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Recent Strategies in Organic Reactions Catalyzed by Phase Transfer Catalysts and Analyzed by Gas Chromatography

P. A. Vivekanand and Maw-Ling Wang*

*Department of Environmental Engineering,
Safety and Health, Hungkuang University,
Shalu District, Taichung,
Taiwan*

1. Introduction

The field of catalysis provides chemists with new and powerful tools for the efficient synthesis of complex organic molecules. It is suitable for carrying out chemical and biochemical reactions at a high rate in nature as well as in organic synthesis. Catalysis expert's foresee catalysis among the most promising fields of basic research. This methodology can be applied to solve many fundamental, technological, environmental and social problems that face humanity. It finds application in modern chemical and petrochemical industries. Reactions involving two substances located in different phases of a reaction mixture are often inhibited due to the reagents inability to come into contact with each other. In such reactions, conventional techniques are environmentally and industrially unattractive. Nevertheless these reactions can be successfully promoted by a popular catalysis methodology *viz.*, phase-transfer catalysis (PTC) under mild operating conditions (Sasson & Neumann, 1997; Mahdavi & Tamami, 2005; Barbasiewicz et al., 2006; Sharma et al., 2006; Devulapelli & Weng, 2009; Yang & Peng, 2010). Phase-transfer catalysts are being combined with enzymes in biotechnological processes and with transition metals in supramolecular chemistry and nano technology (Lancaster, 2002).

Currently, this key green approach (Makosza, 2000) is a powerful tool in the manufacture of fine chemicals and pharmaceuticals (Yadav & Bisht, 2004; Yadav & Badure, 2008). It has been recognized as a convenient and highly useful synthetic tool in both academia and industry because of several advantages of PTC *viz.*, operational simplicity, mild reaction conditions with aqueous media, suitability for largescale reactions, etc., which meet the current requirement of environmental consciousness for practical organic synthesis. This technique aids in the transfer of an ionic species from either an aqueous or a solid phase into the organic phase where the chemical reaction takes place. Undoubtedly, PTC offers many substantial advantages for the practical execution of numerous reactions (Wang & Tseng, 2002; Yadav, 2004; Wang & Lee, 2007; Wang & Lee, 2006; Wang et. al., 2003; Vivekanand & Balakrishnan, 2009a, 2009b, 2009c, 2009d, 2009e).

* Corresponding Author

Hence, PTC is now well recognized as an invaluable methodology for organic synthesis from two or more immiscible reactants and its scope and application are the subjects of current research. Consequently, there is an upsurge of interest in the synthesis of many more such catalysts which would be highly advantageous and may be employed as a vital tool in organic syntheses. Phase transfer catalysis will be of curiosity to anyone working in academia and industry that needs an up-to-date critical analysis and summary of catalysis research and applications. Presently, ingenious new analytical and process experimental techniques viz., ultrasound and microwave irradiation assisted PTC transformations (Masuno et al., 2005; Wang & Rajendran, 2006; Wang & Rajendran, 2007a, 2007b; Wang & Chen, 2008; Wang & Chen, 2010; Vivekanand & Wang, 2011; Yang & Lin, 2011; Chatti, et al., 2002; Gumaste et al., 2004; Luo et al., 2004; Chatti et al., 2004; Bogdal et al., 2005; Hejchman et al., 2008; Baelen et al., 2008; Sahu et al., 2009; Awasthi et al., 2009; Greiner et al., 2009; Wang & Prasad, 2010; Fiamegos et. al., 2010) have become immensely popular in promoting various organic reactions.

Chemical kinetics is the study of the reaction rates of chemical reactions taking into account their reaction mechanism. Chemical kinetics is the basis of catalysis; however, catalysis is not a part of the kinetics. Mastering these reaction rates has many practical applications, for instance in understanding the complex dynamics of the atmosphere, in understanding the intricate interplay of the chemical reactions that are the basis of life and in designing an industrial process. Moreover, knowledge of kinetics will be helpful in developing theories that can be used to predict the outcome and rate of reactions.

Now a days, kinetic investigation of heterogeneous catalytic reactions is an indispensable step of the theoretical and applied investigations on catalysis. It facilitates in elucidation of the mechanism of a given heterogeneous catalytic reaction and contributes essentially to the revelation of the catalyst behavior in the course of its synthesis, utilization and recycles. Their examination assists in modeling and selection of optimal catalysts and optimization of catalytic reactors. Consequently, the growth of theory and practice in catalysis is implausible without unfolding extensive kinetic investigations.

Catalytic reactions and reaction kinetics are usually monitored using well-established analytical techniques such as gas chromatography (GC). For determining the kinetics of any reaction, samples were collected from organic layer at regular intervals, diluted with suitable solvents and finally injected into GC for analysis. Retention time and area of reactants were obtained from the chromatograph. Using the obtained data's, rate constants were evaluated from the kinetic plot. Thus, gas chromatography identifies compounds by chromatography retention time and thereby, making the method a highly accurate procedure and an essential method in the analysis of organic reactions. The analysis of compounds by GC is very fast, accurate and reliable. Further small samples can be analyzed with high resolution.

Anionic compounds, including anions of organophosphoric acids, carboxylic acids and phenols in aqueous samples can be directly determined by liquid chromatography (LC) or ion chromatography. Alternatively, gas chromatography (GC) analysis after extraction and derivatization is a very practical option. Generally, these types of GC procedures are based on the isolation of anionic analytes from the aqueous samples followed by purification, desiccation, derivatization and analysis by GC (Mikia, et al., 1997). Capillary electrophoresis

and ion chromatography identify inorganic anions by retention time or migration time. Nevertheless, a sample contaminated with matrix is often difficult to analyze.

Analysis of inorganic anions in forensic chemistry (Sakayanagi, et al., 2006), iodide anion (Lin, et al., 2003), flavonoids (Yiannis, et al., 2004), haloacetic acids in drinking waters (Cardador, et al., 2008), phenolic metabolites in human urine (Bravo, et al., 2005), phenols (Fiamegos, et al., 2008) etc., have been carried out using GC under PTC conditions.

In view of the success and vitality of GC analysis in PTC assisted organic reactions, we have proposed to present recent happenings in the field of PTC and to study its applications to various organic reactions that were monitored by gas chromatography. Further, kinetics of various organic reactions catalyzed by PTC carried out under a wide range of experimental conditions will be presented. Much of our current effort is devoted to exploring the kinetic aspects of the reactions, the role of the catalyst structure, and influence of experimental parameters. The roles of these species in the overall catalytic organic reactions are investigated so as to understand whether they are mere spectators or participate in the reaction and how their presence affects the overall reaction kinetics.

Divided into five sections, the chapter explores, Suzuki-coupling, epoxidation, C-alkylation, N-alkylation and O-alkylation reactions. Helping readers to better understand the kinetics of the PTC reactions that are analyzed by GC, the examples in the chapter substantiates the development of more effective PTC processes achieved during the last few decades, enabling industry to embark on a safer and more efficient synthesis of organic compounds for the manufacture of a wide array of products.

2. Phase transfer catalyst assisted organic reactions followed by gas chromatography

2.1 N-alkylation

Imide derivatives are organic compounds with numerous applications in biology (Langmuir et al., 1995; Settimo et al., 1996) as well as in synthetic (Ohkubo, et al. 1996) and polymer chemistry (Iijima, et al., 1995). GC analysis of PTC assisted N-alkylation reactions are well documented (Jankovic, et al., 2002; Mijin, et al., 2004 & Mijin, et al., 2008). Synthesis of N-butylphthalimide (PTR) can be achieved by reacting 1-bromobutane and potassium salt of phthalimide in a liquid (water)-liquid (organic solvent) two-phase medium catalyzed by quaternary ammonium salt. Nonetheless, the hydration of potassium salt of phthalimide in aqueous solution is serious which results in poor yield.

Herein, we discuss the kinetics of synthesis of N-butylphthalimide (PTR) (Scheme 1) that was analyzed by GC (Wang, et al., 2005). The kinetic experiments were run in an ordinary smooth-wall, three-necked flask, fitted with an agitator, reflux condenser and sampling port. All ingredients *viz.*, potassium phthalimide (excess agent), TBAB and acetonitrile, were placed in the flask and stirred at 800 rpm for about 30 min at 70 °C (Wang, et al., 2005). Measured quantities of *n*-bromobutane (limiting agent) and toluene (internal standard) were then added to reactor. The reaction mixture was stirred at 800 rpm. Samples of the organic phase were withdrawn at regular time intervals by stopping the stirrer for 15-30 sec such that the organic phase had separated well enough to get a good sample, then analyzed by GC using an internal standard method. The conditions for the GC analysis are as follows: Shimadzu GC 17A, J&W

Scientific Inc., capillary column (db-1 column); 100% poly(dimethylsiloxane) stationary phase; 15m x 0.525m column dimension; carrier gas, nitrogen (60 ml/min); flame ionization detector; injection temperature: 250 °C (Fig. 1). An aliquot of reaction mixture (0.5 ml) was injected and the retention times for acetonitrile, 1-bromobutane, toluene and *N*-butylphthalimide are presented in Table 1. The structure of the product **3** was confirmed through GC mass spectroscopy (Fig. 2), which showed a molecular ion peak at 203 (M^+).

Scheme 1. *N*-alkylation of potassium salt of phthalimide catalyzed by TBAB (Wang, et al., 2005).

Fig. 1. GC analysis (temperature programming) condition for following *N*-Alkylation of potassium salt of phthalimide

Entry No	Solvent/Reactant/ Internal Standard/Product	Retention Time (Min.)
1	Acetonitrile	1.42
2	1-Bromobutane	3.03
3	Toluene	3.50
4	N-(<i>n</i> -butyl)phthalimide	12.79

Table 1. Determination of retention time for compounds in the N-alkylation reaction mixture by GC analysis

Fig. 2. GC-MS analysis of N-(*n*-butyl)phthalimide

2.1.1 Reaction mechanism and kinetic model

PTC assisted *N*-alkylation of potassium salt of phthalimide (PTK) with organic substrate was carried out in a solid-liquid solution (organic solvent) under phase-transfer catalysis conditions (Scheme 1).The reaction was carried out in the absence of water so as to avoid hydration. On comparing the reaction under liquid (organics solvent)-liquid (water) phase-transfer catalysis conditions (LL-PTC) with solid-liquid solution (organic solvent) under phase-transfer catalysis conditions (SL-PTC), the later method is advantageous because reaction rate is greatly enhanced and the yield of the product is increased. In the beginning of the reaction, the active catalyst N-(tetrabutylammonium) phthalimide (PTQ) is produced from the reaction of PTK, dissolved in organic solvent, with catalyst QBr. The inorganic salt KBr precipitated as a solid form from the organic-phase solution. Then, PTQ reacts with organic-phase reactant RX to produce the desired product PTR (Scheme 2).

Scheme 2. Mechanism for the *N*-alkylation of potassium salt of phthalimide catalyzed by TBAB.

In the Scheme 2, $QX_{(org)}$ and $RX_{(org)}$ represent the quaternary ammonium salt in the organic-phase solution and organic-phase reactant (*n*-bromobutane), respectively. The subscripts "org" and "s" denote the species in organic-phase and in solid-phase, respectively. The overall reaction is expressed as:

As shown in eq 2, the reaction is fast and reaches equilibrium in a short time. Thus, the equilibrium constant K_1 is defined as:

$$K_1 = \frac{[KX]_{org} [PTQ]_{org}}{[PTQ]_{org} [QX]_{org}} \quad (6)$$

As stated, the inorganic salt KX precipitates from the organic solution and the equilibrium constant K_2 is defined as:

$$K_2 = \frac{[KX]_s}{[KX]_{org}} \quad (7)$$

The rate equation of the intrinsic reaction is given in Eq. (4):

$$\frac{d[PTR]_{org}}{dt} = -\frac{d[RX]_{org}}{dt} = k_{int} [PTQ]_{org} [RX]_{org} \quad (8)$$

where k_{int} is the intrinsic rate constant. The material balance for the catalyst is given by:

$$[QX]_{org,i} = [QX]_{org} + [PTQ]_{org} \quad (9)$$

where $[QX]_{org,i}$ is the initial concentration of QX . On solving Eqs. (6), (7) and (9), we obtain:

$$[PTQ]_{org} = f_c [QX]_{org,i} \quad (10)$$

where f_c is given as

$$f_c = \frac{1}{1 + \frac{1}{K_1 K_2} \frac{[KX]_s}{[PTK]_{org}}} \quad (11)$$

We assume that the concentrations of $[KX]_s$ and $[PT-K]_{org}$ are kept at constant values after the induction period of the reaction. Therefore, as shown in Eq. (10), $[PTQ]_{org}$ is kept at a constant value. For this, Eq. (7) can be expressed as:

$$-\frac{d[RX]_{org}}{dt} = k_{app}[RX]_{org} \quad (12)$$

where k_{app} is the apparent rate constant of the pseudo first-order rate law.

$$k_{app} = k_{int}[PTQ]_{org} = k_{int}f_c[QX]_{org,i} \quad (13)$$

Eq. (12) is integrated:

$$-\ln(1 - X) = k_{app}t \quad (14)$$

where X is the conversion of 1-bromobutane (RX), i.e.

$$X = 1 - \frac{[RX]_{org}}{[RX]_{org,i}} \quad (15)$$

where $[RX]_{org,i}$ is the initial concentration of RX in the organic-phase solution. From Eq. (14), it is obvious that the reaction follows a pseudo first-order rate law. By plotting $-\ln(1 - X)$ versus t , the apparent rate constant k_{app} is obtained experimentally from the slope of the straight line.

In general, the hydration of potassium salt of phthalimide in aqueous solution is a serious problem and meager yield of products were obtained when the reaction of potassium salt of phthalimide and organic substrate was carried out under liquid (organics solvent)-liquid (water) phase-transfer catalysis conditions (LL-PTC). Hence, in this work, phase-transfer catalysis was successfully employed to synthesize *N*-alkylphthalimide (PTR) from the reaction of potassium salt of phthalimide (PTK, as excess reagent) with alkylating agent (RBr, as limiting reagent) in solid-liquid phase-transfer catalysis conditions (SL-PTC). Under appropriate conditions, a high yield of the product was obtained. The product was successfully separated and purified from the solid-liquid phase reaction solution. The kinetic results show a material balance between reactants and products, i.e., the consumption of the amount of reactant (*n*-bromobutane) equals to the sum of the generation of the amount of the product (*N*-alkylphthalimide). From GC analysis (Fig.2 and Table 1) and kinetic results, no byproducts were observed during or after the reaction system, indicating that only PTR was produced from the reactant RBr by phase transfer catalysis conditions. Therefore, the consumption of the reactant equals the production of product. The kinetics results obtained from the plot of $-\ln(1-X)$ vs. time using GC analysis under various conditions are discussed in the following sections.

2.1.2 Influence of stirring speed

The effect of agitation speed on the rate of the reaction under standard reaction conditions were investigated by varying the agitation speed in the range of 0-1100 rpm. From the plot of $-\ln(1-X)$ vs. time, the apparent rate constants (k_{app}) were evaluated (Fig. 3). It is clear that

the reaction follows the pseudo first-order rate law. The conversion is increased with the increase in agitation speed up to 400 rpm, but there is no significant improvement in the reaction by further increasing the agitation speed from 400 to 1,000 rpm. This phenomenon indicates the less influence of the external mass transfer resistance on the reaction beyond 200 rpm. Therefore, the agitation speed was set at 800 rpm for studying the reaction phenomena at which the resistance of mass transfer stays at a constant value. We observed similar trend in the kinetic study of synthesizing 1-(3-phenylpropyl)pyrrolidine-2,5-dione under solid-liquid phase-transfer catalytic conditions (Wang & Chen, 2008).

Fig. 3. Effect of stirring speed on the rate of *N*-alkylation of PTK: 6 mmol of PT-K, 0.7 mmol of TBAB, 50 mL of acetonitrile, 4 mmol of *n*-bromobutane, 0.5 g of toluene (internal standard), 70 °C. (Reprinted with permission from Wang, et al., 2005. Copyright (2011) Elsevier).

2.1.3 Effect of different catalysts

In this work, eight quaternary ammonium salts *viz.*, THAB, TBAB, TOAB, BTEAB, QSO₃, THAB, TBAB and TOAB were used to examine their reactivity. In principle, there is no universal rule to guide in selecting an appropriate phase-transfer catalyst except that determined from experiments. The reason is that different reactions need various catalysts to enhance the rate and to promote the yields. From the plot $-\ln(1-X)$ vs time, the rate constants were obtained (Fig. 4). The order of the reactivities of these onium salts is: THAB > TBAB > TOAB > BTEAB > QSO₃. TEAB and QSO₃ (4-(trialkylammonium) propansulfate), which are more hydrophilic, do not possess high reactivity. THAB, TBAB and TOAB of appropriate hydrophilic and hydrophobic properties exhibit high reactivity to obtain high conversion of 1-bromobutane. Further, it is favorable for the reaction in choosing quaternary ammonium salts of larger carbon numbers. The reason is that the lipophilicity is strong using the quaternary ammonium salts of larger carbon number (Wang & Rajendran, 2007b, 2007c; Wang & Chen, 2008).

Fig. 4. A plot of $-\ln(1-X)$ of 1-bromobutane vs. time with different quaternary ammonium salts; 4 mmol of 1-bromobutane, 6 mmol of phthalimide potassium salt, 50 ml of acetonitrile, 0.7 mmol of PTC, 0.5 g of toluene (internal standard), 800 rpm, 70 °C. (Reprinted with permission from Wang, et al., 2005. Copyright (2011) Elsevier).

2.2 O-alkylation

In this work, ultrasonic irradiation assisted synthesis of dimethoxydiphenylmethane (DMODPM) from the reaction of methanol and dichlorodiphenylmethane (DCDPM) was successfully carried out in a liquid-liquid phase-transfer catalytic (LLPTC) reaction (Scheme 3) (Wang & Chen, 2009). Hydrolysis of the ketal product in acidic solution is avoided by carrying out the reaction in a basic solution. Two major advantages of carrying out the reaction under PTC conditions are i) it enhances the reaction and increases the yield and ii) also minimizes the by products.

Scheme 3. Synthesis of DMODPM under LLPTC conditions(Wang & Chen, 2009).

The effects of the reaction conditions on the conversion of DCDPM, as well as the apparent rate constant ($k_{app,1}$) of the first reaction in the organic-phase solution, were investigated in detail. The product DMODPM and the reactants (DCDPM and ethanol) were all identified by GC-MS and NMR and IR spectroscopies. The GC mass spectrum of **6** showed a peak at

Fig. 5. GC-MS chromatogram of dimethoxydiphenylmethane(**6**).

m/z 228 (M^+) (Fig.5) Their concentrations (or contents) were analyzed by GC with GC17A model instrument (Shimadzu). The stationary phase was 100% poly(dimethylsiloxane). The carrier gas was N_2 (30 mL/min). The column was db-1 type.

2.2.1 Reaction mechanism and kinetic model

We believe that methanol first dissolves and reacts with KOH to produce potassium methoxide (CH_3OK or MeOK) in the aqueous solution. Then, CH_3OK further reacts with TBAB catalyst (QBr) to form tetrabutylammonium methanoxide (MeOQ or QOR), which is an active organic-soluble intermediate. This active intermediate (MeOQ) then reacts with DCDPM through two sequential reaction steps in the organic phase to produce the desired product, dimethoxydiphenylmethane (DMODPM). The reaction mechanism of the overall reaction is expressed in Scheme 4.

Scheme 4. Mechanism of DMODPM synthesis under LLPTC conditions.

where ROH, ROK, and QOR represent methanol, potassium methoxide, and tetrabutylammonium methanoxide, respectively; CMODPM and DMODPM are the monochloro-substituted (chloromethoxydiphenylmethane) and dichloro-substituted (dimethoxydiphenylmethane) products, respectively; and QX is the quaternary ammonium salt, where X can be either chloride or bromide. k_1 and k_2 are the two intrinsic rate constants of the organic-phase reactions.

For a two-phase phase-transfer catalytic reaction, the rate is usually determined by four steps, i.e., (a) the ionic aqueous-phase reaction, (b) the organic-phase reaction, (c) the mass transfer of species QOR (active intermediate) from the aqueous phase to the organic phase, and (d) the mass transfer of species of the regenerated catalyst QBr from the organic phase to the aqueous phase. The mass transfers of species from the aqueous phase to the organic phase and *vice versa* are all fast. The ionic aqueous-phase reaction is also very fast. Therefore, it is obvious that the organic-phase reaction, which is usually slow, is the rate-determining step. The ionic reaction in aqueous solution is fast. Also, MeOQ formed from the reaction of potassium methoxide and tetrabutylammonium bromide (TBAB) is an organic-soluble compound. The transfer of MeOQ from the aqueous phase to the organic phase is also fast. Therefore, the two sequential reactions in the organic phase are the rate-determining steps for the whole reaction. From the GC spectrum of the reaction samples, only DMODPM product was observed and no CMODPM was observed. This fact indicates that the second reaction is faster than the first one. Following the Bodenstein steady-state assumption, the production rate of CMODPM equals the consumption rate of CMODPM in the reaction solution. Once CMODPM is produced, it reacts with QOR very quickly to produce the final product DMODPM in the second reaction of the organic phase. Thus, the first reaction in the

organic phase is the rate-determining step. Also, CMODPM was not observed. Thus, the rate of the change of CMODPM with respect to time was set to be zero, as shown in Eq 16. Consequently, the first reaction in the organic phase is the rate-determining step. Thus, we have

$$\frac{d[\text{CMODPM}]_{\text{org}}}{dt} = 0 \quad (16)$$

where the subscript “org” denotes the species in the organic solution. The material balances for DCDPM, CMODPM, and DMODPM in the organic-phase solution are

$$-\frac{d[\text{DCDPM}]_{\text{org}}}{dt} = k_1[\text{DCDPM}]_{\text{org}}[\text{QOR}]_{\text{org}} \quad (17)$$

$$-\frac{d[\text{CMODPM}]_{\text{org}}}{dt} = k_1[\text{DCDPM}]_{\text{org}}[\text{QOR}]_{\text{org}} - k_2[\text{CMODPM}]_{\text{org}}[\text{QOR}]_{\text{org}} \quad (18)$$

$$\frac{d[\text{DMODPM}]_{\text{org}}}{dt} = k_2[\text{QOR}]_{\text{org}}[\text{CMODPM}]_{\text{org}} \quad (19)$$

Combining eqs. (16) and (18) results in,

$$[\text{CMODPM}]_{\text{org}} = \frac{k_1}{k_2}[\text{DCDPM}]_{\text{org}} \quad (20)$$

From eqs. (17), (19) and (20), we get

$$-\frac{d[\text{DCDPM}]_{\text{org}}}{dt} = \frac{d[\text{DMODPM}]_{\text{org}}}{dt} \quad (21)$$

This result indicates that the consumption rate of DCDPM equals the production rate DMODPM in the organic phase. No other byproducts were observed during or after the reaction. Therefore, by integrating the equation after combining Eqs 17, 20, and 21, we have

$$-\ln(1 - X) = k_{\text{app}}t \quad (22)$$

where $k_{\text{app},1}$ is the apparent rate constant and X is the conversion of DCDPM, i.e.

$$X = \frac{[\text{DMODPM}]_{\text{org}}}{[\text{DCDPM}]_{\text{org},i}} = \frac{[\text{DCDPM}]_{\text{org},i} - [\text{DCDPM}]_{\text{org}}}{[\text{DCDPM}]_{\text{org},i}} \quad (23)$$

$$k_{\text{app},1} = k_1[\text{QOR}]_{\text{org}} \quad (24)$$

where the subscript i represents the initial conditions of the species. The rate at which the reactant DCDPM is consumed can be calculated from Eq 17 and the rate at which the final product DMODPM is produced can be calculated from Eq 19. By applying the pseudo-steady-state approach, the rate of the final product (DCDPM) can be calculated from Eq 17.

As shown in Eq 22, it is obvious that the reaction follows a pseudo-first-order rate law. The $k_{\text{app},1}$ values were obtained by plotting the experimental data for $-\ln(1 - X)$ vs. time (t). Thus,

the reaction rate was calculated from Eq 17. Unexpected products were noticed in the absence of KOH and phase-transfer catalyst. However on the addition of KOH and PTC, DMODPM product was obtained in a small quantity. Therefore to enhance the reaction rate greatly, ultrasonic irradiation was employed in the reaction. The kinetics results obtained based on GC analysis (Fig. 6) under various conditions is discussed in the following sections.

Fig. 6. GC analysis (temperature programming) condition for following O-alkylation

2.2.2 Effect of ultrasonic power and frequency

To ascertain the influence of various ultrasonic frequencies on the rate of the two phase reaction of DCDPM and methanol with same output power of 300 W, the ultrasonic frequency was varied in the range of 20-50 kHz under otherwise similar conditions using TBAB as the catalyst. The kinetic profile of the reaction is obtained by plotting $-\ln(1 - X)$ versus time (Fig. 7). From these observed results, it can be inferred that ultrasonic assisted phase-transfer catalysis significantly increases the rate of the reaction.

Fig. 7. Effect of the ultrasonic frequency on the conversion of DCDPM. Conditions: 0.228 g of TBAB, 90 mmol of methanol, 2.75 mmol of DCDPM, 40 mL of chlorobenzene, 5 g of KOH, 10 mL of water, 0.1 g of toluene, 400 rpm, 60 °C 300 W. (Reprinted with permission from Wang & Chen, 2009. Copyright (2011) American Chemical Society)

Without the application of ultrasonic power to the reaction solution, the conversion of DCDPM is low. The reaction follows a pseudo-first-order rate law, and the conversion is increased with higher ultrasonic frequency, indicating that ultrasonic waves enhance the nucleophilic substitution. The chemical effects of the ultrasound can be attributed to intense local conditions generated by cavitation bubble dynamics, i.e., the nucleation, formation, disappearance, and coalescence of vapor or gas bubbles in the ultrasonic field. However, in the phase-transfer catalytic reaction, rate enhancements are typically due to mechanical effects, mainly through an enhancement of mass transfer. The use of sonication techniques for chemical synthesis has also attracted considerable interest in recent years, because they can enhance the selectivity and reactivity, increase the chemical yields, and shorten the reaction time. In addition, there is no decomposition of phase-transfer catalysts under the experimental conditions. In this work, we found that the $k_{app,1}$ values with ultrasonic conditions (unconventional method) under the present experimental conditions are higher than those of the silent conditions (conventional method) (Wang & Rajendran, 2006; Wang &

Rajendran, 2007b, 2007c; Wang and Chen, 2010; Vivekanand & Wang, 2011). Similar increase in rate constant values was observed on varying ultrasonic power (Fig. 8). The corresponding $k_{app,1}$ values are shown in Table 2.

Fig. 8. Effect of the ultrasonic power on the conversion of DCDPM. Conditions: 0.228 g of TBAB, 90 mmol of methanol, 2.75 mmol of DCDPM, 40 mL of chlorobenzene, 5 g of KOH, 10 mL of water, 0.1 g of toluene, 400 rpm, 60 °C, 40 kHz. (Reprinted with permission from Wang & Chen, 2009. Copyright (2011))

Ultrasonic Power (W)	100	200	300	400	500	600
$k_{app} (\times 10^3, \text{min}^{-1})$	4.0	7.1	10.3	12.4	14.2	15.2

a- Gas chromatographic analysis

Table 2. Effect of ultrasonic power on the apparent rate constants ($k_{app,1}$) for the phase-transfer catalytic reaction of MeOH and DCDPM^a

2.3 C-alkylation

Recently, the kinetics of monoalkylation of benzyl cyanide with *n*-bromopropane (BP) has been studied under phase transfer catalysis (PTC) conditions using aqueous potassium hydroxide as the base and tetrabutylammonium bromide as phase transfer reagent under

ultrasonic condition (Vivekanand & Wang, 2011) (Scheme 5). Gas chromatography analyzed reaction was carried out at 50 °C under pseudo-first-order conditions by employing *n*-bromopropane as a limiting reactant and benzyl cyanide as a excess agent (Fig. 9).

Fig. 9. GC Chromatogram of C-alkylation of benzyl cyanide. A:1-bromopropane (Retention time = 2.15 min.); IS:Toluene (Retention time = 4.40 min.); B:Chlorobenzene (Retention time = 6.19 min.); C:Benzylcyanide (Retention time = 12.52 min.); Product: 2-Phenylvaleronitrile (Retention time = 14.35 min.).

Scheme 5. Alkylation of benzyl cyanide under PTC assisted ultrasonic condition.

The kinetic results indicates a material balance between reactant and products, i.e., the consumption of the amount of reactant (BP) equals to the sum of the generation of the amount of the product (2-phenylvaleronitrile) under ultrasonic conditions. Thus, rate of the decrease of *n*-bromopropane is consistent with the rate of production of 2-phenylvaleronitrile. Pseudo-first order kinetics was indicated by the linearity of the plot of $-\ln(1-X)$ versus time. The effect of various experimental parameters on the rate of the reaction has been studied; based on the experimental results, an interfacial mechanism was proposed. Similar PTC assisted C-alkylation reactions were analyzed by GC under various reaction conditions and an interfacial mechanism was proposed for these alkylation reactions (Vivekanand and Balakrishnan, 2009b, 2009c).

2.3.1 Effect of organic solvents

In this work, cyclohexanone, chlorobenzene, anisole, benzene, cyclohexane, were chosen as organic solvents to investigate their reactivities. From the plot of $-\ln(1-X)$ versus time, the rate constants are obtained. As shown in Table 3, the dielectric constants (ϵ) for these organic solvents are in the order Cyclohexanone ($\epsilon = 8.2$) > Chlorobenzene ($\epsilon = 5.6$) > Anisole ($\epsilon = 4.3$) > Benzene ($\epsilon = 2.28$) > Cyclohexane ($\epsilon = 2.02$). The order of the reactivity of the reactions in these six organic solvents is Cyclohexanone > Chlorobenzene > Anisole > Benzene > Cyclohexane. The dielectric constants are usually used as the main index in choosing an appropriate organic solvent in a PTC system; i.e., the reaction rate increases with increasing dielectric constant of the organic solvent. As the dielectric constant values of solvents increases, the activity of the nucleophilic reagent and also the distance between the bromide atom and the propyl group is increased. Therefore, the rate of the reaction increases (Wang and Chen, 2009 & Wang et al., 2009).

	Solvents				
	Cyclohexane	Benzene	Anisole	Chlorobenzene	Cyclohexanone
ϵ^a	2.02	2.28	4.3	5.6	8.2
$k_{app} (\times 10^{-3}, \text{min}^{-1})$	2.2	2.9	5.7	7.0	9.8

a-Dielectric constant.

Table 3. Effect of the organic solvents on the apparent rate constants (k_{app}) under ultrasonic condition: 21.93×10^{-2} mol of benzyl cyanide, 10g of KOH, 20 mL of H_2O , 0.1 g of internal standard (toluene), 20 mL of solvent, 21.96×10^{-3} mol of *n*-bromolpropane, 0.3 g of TBAB, 600 rpm, 50 $^\circ\text{C}$; under ultrasound conditions (50 kHz, 300 W). (Reprinted with permission from Vivekanand & Wang, 2011. Copyright (2011) Elsevier).

2.4 Suzuki cross coupling reaction

Suzuki cross coupling reaction (Miyaura and Suzuki, 1995; Corbet and Mignani, 2006) has been recognized as a powerful and convenient tool for the carbon-carbon bond forming

methods in the synthesis of pharmaceutical agents, organic materials, as well as natural products (Tomori, et al., 2000 & Kertesz et al., 2005). As a consequence, a considerable number of homogenous palladium catalysts have been used to obtain high yields of desired product.

A good number of Suzuki cross coupling reaction have been realized in organic solvents because of the solubility of typical reaction components like aryl, allyl or benzyl halides and boronic acids as well as their coupling products. In recent times, there has been great interest in developing green chemical reactions that make carbon-carbon bonds using water as a solvent and applying these reactions in academic and industrial lab settings (Deveau & Macdonald, 2004; Li, 2005; Liu, et al., 2006). Hence researchers started to deal with the coupling reaction in aqueous two-phase systems (Genet et al., 1995) with water-soluble palladium complexes as catalysts allowing easy separation of the water phase which contains the palladium catalyst and a strong base to bind the formed hydrogen halide. In such biphasic systems, phase-transfer reagents were added to promote the transport of the water-soluble palladium catalyst to the interface of the reactant. Enhancement effect on the reaction rate was observed depending on the structure of the added amphiphiles. Thus coupling of broad range of aryl halides with organoboron compounds can be readily promoted by use of a phase transfer catalyst in a biphasic solvent system (Y.G.Wang et al., 2007 & Sahu et al., 2009). Specifically, this procedure is efficient for the cross-coupling of aryl halides with electron-withdrawing substituents and sterically demanding substituents (Miura et al., 2007). The phase-transfer catalyst system efficiently promotes the cross-coupling of electronic variation in the aryl halides.

Paetzold and Oehme (2000) reported the palladium-catalysed cross coupling of 1-iodoanisole with phenylboronic acid in an aqueous solution of sodium carbonate in the presence of different phase transfer catalysts (Scheme 6). The coupling reaction was analyzed by GLC (column HP 1; program: 2 min at 50 °C then 10°C/min up to 260 °C). Gas Chromatography analysis revealed that on increasing concentration of the PTC, the rate of the reaction was increased and the formation of byproducts was suppressed.

Scheme 6. Palladium-catalyzed cross coupling of iodoanisole with phenylboronic acid in the presence of PTC.

Majority of PTC's gave yields of >90% except cetylammmonium tetrafluoroborate (Table 4; entry 1) which inhibits the reaction. The amphiphiles with low hydrophilic lipophilic balance (Table 4; entries 2, 5-9) and short chain amphiphiles (Table 4; entries 15 and 16) gave lower activities. Not only, the cetyltrimethylammonium bromide was favored as phase transfer reagent (Table 4; entry 10), but also zwitterionic amphiphiles, e.g.,

alkyldimethylammonium propane sulfonates (Table 4; entries 3 and 14) are excellent promoters. Dependence of anion was observed by authors while tetraalkylammonium salts were employed as PTC's (Table 4; entries 3, 4, 10-14). In addition to yield enhancement, the authors also reported that in presence of PTC, the selectivity increases by the suppression of formation of the biphenyl side product (**13**). Further the authors explored the reaction in presence of supported detergents(Paetzold et al., 2004).

Entry No.	PTC	Yield (%)	
		60 Min.	360 min.
1	Cetylammonium tetrafluoroborate	20	47
2	Polyoxyethylene(16)methylester C ₁₂	74	95
3	3-Dodecyltrimethylammonium propane sulfonate	89	94
4	Dodecyltrimethylammonium bromide	84	94
5	N-Lauroyl-alanine, sodium salt	85	89
6	N-Lauroyl-proline, sodium salt	84	89
7	Polyoxyethylene(20)sorbitanmonolaurate	78	26
8	Polyoxyethylene(6)lauryl ether	67	75
9	Polyoxyethylene(10)lauryl ether	70	78
10	Cetyltrimethylammonium bromide	98	99
11	Cetyldimethylammonium bromide	89	94
12	Cetyltrimethylammonium tetrafluoroborate	77	92
13	Cetyltrimethylammonium sulfate	78	91
14	3-Cetyldimethylammonium propane sulfonate	90	98
15	Tetra-n-butylammonium bromide	73	88
16	Benzyltrimethylammonium bromide	70	86
17	No Catalyst	65	85

Table 4. Effect of a phase-transfer catalyst in a biphasic solvent system on the Suzuki cross-coupling reactions

The coupling reaction of iodobenzene and phenylboronic acid occurs in aqueous medium in presence of palladium complexes and calix[*n*]arenes with good yields(Baur et al., 2001). The influence of water soluble macrocycles (Fig.10; 14-19) on the Suzuki reaction was analyzed by gas chromatography. The kinetic runs of aryl-aryl coupling reactions were stopped at small levels of conversion to exclude product inhibition effects and the yields were determined by GC. For comparison purpose, control experiments were carried out under identical conditions without addition of any macrocycle (Table 5, entry 9). The initial yields were found to be 4 to 8 times higher compared to the uncatalyzed reaction. Authors attributed the observed increase of initial yields to balance of binding ability of the host molecule and phase transfer properties. In order to avoid competition of organic solvent with the starting materials, apart from iodobenzene no additional organic solvent was employed in the investigation. Of the two bases compared, Cs₂CO₃ was found to be superior to diisopropylamine. All the calixarenes were found to be more superior to β -cyclodextrin. The mono-substituted calyx[4]arene **15**, the macrocyclic system with lowest solubility, was found to be more active than other tested macrocyclic systems.

Fig. 10. Structure of various calixarenes.

Entry No.	Macrocycle (equiv.)	Yield (%)		
		HNPr ₂	Cs ₂ Co ₃	No Base
1	18 (10 mol %)	2.4	-	-
2	19 (10 mol %)	2.9	-	-
3	19 (25 mol %)	2.6	-	-
4	17 (10 mol %)	5.8	8.1	1.1
5	17 (25 mol %)	7.5		
6	16 (10 mol %)	2.2	5.5	0.1
7	15 (10 mol %)	3.6	12.7	0.1
8	14 (10 mol %)	2.1	3.4	-
9	-	≅1.0	3.2	-

Table 5. Suzuki coupling reaction in presence of different macrocycles.

2.5 Epoxidation

The high-additive-value epoxides are extensively used in insulating materials, adhesives, coating materials, construction materials and electronic parts. Due to growing attraction of PTC assisted epoxidation reactions, we examined the epoxidation of dicyclopentadiene (**19**) in presence of sodium tungstate, phosphoric acid and hydrogen peroxide under phase transfer catalysis conditions by gas chromatography(Wang et al., 2004). High conversion of dicyclopentadiene and a trace amount of by-product were obtained.

The kinetics of the reaction was carried out in a 150 ml three-necked Pyrex flask, which permitted agitating the solution, inserting thermometer, taking samples and adding the feed. Known quantities of sodium tungstate and phosphoric acid were completely dissolved in hydrogen peroxide aqueous solution for preparing the active catalyst. The solution was put into the reactor, which was submerged into a well-controlled temperature water bath within ± 0.1 °C. Then, measured quantities of Aliquat 336 in chloroform, dicyclopentadiene in chloroform and biphenyl (internal standard) were introduced to the reactor to start the reaction. Samples were collected from the organic layer of the mixture (by stopping the stirring for 10–15 s each time) at regular time intervals. The samples were analyzed by gas chromatography (Shimadzu, 17A) for the three products; 1,2-epoxy-3a,4,7,7a-tetrahydro-4,7-methano-indene (**20**), 5,6-epoxy-3a,4,5,6,7,7a-hexahydro-4,7-methano-indene (**21**) and 1,2,5,6-diepoxy-octahydro-4,7-methano-indene (**22**). Gas chromatography (GC) mass analysis reveals molecular ion peaks at 148 (M⁺) (Fig. 11a) , 148(M⁺) (Fig. 11b) and 164 (M⁺) (Fig. 11c) for compounds **20**, **21** and **22** respectively. The GC analyzing conditions were:

- Column: 30m x 0.525mm i.d. capillary column containing 100% poly(dimethylsiloxane)
- Injection temperature: 250°C
- Carrier gas: N₂ at a flow rate of 20 mL/min
- Elution time of reactant A and products B, C, D: 3.82, 6.67, 7.24, and 9.43 min, respectively
- Detector: flame ionization detector (FID)

Fig. 11. Continued

Fig. 11. GC-MS analysis of (a) 1,2-epoxy-3a,4,7,7a-tetrahydro-4,7-methano-indane(**20**), (b) 5,6-epoxy-3a,4,5,6,7,7a-hexahydro-4,7-methano-indene(**21**);(c) 1,2,5,6-diepoxy-octahydro-4,7-methano-indene (**22**).

Initially, from the ion exchange reaction (between hydrogen peroxide, phosphoric acid, sodium tungstate and quaternary ammonium salt in the aqueous phase), the active catalyst $Q_3\{PO_4[W(O)(O_2)_2]_4\}$ was generated. In general, there are eight active oxygen atoms on each molecule of the active catalyst $Q_3\{PO_4[W(O)(O_2)_2]_4\}$. Nevertheless, we assume that each time only one active oxygen atom of the active catalyst is consumed in reacting with dicyclopentadiene in each reaction step. The remaining seven oxygen atoms are no longer active and needed for regeneration, i.e., the molecular formula of the catalyst after reaction is assumed to be $Q_3\{PO_4[W(O)(O_2)_2]_3[W(O)(O_2)(O)]\}$. Thus, three products, which include the epoxidation of two single-site double bonds and one two-site double bond of dicyclopentadiene molecule, are produced. The reaction mechanism is thus proposed as shown in Scheme 7.

Scheme 7. Mechanism of dicyclopentadiene's epoxidation under PTC conditions. (Reprinted with permission from Wang, et al., 2004. Copyright (2011) Taylor and Francis).

where $k_{a,1}$, $k_{a,2}$, and $k_{a,3}$ are the three aqueous-phase intrinsic rate constants, k_1 , k_2 , k_3 , and k_4 are the four organic-phase intrinsic rate constants and k_{QPW} and k_{QPWO} are the mass transfer coefficients of the regenerated catalyst $\text{Q}_3\{\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_3[\text{W}(\text{O})(\text{O}_2)(\text{O})]\}$ and the active catalyst $\text{Q}_3\{\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4\}$, respectively. Thus, the entire reaction involves the following steps:

- the ion exchange, the complex reaction in the aqueous phase,
- formation of the active catalyst at the interface between two phases,
- the epoxidation in the organic phase, and
- the mass transfer of active catalyst.

Thus based on the experimental result, the conversion follows pseudo first-order rate law, i.e.,

$$\frac{d[\text{DCPDI}]_{\text{org}}}{dt} = k_{\text{app}} [\text{DCPDI}]_{\text{org}} \quad (25)$$

where $[\text{DCPDI}]_{\text{org}}$ is the concentration of dicyclopentadiene in the organic phase. The subscript "org" denotes the characteristics of the species in the organic phase. In the beginning of experiment, we have

$$t = 0, [\text{DCPDI}]_{\text{org}} = [\text{DCPDI}]_{\text{org}, i} \quad (26)$$

The subscript "i" denotes the characteristics of the species at the initial condition. On solving equations (25) and (26), we have

$$-\ln(1 - X) = k_{app}t \quad (27)$$

where k_{app} is the apparent rate constant. X is the conversion of dicyclopentadiene, i.e.,

$$X = 1 - \frac{[DCPDI]_{org}}{[DCPDI]_{org,i}} \quad (28)$$

Assuming that the individual organic-phase reaction follows pseudo first-order rate law, we have

$$-\frac{d[DCPDI]_{org}}{dt} = -(k_1 + k_2)[QPWO]_{org}[DCPDI]_{org} \quad (29)$$

where $[QPWO]_{org}$ is the concentration of the active catalyst in the organic phase QPWO (i.e., $Q_3\{PO_4[W(O)(O_2)_2]_4\}$).

For a constant concentration of active catalyst in the organic phase, Eq (28) is reduced to

$$k_{app} = (k_1 + k_2)[QPWO]_{org} \quad (30)$$

As shown in the above equation, k_{app} represents the sum of two apparent rate constants of the two primary reactions, which are indicated in the reaction mechanism. From Eq (27), the apparent rate constant k_{app} can be obtained by a plot of $-\ln(1-X)$ versus time.

2.5.1 Effect of the amount of Aliquat 336

As shown in Table 6, the apparent rate constant value increases sharply with the increase in the amount of Aliquat 336 only upto 0.95×10^3 mol. Nevertheless, the apparent rate constant does not continue to increase when the catalyst loading exceeded 0.95×10^3 mol. We attribute the aforesaid fact to limited quantity of the active catalyst that is generated using a limiting amount of Na_2WO_4 and H_3PO_4 .

Generally, only the active catalyst $Q_3\{PO_4[W(O)(O_2)_2]_4\}$ promotes the reaction. The production of the active catalyst from the reaction of quaternary ammonium salt, sodium tungstate, hydrogen peroxide, and phosphoric acid takes place only in a stoichiometric quantity. The free sodium tungstate, phosphoric acid, quaternary ammonium salt and hydrogen peroxide do not enhance the reaction. Consequently, increasing the amount of Aliquat 336 does not enhance the reaction. We observed, the products (20), (21) and (22) being produced when an appropriate amount of Aliquat 336 was employed. On the other hand if a small amount of Aliquat 336 was used, only products (20) and (21) were produced.

2.5.2 Effect of the H_2O_2

Table 7 indicates the effect of amount of H_2O_2 on the rate of the reaction. The rate decreased with the increase in the volume of H_2O_2 . Nonetheless, this variation is not significant. The foremost cause is probably that the oxidation of dicyclopentadiene by free H_2O_2 takes place when a larger volume of H_2O_2 is employed. The active catalyst distributes between aqueous and organic phases, and most of the active catalyst is soluble in the organic phase. Therefore, the active catalyst of a slight portion dissolves in the aqueous phase by increasing

the volume of H₂O₂. Hence, the concentration of the active catalyst in the organic phase is slightly decreased by increasing the volume of hydrogen peroxide. The reaction between the active catalyst and the reactant takes place in the organic phase. Thus, the reaction rate slightly decreased with the increase in the volume of hydrogen peroxide due to low concentration of active catalyst in the organic phase(Wang and Rajendran, 2007a,b & Wang and Chen, 2008).

Amount of Aliquat 336 x 10 ³ (mol)	1.24	1.07	0.95	0.77	0.58	0.39	0.21	0.08	0
<i>k</i> _{1,app} x 10 ² (min ⁻¹)	2.79	2.99	3.15	3.15	1.61	1.91	1.17	0.44	0.12
<i>k</i> _{2,app} x 10 ² (min ⁻¹)	1.51	1.57	1.70	1.70	0.81	0.96	0.56	0.19	0
<i>k</i> _{3,app} x 10 ² (min ⁻¹)	0.63	0.69	0.79	0.79	0.20	0.42	0.25	0	0
<i>k</i> _{4,app} x 10 ² (min ⁻¹)	1.11	1.24	1.41	1.41	0.55	0.82	0.40	0	0

Table 6. Influence of the amount of catalyst on the conversion of dicyclopentadiene based on GC analysis

Volume of H ₂ O ₂ (mL)	65	55	45	35	25
<i>k</i> _{1,app} x 10 ² (min ⁻¹)	1.97	2.13	2.26	2.71	2.37
<i>k</i> _{2,app} x 10 ² (min ⁻¹)	1.23	1.35	1.39	1.61	1.53
<i>k</i> _{3,app} x 10 ² (min ⁻¹)	0.50	0.57	0.63	0.67	0.62
<i>k</i> _{4,app} x 10 ² (min ⁻¹)	0.90	1.04	1.04	1.22	1.11

a-by GC analysis

Table 7. Influence of the volume of hydrogen peroxide on the conversion of dicyclopentadiene^a

Previously, we reported (Wang & Huang, 2003) GC analyzed comparison of epoxidation conversion of olefins under phase transfer catalysis conditions. The results are shown in Table 8. In Olefins (23-38), the double bond in the ring is more easily oxidized than that of the terminal one using hydrogen peroxide as an oxidant. We compared the epoxidation results of olefins (27), (29) & (31) with those of olefins (34), (36) & (38). The results indicates higher conversion of olefins with double bond in five-carbon, six-carbon and eight-carbon rings than that of the aliphatic terminal bond. With minimum steric hindrance, only two hydrogen atoms appear on the double bond of the ring. On the other hand, there is larger steric hindrance for the double bond of the chain end when using the large-sized catalyst (Q₃[PO₄[W(O)O₄]₄]). Due to this phenomenon, it is difficult for the oxygen atom in the active complex catalyst to combine with the terminal carbon-carbon double bond.

As stated previously, the double bond of the ring can easily be epoxidized. Therefore, conversion of dicyclopentadiene (19) is larger than that of the olefins (23), & (25), which have only one double bond in the ring. Three different products were obtained from olefin (19) for the two double bonds in the ring. Since, six-carbon ring epoxide is more stable, conversion of olefin (27) is higher than olefin (29). On comparing the conversion of olefins (27), (29) & (30), we found that the conversion of 1,5- cyclooctadiene (100%) was the highest and the conversion of cyclohexene (92%) was the lowest. The reason for this is

that the six-carbon ring is the most stable, whereas the eight-carbon ring is the most unstable.

The conversion of straight chain compounds [(34), (36) & (38)] was much lower than those of the above reactants [(19), (23) (25), (27), (29), & (31)]. Comparing the results of (34) and (36), the conversion of 1-hexene was larger than that of 1-octene. Generally, the double bonds of the six-carbon chain have more chances to be attacked by the active catalyst than those of the 8-carbon chain. In the case of (38), there are two double bonds on the chain end of 1,7-octadiene. However, epoxidation of 1,7-octadiene gave only one product because of the short reaction time. Nevertheless *bis*-epoxy product was noticed on extending the reaction time.

Entry	Olefin	Product	Conversion ^a
1	23	24	75
2	25	26	92
3	19	20 21 22	98
4	27	28	98
5	29	30	92
6	31	32 33	100

7			25
8			10
9			20

a Gas chromatography (Shimadzu GC 9A with FID using 100% poly(dimethylsiloxane), capillary column, 30m_0.525 mm and nitrogen as the carrier gas).

Table 8. Structural influence of different olefins on their epoxidation under PTC conditions (Wang & Huang, 2003) analyzed by GC^a. (Reprinted with permission from Wang & Huang, 2003. Copyright (2011) Springer).

3. Conclusions

Current chapter describes recent developments and a perspective in kinetics of phase transfer catalysis assisted organic reactions analyzed by Gas Chromatography. The combination of PTC with sonochemistry can also be an interesting approach for determining efficient reaction conditions, provided that PTC remains stable under exposure to ultra-sounds. Research reports from leading laboratories that touch on all the themes noted herein and many others are assembled. The topics are organized by five broad groupings, *viz.*, N-alkylation, O-Alkylation, C-alkylation, Suzuki coupling and epoxidation. The N-alkylation study reveals that the stirring speed has positive influence on rate of the reaction only up to 400 rpm and the favorable quaternary ammonium salt for the reaction will be the one with larger carbon numbers. In the ultrasonic irradiation assisted synthesis of dimethoxydiphenylmethane, higher the ultrasonic frequency and power, higher will be the rate constant values. C-alkylation study indicates the influence of dielectric constant values on the rate of the reaction. GC-analyzed Suzuki coupling reactions indicates the application of PTC in these reactions. Kinetics of epoxidation of dicyclopentadiene shows that the rate of the reaction depends only upto certain amount of catalyst. Nevertheless the volume of hydrogen peroxide has a negative influence on the rate of the reaction. Thus, PTC approach leads in establishing genuinely sustainable chemical industrial processes within the context of the forthcoming paradigm shift in worldwide production of highly valuable substances.

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Phone: +86-21-62489820
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