PTC, 18-crown-6, was carried out by Jose *et al.* [11]. They observed that the initial rate increased with concentration of the catalyst and benzyl alcohol, and developed a homogeneous rate equation. Lele *et al.* [12] investigated the effect of PTC on some fast and very slow reactions and reported enhancement factors of 200 in the case of fast reactions and 7 in the case of slow reactions. Enhancement factor is defined as the ratio of rates of reaction with and without PTC. Similarly in the reaction of diphenyl chlorophosphate with sodium phenolate to give triphenyl

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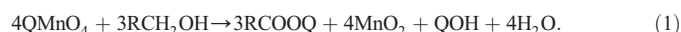
phosphate using Aliquat336, the enhancement factor was found to be 90 by Kumar and Sharma [13]. The enhancement factor of 4 to 9 was obtained by Sankarshana and Rao [14] in the oxidation of higher alcohols employing different types of PTC.

It is evident that the conventional reactions involving heterogeneous phases can be performed easily at accelerated rates and at normal conditions. In the present study, the reaction involves the permanganate oxidation of 2-methyl-1-butanol under homogeneous and heterogeneous conditions. Enhancement factor was determined using different PTCs under heterogeneous conditions. The rate constants obtained under homogeneous and heterogeneous conditions are compared. For this purpose, Aliquat336 was the catalyst employed. The advantage of using Aliquat336 is its insolubility in the aqueous phase. It can be recycled along with the unconverted substrate in the organic phase. Also, the product thus formed can be easily separated from the aqueous phase by acidification.

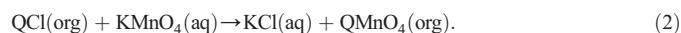
2. Experimental

2.1. Kinetics under homogeneous conditions

The experimental set-up consisted of a $0.25 \times 10^{-3} \text{ m}^3$ cylindrical borosilicate glass reactor. The reactor was provided with a stirrer and was placed in a temperature bath. The oxidation reaction of 2-methyl-1-butanol (RCH_2OH) with tricaprylyl methylammonium permanganate (QMnO_4) was carried out in the reactor and the reaction is represented as follows.



For each homogeneous kinetic run a solution of RCH_2OH of known concentration in benzene was prepared. QMnO_4 solution was prepared by dissolving the PTC, tricaprylyl methylammonium chloride (Aliquat336, quaternary ammonium chloride, QCl). QCl of known quantity in benzene was brought into contact with potassium permanganate (KMnO_4) solution and thoroughly mixed. The benzene solution containing QCl became purple indicating the formation of QMnO_4 according to the reaction given below:



QCl is insoluble in the aqueous phase. Hence, the reaction occurs at the interface. Purple benzene i.e. quaternary ammonium permanganate (QMnO_4) solution was separated and the concentration was determined by measuring its absorbance in a UV-spectrophotometer (Shimadzu 160, Japan). The absorbance values were converted to the concentration ($\text{kmol} \cdot \text{m}^{-3}$) from the calibration curve. The calibration was made as follows. As mentioned above purple benzene (QMnO_4) was prepared by taking a known quantity of QCl in benzene and excess of KMnO_4 in aqueous phase. A sample solution of the QMnO_4 was diluted with benzene and made suitable for measurement of absorbance in the UV-spectrophotometer.

For a particular reaction QMnO_4 solution was adjusted to the required concentration by adding pure benzene. $0.075 \times 10^{-3} \text{ m}^3$ of this solution was mixed with $0.075 \times 10^{-3} \text{ m}^3$ of known concentration of RCH_2OH in benzene at the same temperature. At this point the reaction commenced as per Reaction (1). Samples were taken from the reactor at different time intervals as the reaction proceeded, to determine the fall in concentration of QMnO_4 by measuring the absorbance.

In all the experiments, the concentration, of RCH_2OH was maintained in large excess, so that its change during the reaction is insignificant resulting in a pseudo order situation. MnO_2 in the reaction can be considered as negligible. The conditions for these homogeneous kinetic runs were as follows. Concentration of QMnO_4 , $C_{\text{QO}} = 1.13$ to $9.03 \times 10^{-4} \text{ kmol} \cdot \text{m}^{-3}$. Concentration of RCH_2OH , C_{AO} was

varied between 0.093 and $0.278 \text{ kmol} \cdot \text{m}^{-3}$. Temperature, T , was set at 303.15 K . To study the temperature effect, runs were made in the range of 297.15 to 323.15 K , keeping C_{AO} and C_{QO} constant at 0.278 and $3.39 \times 10^{-4} \text{ kmol} \cdot \text{m}^{-3}$ respectively.

2.2. Kinetics under heterogeneous conditions and enhancement factor

The setup consisted of a glass reactor of 0.08 m diameter, 0.1 m height and $0.5 \times 10^{-3} \text{ m}^3$ capacity with four baffles and a stirrer for mixing. The speed of the stirrer was controlled by means of a regulator. The reactor was kept in a temperature bath.

2.3. Comparison of enhancement factor

To determine the enhancement factor, runs were made with and without phase transfer catalyst under otherwise similar conditions. Aliquat336, TEBAC, TBAB, tetra butyl ammonium iodide (TBAI) and tetra butyl ammonium hydrogen sulfate (TBAHS) were the 5 catalysts used for the oxidation of RCH_2OH . For the experiments with no PTC, $0.05 \times 10^{-3} \text{ m}^3$ of benzene solution with $0.925 \text{ kmol} \cdot \text{m}^{-3}$ concentration of RCH_2OH was stirred with $0.1 \times 10^{-3} \text{ m}^3$ of aqueous solution containing $3.164 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$ of KMnO_4 . The temperature and the speed of agitation were 308.15 K and $450 \text{ r} \cdot \text{min}^{-1}$ respectively. Sample was collected from the aqueous phase to determine the concentration of KMnO_4 . Similarly, the runs were made using five different PTCs. In these runs the initial concentration of each of the PTC was maintained at $2.26 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$ and the sample was taken at the intervals of 1800 s .

2.4. Heterogeneous kinetics

The kinetics of the phase transfer catalytic oxidation of RCH_2OH by permanganate ion in heterogeneous system consisting of organic and aqueous phases was determined using Aliquat336 as the PTC. This was found to be the best among the catalysts studied. The rate constant k_{ht} was determined by varying (a) the concentration of Aliquat336, C_{QCl} (b) the concentration of RCH_2OH , C_{A} , and (c) the temperature, T . Known weights of Aliquat336 and RCH_2OH were dissolved in $0.05 \times 10^{-3} \text{ m}^3$ of benzene solution. This solution was mixed with $0.1 \times 10^{-3} \text{ m}^3$ aqueous phase containing known concentration of KMnO_4 , C_{K} , and stirred. At a particular time, agitation was stopped and the contents in the reactor were allowed to separate into two layers. Then, a sample was withdrawn from the aqueous layer to determine C_{K} . The combined operation took a total time of about 45 to 50 s . During this time any reaction may be neglected. After the sample was taken, the experiment was continued by restarting the agitation.

The conditions at which these runs were made are as follows. C_{K0} was $3.164 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$ in aqueous phase. C_{QCl0} was changed from 2.71 to $6.78 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$. C_{AO} was varied from 0.74 to $1.30 \text{ kmol} \cdot \text{m}^{-3}$. All the experiments were carried out at 303.15 K . To study the temperature effect on the reaction, few runs were made from 302.15 to 323.15 K .

3. Results and Discussion

3.1. Kinetics under homogeneous conditions

The rate equation for the disappearance of QMnO_4 in Reaction (1) is represented as

$$-r_{\text{hm}} = -\text{d}C_{\text{Q}}/\text{d}t = k_{\text{hm}} C_{\text{Q}}^a C_{\text{A}}^b = k_{\text{hm}}^* C_{\text{Q}}^a. \quad (3)$$

Since the initial C_{A} in Eq. (3) was large, it can be essentially considered to remain at its initial concentration value of C_{AO} , during the course of the reaction i.e. $C_{\text{AO}} = C_{\text{A}}$. Hence the product $k_{\text{hm}} C_{\text{AO}}^b$, can be

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