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Role of Mass Transfer in Phase Transfer Catalytic Heterogeneous Reaction Systems

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1. Introduction

Conventional techniques [1] for removing the constraints of mutual insolubility of aqueous phase with organic phase are industrially unattractive and polluting. A plausible technique now widely known as "phase transfer catalysis" (PTC) has emerged as a broadly useful tool [2–7] in solving the predicament of insolubility of aqueous phase with organic phase. In this methodology, involving a substrate (in the organic layer) and an anionic reagent or a nucleophile (in the aqueous layer), reacting anions are continuously introduced into the organic phase. Currently, PTC is an important choice in organic synthesis and is widely applied in the manufacturing processes of specialty chemicals, such as pharmaceuticals, perfumes, dyes, additives, pesticides, and monomers. Further, the recent tendency toward "green and sustainable chemistry" has again attracted strong attention to this technique [8-13]. In the last five decades, a steadily increasing number of papers and patents dealing with phase transfer topics and related to their applications have been published in the literature [14-30].

It is understood that the complicated nature of the PTC system stems from the two mass-transfer steps and two reaction steps in the organic and aqueous phases. In addition, the equilibrium partitions of the catalysts between two phases also affect the reaction rate. The difficulty in realizing the mass-transfer rates of catalysts between two phases is probably due to the uneasy identification of the catalyst (or intermediate product) during reactions. Inoue *et al.* [31] investigated mass transfer accompanied by chemical reaction at the surface of a single droplet. They studied the mass-transfer effect for both neglecting and accounting for the mass-transfer resistance in the continuous phase.

Wang and Yang [32] investigated the dynamic behavior of phase transfer- catalyzed reactions by determining the parameters accounting for mass transfer and the kinetics in a two-phase system. However, the main disadvantage of PTC in the industrial application of soluble phase-transfer catalyst (PTC) applications, such as quaternary ammonium salts, is the need to separate the catalysts from the reaction mixture and its subsequent reuse or disposal. Hence, from industrial point of view, polymer-anchored catalyst is more desirable in order to simplify catalyst separation from the reaction mixture and its reuse thereby the need for complex chromatographic techniques can be avoided for product separation and isolation [33–38]. To circumvent the problem of separation of catalyst from the reaction mixture, for the first time Regen [39] reported anchoring the phase transfer catalysts to a polymer backbone and suggested the name "Triphase Catalysis". Quaternary onium salts,

crown ethers and cryptands have all been immobilized on various kinds of supports, including polymers (most commonly (methylstyrene-costyrene) resin crosslinked with divinylbenzene), alumina, silica gel, clays, and zeolites [40–51]. Kinetics of triphase phase-transfer-catalyzed reactions [52] are influenced by (i) mass transfer of reactant from bulk liquid to catalyst surface; (ii) diffusion of reactant through polymer matrix to active site; (iii) intrinsic reaction rate at active site; (iv) diffusion of product through polymer matrix and mass transfer of product to external solution; (v) rate of ion exchange at active site. In heterogeneous conditions, for a proper mass transfer to occur, both the liquid phases should be in contact with catalyst. Thus, mass transfer of reactant from bulk solution to catalyst surface and mass transfer of the product to the bulk solution are the significant steps involved. The reaction mechanism of these PTC's system is often complicated and several factors affect the conversion of reactants. With all these antecedents, in this chapter, a kinetic and mathematical model of phase-transfer catalysis concerning mass transfer with various organic reactions will be presented. An extensive detail has been made on the effects of mass transfer in the PTC reaction systems. Further, it is proposed to present the diffusion resistance of an active phase-transfer catalyst in the organic phase and mass-transfer resistance between the droplet and the bulk aqueous phase.

2. Influence of mass transfer in various PTC assisted organic reactions

2.1 O-Alkylation

Previously, we reported a simplified model [53] to predict the dynamic behavior of the allylation for 2, 4, 6-tribromophenol catalyzed by tetra-*n*-butylammonium bromide. The intermediate product viz., of tetra-*n*-butylammonium 2,4,6-tribromophenoxide ((C$_6$H$_2$)-Br$_3$OBu$_4$N) was successfully identified [54]. Kinetic run was started by dissolving a known quantity of potassium hydroxide and 2,4,6-tribromophenol in water. The solution was then introduced into the reactor, which was thermostated at the desired temperature. A measured quantity of allyl bromide and diphenyl ether (internal standard), were dissolved in the chlorobenzene solvent and then added to the reactor. To start the reaction, tetra-*n*-butylammonium bromide (TBAB) was then added to the reactor. Aliquot samples (0.8 mL) were collected from the reactor at regular intervals of time. After the separation of organic phase from aqueous phase, 0.1 mL of the organic-phase sample was immediately diluted with 4.5 mL of methanol and the sample was analyzed by HPLC analysis. A general schematic diagram of phase-transfer catalysis for the allylation of 2, 4, 6-tribromophenol is presented in Scheme 1.
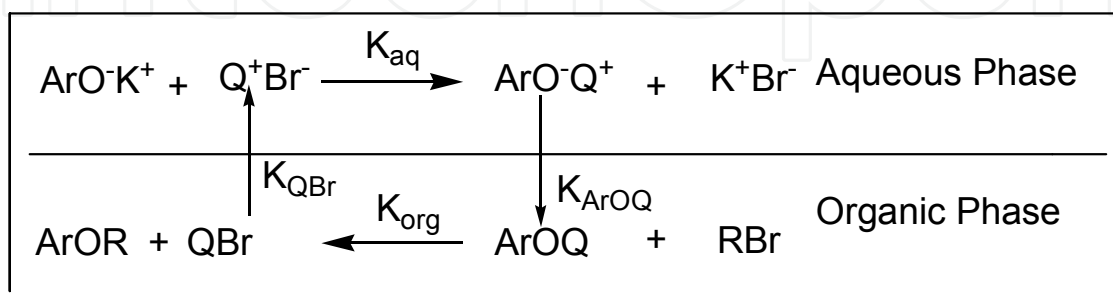
Scheme 1. O-Alkylation of 2,4,6-tribromophenol under PTC Conditions

where the parameters, K_{aq}, K_{org}, K_{ArOQ} and K_{QBr} are given in the Nomenclature section.

In order to formulate a mathematical model to describe the dynamic behavior of the two-phase reaction shown above, a two-film theory is employed to consider the mass transfer of the catalysts between two phases. Hence, those equations which model the two-phase reaction are presented below. The rate of change for ArOQ in the organic phase is the difference of mass-transfer rate and organic-phase reaction rate.

$$\frac{dC_{ArOQ}^{org}}{dt} = K_{ArOQ}A\left(C_{ArOQ}^{aq} - \frac{C_{ArOQ}^{org}}{m_{ArOQ}} \right) - K_{org}C_{RBr}^{org}C_{ArOQ}^{org} \tag{1}$$

The rate of change for ArOQ in the aqueous phase is the difference of aqueous-phase reaction rate and mass transfer rate.

$$\frac{dC_{ArOQ}^{aq}}{dt} = K_{org}C_{ArOK}^{aq}C_{QBr}^{aq} - K_{ArOQ}Af\left(C_{ArOQ}^{aq} - \frac{C_{ArOQ}^{org}}{m_{ArOQ}} \right) \tag{2}$$

Similarly, the rate of change for QBr either in the organic phase or in the aqueous phase is obtained as shown in (3) and (4).

$$\frac{dC_{QBr}^{org}}{dt} = K_{org}C_{ArOQ}^{org}C_{RBr}^{org} - K_{QBr}A\left(C_{QBr}^{org} - m_{QBr}C_{QBr}^{aq} \right) \tag{3}$$

$$\frac{dC_{QBr}^{aq}}{dt} = K_{QBr}Af\left(C_{QBr}^{org} - m_{QBr}C_{QBr}^{aq} \right) - K_{aq}C_{ArOK}^{aq}C_{QBr}^{aq} \tag{4}$$

The reaction rate of ArOK in the aqueous phase is

$$\frac{dC_{ArOK}^{aq}}{dt} = -K_{aq}C_{ArOK}^{aq}C_{QBr}^{aq} \tag{5}$$

The reaction rate of RBr in the organic phase is

$$\frac{dC_{RBr}^{org}}{dt} = -K_{org}C_{ArOQ}^{org}C_{RBr}^{org} \tag{6}$$

In the above equations, "f" is defined as the ratio of the volume of organic phase (V_0) to the volume of aqueous phase (V_a), i.e.

$$f = \frac{V_o}{V_a} \tag{7}$$

The distribution coefficients of catalysts m_{ArOQ} and m_{QBr} are defined as

$$m_{ArOQ} = \frac{C_{ArOQ}^{org(s)}}{C_{ArOQ}^{aq(s)}} \tag{8}$$

$$m_{QBr} = \frac{C_{QBr}^{org(s)}}{C_{QBr}^{aq(s)}} \tag{9}$$

where the superscript "s" denotes the characteristics of the species at the interphase.
The conversion of allyl bromide (RBr) is defined as X,

$$X = 1 - \frac{C_{RBr}^{org}}{C_{RBr,0}^{org}} \tag{10}$$

where the subscript "0" denotes the initial concentration of allyl bromide. The total number of moles of catalyst (Q_o) and the total number of moles of 2,4,6-tribromophenol (E_o) initially are

$$Q_0 = V_o \left(C_{ArOQ}^{org} + C_{QBr}^{org} \right) + V_a \left(C_{ArOQ}^{aq} + C_{QBr}^{aq} \right) \tag{11}$$

$$E_0 = V_o \left(C_{ArOQ}^{org} + \left[C_{RBr,0}^{org} - C_{RBr}^{org} \right] \right) + V_a \left(C_{ArOK}^{aq} + C_{ArOQ}^{aq} \right) \tag{12}$$

The initial conditions of the above equations are

$$C_{QBr}^{org} = 0, \ C_{QBr}^{aq} = C_{QBr,0}^{aq}, \ C_{RBr}^{org} = C_{RBr,0}^{org}; \ t = 0$$
$$C_{ArOQ}^{org} = 0, \ C_{ArOQ}^{aq} = 0, \ C_{ArOK}^{aq} = C_{ArOK,0}^{aq}; \ t = 0 \tag{13}$$

The parameters m_{QBr}, m_{ArOQ}, $K_{QBr}A$, $K_{ArOQ}A$, K_{aq} and K_{org} for the allylation of 2,4,6-tribromophenol in a two phase catalyzed reaction [54] are as follows:

$$m_{QBr} = 7.1 \times 10^{-2} - 0.56 C_{QBr}^{aq} \tag{14}$$

$$m_{ArOQ} = (8.02 + 0.05T) + (78.33T - 1165) C_{ArOQ}^{aq} \tag{15}$$

$$K_{QBr}A = 2.69 \qquad \text{min}^{-1} \tag{16}$$

$$K_{ArOQ}A = 3.84 + 0.06T \qquad \text{min}^{-1} \tag{17}$$

$$K_{aq} = 3.2 \times 10^7 \exp \left[\frac{-4840}{T + 273.16} \right] \qquad M^{-1} \text{min}^{-1} \tag{18}$$

$$K_{org} = 3.3 \times 10^9 \exp \left[\frac{-7016}{T + 273.16} \right] \qquad M^{-1} \text{min}^{-1} \tag{19}$$

After a small induction period, the concentration of ArOQ is kept at a constant value and hence, the pseudo-steady-state hypothesis (PSSH) can be made in the system under investigation, i.e.,

$$\frac{dC_{ArOQ}^{org}}{dt} = \frac{dC_{ArOQ}^{aq}}{dt} = 0 \tag{20}$$

Thus, (1) and (2) become

$$C_{ArOQ}^{aq} = \left(\frac{1}{m_{ArOQ}} + \frac{K_{org} C_{RBr}^{org}}{K_{ArOQ}A} \right) C_{ArOQ}^{org} \tag{21}$$

$$K_{aq}C_{ArOK}^{aq}C_{QBr}^{aq} = K_{ArOQ}Af\left(C_{ArOQ}^{aq} - \frac{C_{ArOQ}^{org}}{m_{ArOQ}}\right) \tag{22}$$

Eliminating C^{aq}_{ArOK} from (21) and (22), we obtain

$$C_{QBr}^{aq} = \frac{fK_{org}C_{RBr}^{org}}{K_{aq}C_{ArOK}^{aq}}C_{ArOQ}^{org} \tag{23}$$

In a similar way, the following equation is held for QBr:

$$\frac{dC_{QBr}^{org}}{dt} = \frac{dC_{QBr}^{aq}}{dt} = 0 \tag{24}$$

From (3), (4), and (23), we have

$$C_{QBr}^{org} = \frac{K_{org}C_{ArOQ}^{org}C_{RBr}^{org}}{K_{QBr}A} + m_{QBr}C_{QBr}^{aq} \tag{25}$$

Substituting (23) into (25)

$$C_{QBr}^{org} = K_{org}C_{ArOQ}^{org}C_{RBr}^{org}\left[\frac{1}{K_{QBr}A} + \frac{m_{QBr}f}{K_{aq}C_{ArOK}^{aq}}\right] \tag{26}$$

Combining (11), (21), (23), and (26), we have

$$C_{ArOQ}^{org} = \frac{Q_o}{V_o}\left\{1 + \frac{1}{fm_{ArOQ}} + \frac{K_{org}C_{RBr}^{org}}{fK_{ArOQ}A} + \left(1 + fm_{QBr} + \frac{k_{aq}C_{ArOK}}{K_{QBr}A}\right)\frac{K_{org}C_{RBr}^{org}}{K_{aq}C_{ArOK}^{aq}}\right\}^{-1} \tag{27}$$

Applying the Damkohler numbers of ArOQ and QBr, respectively, as

$$Da_{A_{rOQ}} = \frac{K_{org}C_{RBr}^{org}}{K_{ArOQ}A} = \frac{K_{org}(1-X)C_{RBr,0}^{org}}{K_{ArOQ}A} \tag{28}$$

$$Da_{QBr} = \frac{K_{aq}C_{ArOK}^{aq}}{K_{QBr}A} \tag{29}$$

The concentration of ArOK in the aqueous phase can be obtained from the material balance of 2,4,6-tribromophenol, which is shown in (12). As shown in (28) and (29), the Damkohler number indicates the ratio of the chemical reaction rate to the mass-transfer rate of the catalyst. An effective fraction of catalyst, η, which is defined as the ratio of the observed two-phase reaction rate to the organic-phase reaction rate with catalyst completely used, is given as

$$\eta = \frac{K_{app}C_{RBr}^{org}}{K_{org}\left(\dfrac{Q_0}{V_o}\right)C_{RBr}^{org}} = \frac{V_o C_{ArOQ}^{org}}{Q_0} \tag{30}$$

where

$$K_{app} = K_{org}C^{org}_{ArOQ} \qquad (31)$$

Thus, η can be expressed as

$$\eta = \frac{1}{1 + \dfrac{\alpha}{f} + (1+\beta)R} \qquad (32)$$

where

$$\alpha = \frac{1}{m_{ArOQ}} + Da_{ArOQ} \qquad (33)$$

$$\beta = fm_{QBr} + Da_{QBr} \qquad (34)$$

$$R = \frac{K_{org}C^{org}_{RBr}}{K_{aq}C^{aq}_{ArOK}} \qquad (35)$$

The parameters "α" and "β" reflect the effects of the equilibrium distribution of catalysts between two phases and the mass transfer of catalysts across the interphase. "R" is a ratio of the reaction velocity in the organic phase to that of velocity in the aqueous phase. Thus, the concentrations of ArOQ and QBr either in the organic phase or in the aqueous phase can be represented by the following equations:

$$C^{org}_{ArOQ} = \frac{\dfrac{Q_0}{V_o}}{1 + \dfrac{\alpha}{f} + (1+\beta)R} \qquad (36)$$

$$C^{aq}_{ArOQ} = \left(\frac{Q_0}{V_o}\right)\eta\alpha \qquad (37)$$

$$C^{org}_{QBr} = \left(\frac{Q_0}{V_o}\right)\eta\beta R \qquad (38)$$

$$C^{aq}_{QBr} = \left(\frac{Q_0}{V_o}\right)\eta fR \qquad (39)$$

By solving the nonlinear algebraic equations of (11), (12), (32), (36), (37), (38), and (39) with the specified parameters or the operating conditions, the simulation results for f = 1 are given in Figures 1-3.

As given in (28) and (29), the Damkohler number (D_a) is defined as the ratio of the reaction rate to the mass transfer rate. From the plot of D_a vs. the conversion of allyl bromide, it is obvious that the Damkohler number of ArOQ, which also depends on the initial concentration of allyl bromide, is much less than unity for the whole range of conversion

(Figure 1). Thus, the reaction rate of the organic-phase reaction is much lower than the mass-transfer rate of ArOQ. Hence, the mass-transfer resistance of ArOQ from the aqueous phase to the organic phase is negligible when compared with the reaction rate in the organic phase. In addition, the Damkohler number of ArOQ increases with the increase of temperature for a certain value of conversion. This is attributed to the increase in the organic phase reaction rate at a higher temperature while the resistance of mass transfer of ArOQ is very small.
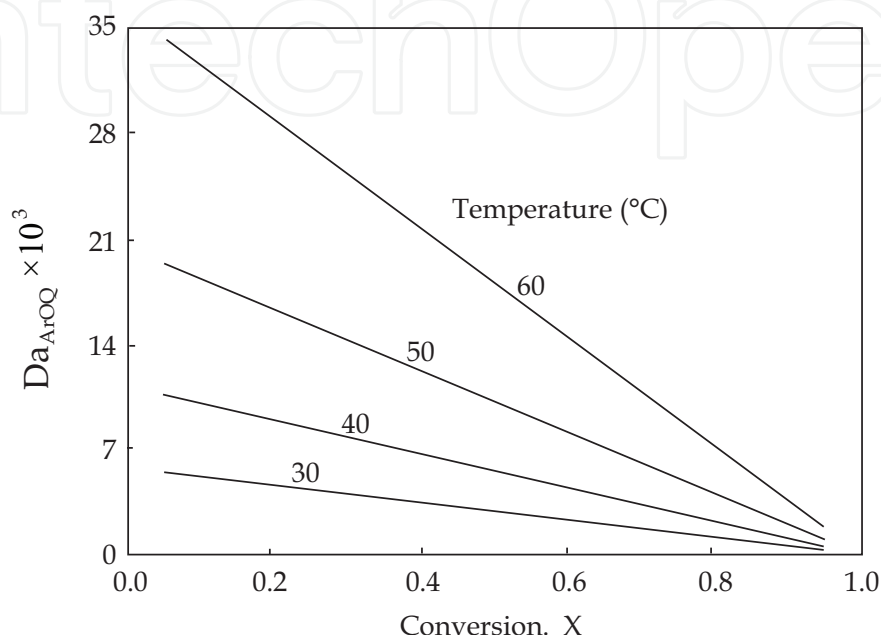
Fig. 1. Dependence of the ratio of the reaction to the mass transfer rate for ArOQ (Da_{ArOQ}) on conversion (X) at different temperatures: 0.7 g of allyl bromide, 3.0 g of 2,4,6-tribromophenol, 0.2 g of TBAB catalyst, 1.0 g of KOH, 50 mL of H_2O, 50 mL of chlorobenzene. (Adapted from Ref. [53], by permission)

The order of magnitude of the Damkohler number of QBr (Da_{Br}) for the whole range of conversion is about unity (Figure 2). These results reflect the fact that the mass-transfer rate of QBr from the organic phase to the aqueous phase is slightly larger than the reaction rate in the aqueous phase. A plot of R value, which denotes the relative reactivity of the organic phase to the aqueous phase *vs.* conversion, is given in Figure 3. The R value is less than unity. In combining the results from Figures 1-3, the step of the organic-phase reaction is confirmed as the rate-determining step of the whole reaction quantitatively rather than qualitatively by other investigators in the published documents.

From the plot of η *vs.* X, it was found that about 75-90% of the catalyst exists in the form of ArOQ remaining in the organic phase. Further, we found that the concentration of ArOQ in the organic phase increases when the initial amount of catalyst added to the reactor increases. Some of the salient features of the study are:

i. The reaction system was simulated by the proposed model in conjunction with the system parameters, such as mass-transfer coefficients of catalysts, distribution coefficients of catalysts and the intrinsic reaction rate constants either in the organic phase or in the aqueous phase.

ii. The Damkohler numbers, which directly reflect the relative rate of chemical reaction to the mass transfer of the catalysts, are defined.

iii.   The mass-transfer resistance of catalysts from the aqueous phase to the organic phase is
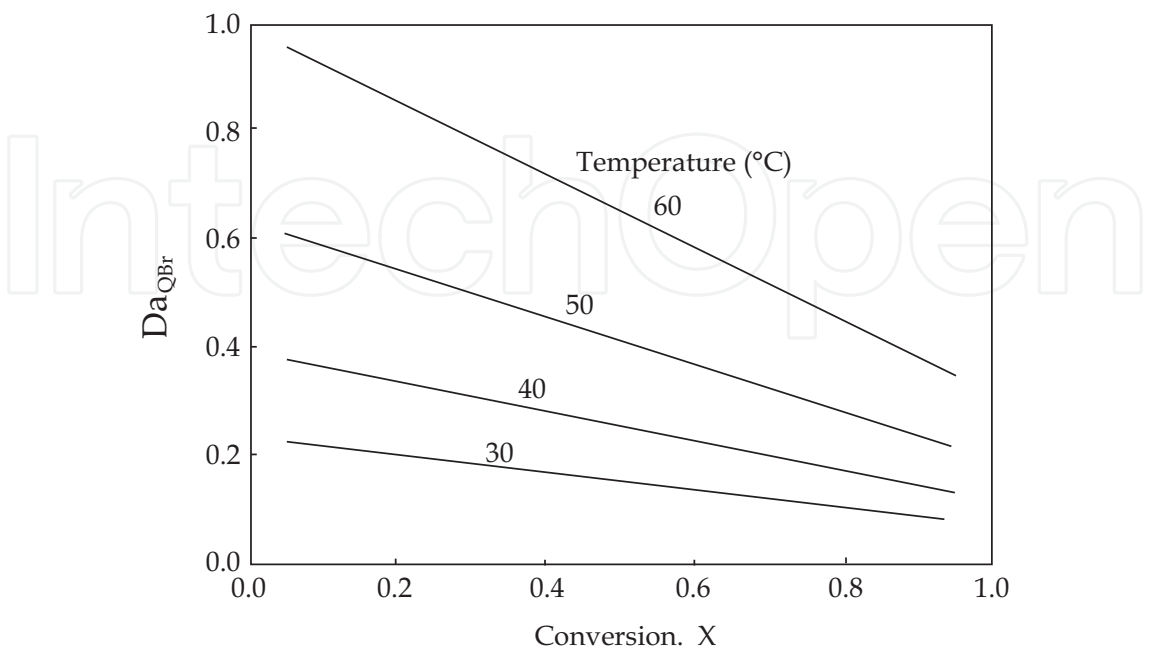   negligible.

Fig. 2. Dependence of the ratio of the reaction to the mass transfer rate for QBr (Da_{QBr}) on
conversion (X) at different temperatures: 0.7 g of allyl bromide, 3.0 g of 2,4,6-tribromophenol,
0.2 g of TBAB catalyst, 1.0 g of KOH, 50 mL of H_2O, 50 mL of chlorobenzene. (Adapted from
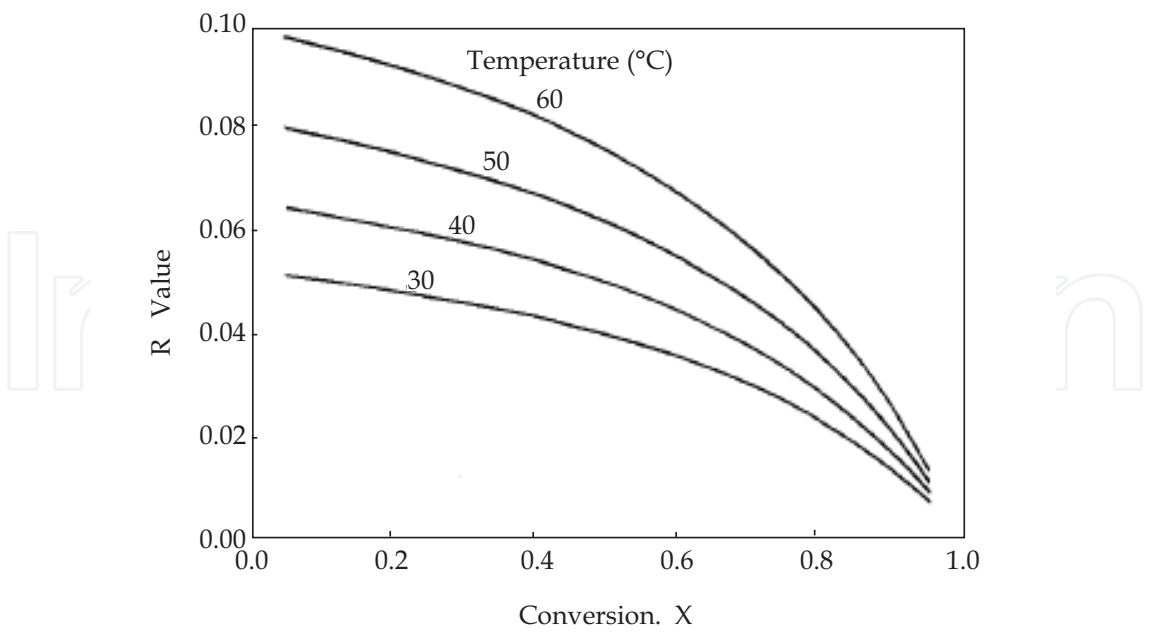Ref. [53], by permission)

Fig. 3. Dependence of the ratio of the organic-phase reaction to the aqueous-phase reaction
rate (R value) on conversion (X) at different temperatures: 0.7 g of allyl bromide, 3.0 g of
2,4,6-tribromophenol, 0.2 g of TBAB catalyst, 1.0 g of KOH, 50 mL of H_2O, 50 mL of
chlorobenzene. (Adapted from Ref. [53], by permission)

Later, we investigated the reaction of 2,4,6-tribromophenol with allyl bromide catalyzed by triphase catalyst (polymer supported tributylamine chloride) in an organic/alkaline solution [55]. The apparent reaction rates were observed to obey the pseudo-first-order kinetics with respect to the organic reactant when excess 2,4,6-tribromophenol was used. Also, a kinetic model in terms of the intrinsic reactivity and intra-particle diffusion limitations for a spherical catalyst is proposed to describe the triphase catalytic reaction system. The pseudo-steady-state approach to the mass balance equation was employed to get the solution. The effective diffusivity of the reactants within the catalyst was obtained from this model and used to predict the observed reaction rate. The apparent reaction rate constants were measured at various agitation speeds using 40-80 mesh of catalyst. Kinetic results indicate that the mass-transfer resistance outside the catalyst can be neglected for agitation speeds higher than 600 rpm (Figure 4)
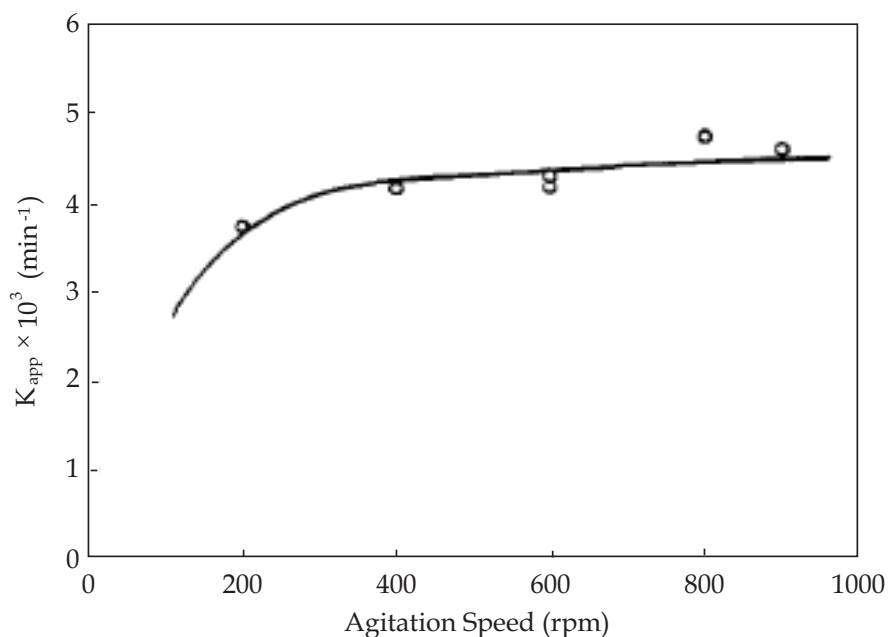

Fig. 4. Effects of the agitation speed on the apparent reaction rate constant: 9.06 x 10⁻³ mol of 2,4,6-tribromophenol; 50 mL of water; 1.567 mole ratio of allyl bromide to 2,4,6-tribromophenol; 1.97, mole ratio of KOH to 2,4,6-tribromophenol; 0.488 g of catalyst pellet (40-80 mesh); 50 mL of chlorobenzene; 50 °C. (Adapted from Ref. [55], by permission)

2.2 Substitution reaction between hexachlorocyclotriphosphazene and sodium 2,2,2-trifluoro-ethoxide

Effects of mass transfer and extraction of quaternary ammonium salts on the conversion of hexachlorocyclotriphosphazene were investigated in detail [56]. Initially, a known quantity of sodium hydroxide, trifluoroethanol, and tetra-n-butylammonium bromide were introduced into the reactor which was thermostated at the desired temperature. Measured quantities of phosphazene reactant, $(NPCl_2)_3$ and n-pentadecane (internal standard) were dissolved in chlorobenzene solvent at the desired temperature. Then, the organic mixture was added into the reactor to start a kinetic run. An aliquot sample was withdrawn from the reaction solution at the chosen time. The sample (0.5 mL) was immediately added to 3 mL of

hydrochloric acid to quench the reaction and then the organic-phase contents are analyzed quantitatively by GC using the method of internal standard.
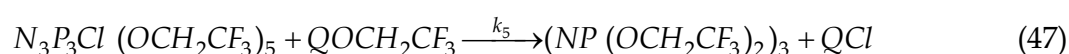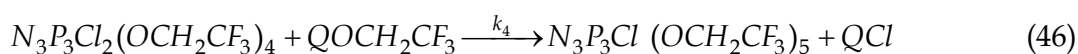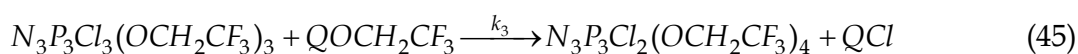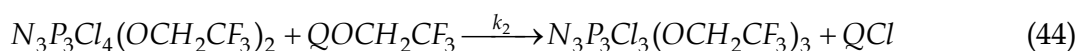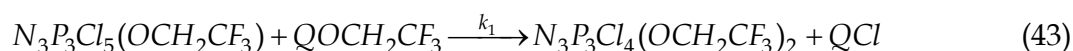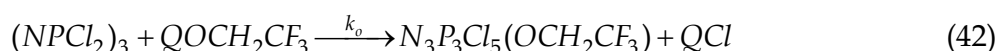
In organic reactions which are driven by S_N2 mechanism under phase transfer catalysis conditions, the substrate and the nucleophile react directly *via* a transittion state to product. The system can be explained by first order reaction by plotting ln [$(NPCl_2)_3$] *vs.* time, which results in a straight line. Thus, the system can be expressed as:

$$-\frac{d[(NPCl_2)_3]_o}{dt} = k_{o,app}[(NPCl_2)_3]_o \tag{40}$$

where,

$$k_{o,app} = k[QOCH_2CF_3]_o \tag{41}$$

The fixed value of $k_{0,,app}$ is called the pseudo-steady-state first-order reaction rate constant. The series reaction of the organic phase was explained by the S_N2 mechanism [57, 58]. The reaction expressions can be written as:

$$(NPCl_2)_3 + QOCH_2CF_3 \xrightarrow{k_o} N_3P_3Cl_5(OCH_2CF_3) + QCl \tag{42}$$

$$N_3P_3Cl_5(OCH_2CF_3) + QOCH_2CF_3 \xrightarrow{k_1} N_3P_3Cl_4(OCH_2CF_3)_2 + QCl \tag{43}$$

$$N_3P_3Cl_4(OCH_2CF_3)_2 + QOCH_2CF_3 \xrightarrow{k_2} N_3P_3Cl_3(OCH_2CF_3)_3 + QCl \tag{44}$$

$$N_3P_3Cl_3(OCH_2CF_3)_3 + QOCH_2CF_3 \xrightarrow{k_3} N_3P_3Cl_2(OCH_2CF_3)_4 + QCl \tag{45}$$

$$N_3P_3Cl_2(OCH_2CF_3)_4 + QOCH_2CF_3 \xrightarrow{k_4} N_3P_3Cl (OCH_2CF_3)_5 + QCl \tag{46}$$

$$N_3P_3Cl (OCH_2CF_3)_5 + QOCH_2CF_3 \xrightarrow{k_5} (NP (OCH_2CF_3)_2)_3 + QCl \tag{47}$$

Thus, the reaction rate can be expressed as,

$$\frac{dy_1}{dy_0} = -1 + k_1 * \frac{y_1}{y_0} \tag{48}$$

$$\frac{dy_2}{dy_0} = k_1 * \frac{y_1}{y_0} - k_2 * \frac{y_2}{y_0} \tag{49}$$

$$\frac{dy_3}{dy_0} = k_2 * \frac{y_2}{y_0} - k_3 * \frac{y_3}{y_0} \tag{50}$$

$$\frac{dy_4}{dy_0} = k_3 * \frac{y_3}{y_0} - k_4 * \frac{y_4}{y_0} \tag{51}$$

$$\frac{dy_5}{dy_0} = k_4 * \frac{y_4}{y_0} - k_5 * \frac{y_5}{y_0} \tag{52}$$

$$\frac{dy_6}{dy_0} = k_5 * \frac{y_5}{y_0} \tag{53}$$

where the dimensionless variables and parameters are defined as

$$y_0 = \frac{[(NPCl_2)_3]_o}{[(NPCl_2)_3]_o^{\,0}}$$

$$y_1 = \frac{[N_3P_3Cl_5(OCH_2CF_3)]_o}{[(NPCl_2)_3]_o^{\,0}}$$

$$y_2 = \frac{[N_3P_3Cl_4(OCH_2CF_3)_2]_o}{[(NPCl_2)_3]_o^{\,0}}$$

$$y_3 = \frac{[NPCl_3(OCH_2CF_3)_3]_o}{[(NPCl_2)_3]_o^{\,0}}$$

$$y_4 = \frac{[N_3P_3Cl_2(OCH_2CF_3)_4]_o}{[(NPCl_2)_3]_o^{\,0}}$$

$$y_5 = \frac{[N_3P_3Cl\ (OCH_2CF_3)_5]_o}{[(NPCl_2)_3]_o^{\,0}}$$

$$y_6 = \frac{[(NP(OCH_2CF_3)_2)_3]_o}{[(NPCl_2)_3]_o^{\,0}}$$

and

$$k_1^* = \frac{k_1}{k_0}, \qquad k_2^* = \frac{k_2}{k_0}, \qquad k_3^* = \frac{k_3}{k_0}, \qquad k_4^* = \frac{k_4}{k_0}, \qquad k_5^* = \frac{k_5}{k_0}$$

where $[(NPCl_2)_3]_O^0$ represents the initial concentration of reactant $(NPCl_2)_3$ in the organic phase and $k_o^* = 1$.

In general, eq. 48-53 can be solved with the following initial conditions of y_i.

$$y_0 = 1, \qquad y_1 = y_2 = y_3 = y_4 = y_5 = y_6 = 0 \tag{54}$$

The solutions are

$$y_{n+1} = \sum_{l=o}^{n+1} \frac{(\prod_{i=0}^{n} k_i^*) y_0^{\,k_l^*}}{\prod_{\substack{i=0 \\ i \neq l}}^{n+1} (k_i^* - k_l^*)}; \qquad n = 0,1,2,3,4 \tag{55}$$

$$y_6 = \sum_{l=0}^{5} \frac{k_5^{*}(\prod_{i=0}^{4} k_i^{*})(y_o^{k_l^{*}} - 1)}{k_l^{*} \prod_{\substack{i=0 \\ i \neq l}}^{5} (k_i^{*} - k_l^{*})} \tag{56}$$

From eqs 55 and 56, the concentrations of the distributed products, $N_3P_3Cl_{6-y}(OCH_2CF_3)_y$, y = 1-6, including the intermediate and final products, are thus determined.

In order to follow the kinetics of phase-transfer catalyzed reactions, it is necessary to sort out the rate effects due to equilibria and anion-transfer mechanism for transfer of anions from the aqueous to the organic phase *i.e.*, the concentration of $QOCH_2CF_3$ would remain constant if Q^+ concentration in the organic phase remained constant throughout the entire course of a kinetic run and the equilibrium constant K is very small.

$$QOCH_2CF_{3\ org} + Cl^-_{\ aq} \xrightleftharpoons{k} QCl_{\ org} + {}^-OCH_2CF_{3\ aq} \tag{57}$$
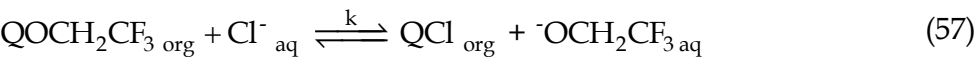
Many experimental runs were carried out to examine the Q^+ values and K values. More than 99.5% of Q^+ stay in the organic phase and K value was calculated to be less than 1×10^{-2}. Therefore, the concentration of $QOCH_2CF_3$ in the organic phase remains constant. Based on this experimental evidence, those factors affecting the reaction are discussed in the following sections.

In PTC systems, it is recognized that the rate-determining step is controlled by the chemical reaction in the organic phase. In systems involving fast mass-transfer rate of catalyst between two phases, the influence of mass transfer on the reaction can be neglected. However, on varying the concentration of $(NPCl_2)_3$, the apparent reaction rate constant values also changes (Table 1). Further, the value of $k_{0.5/2}$, defined as the ratio of the $k_{o,app}$ value using 0.5 g of $(NPCl_2)_3$ to the $k_{o,app}$ value using 2 g of $(NPCl_2)_3$, is increased for increasing reaction temperature. This phenomenon indicates that the present reaction system is both controlled by chemical kinetics and mass transfer.

Organic reactions, which are controlled by purely chemical reaction kinetics, will be independent of the mass of the reactant on the conversion. The effect of the mass of $(NPCl_2)_3$ in presence of different phase transfer catalysts, on the conversion is shown in Table 2. Only in the presence of TEAC the reaction is controlled purely by chemical reaction kinetics. On the other hand other reactions, with different kinds of catalysts, are both controlled by chemical reaction kinetics and mass transfer. A higher influence of mass transfer on the reaction rate is confirmed by higher value of $k_{0.5/2}$.

| | $k_{0,app}$, min^{-1} | | | | | | |
| | mass of reactant, $(NPCl_2)_3$, g | | | | | | |
Temp. °C	0.5	1.0	1.5	2.0	$k_{1.5/2}$	$k_{1/2}$	$k_{0.5/2}$
20	0.36	0.27	0.21	0.17	1.24	1.59	2.11
30	0.58	0.40	0.31	0.24	1.29	1.67	2.42
40	0.87	0.75	0.52	0.31	1.67	2.42	2.81

[a]Reaction conditions: 7 g of $HOCH_2CF_3$, 0.0059 mol of $(NPCl_2)_3$, 3 g of NaOH,   20 mL of water, 9.6 x 10^{-5} mol of TBAB, 50 mL of chlorobenzene.

Table 1. Effects of Mass Transfer on the Reaction System[a]. (Adapted from Ref. [56] by permission)

PTC	$k_{0,app}$, min^{-1} (NPCl$_2$)$_3$, g				Relative Reactivity $k_{0.5/2}$	Q$^+$ in chlorobenzene with adding ROH,[b] %	Q$^+$ in chlorobenzene with out adding ROH,[c] %	Apparent extraction constants with out addding ROH, E$_{app}$[d]
	0.5	1.0	1.5	2.0				
TEAC	0.022	0.022	0.033	0.022	1.00	Trace	0	0
BTMAC	0.039	0.038	0.034	0.033	1.18	4.67	0	0
CTMAB	0.26	0.19	0.17	0.14	1.86	100	4.1	3.7
Aliq.336	0.32	0.25	0.19	0.14	2.3	100	100	∞
BTEAC	0.28	0.23	0.19	0.16	1.75	19.20	0	0
TBAB	0.36	0.27	0.21	0.17	2.10	100	18	18
BTBAB	0.39	0.29	0.22	0.18	2.16	100	31	51

([a]0.0059 mol of (NPCl$_2$)$_3$, 7 g of HOCH$_2$CF$_3$, 3 g of NaOH, 9.6 x 10^{-5} mol of PTC, 50 mL of chlorobenzene, 20 mL of water, 20 °C; [b]7 g of HOCH$_2$CF$_3$,3 g of NaOH, 9.6 x 10^{-5} mol of PTC, 50 mL of chlorobenene, 20 mL of water, 20 °C; [c]3 g of NaOH, 9.6 x 10^{-5} mol of PTC, 50 mL of chlorobenene, 20 mL of water, 20 °C. [d]E$_{app}$= [QY]$_o$/[Q$^+$]/[Y$^-$]$_a$)

Table 2. Effects of Catalysts on the Relative Reactivities[a]. (Adapted from Ref. [56], by permission)

PTC	$k_{0,app}$, min^{-1} (NPCl$_2$)$_3$, g				Rel. Reactivity $k_{0.5/2}$	No PTC reaction (NPCl$_2$)$_3$ %	HOCH$_2$CF$_3$ extracted in solvent +/-	Dielectric constant (temp, °C) ε	App. extraction const. E$_{TBAB}$
	0.5	1.0	1.5	2.0					
1,2-Dichloroethane	0.82	0.59	0.45	0.30	2.73	5	+	10.36(25)	6.1
Chlorobenzene	0.36	0.27	0.21	0.17	2.10	8	-	5.6(25)	<0.1
Dichloromethane	0.36	0.26	0.19	0.14	2.57	5	+	9.08(20)	35
Benzene	0.11	0.09	0.08	0.071	1.55	2	+	2.28(20)	<0.001
Toluene	0.14	0.11	0.095	0.07	2.00	4	+	2.37(25)	<0.001
Hexane	0.046	0.046	0.041	0.04	1.10	0	+	1.89(20)	<0.001
Chloroform	0.059	0.059	0.047	0.043	1.53	2	+	4.8(20)	47

[a] E$_{TBAB}$= [QBr]$_o$/[Q+]$_a$[Br$^-$]$_a$. Reaction conditions: HOCH$_2$CF$_3$ = 7 g, T BAB = 9.6 x 10^{-5} mol, solvent = 50 mL, H$_2$O = 20 mL, NaOH = 3 g, temp = 20 °C

Table 3. Effects of Solvents on the Relative Reactivities[a]. (Adapted from Ref. [56], by permission)

We measured the percentage of quaternary ions in the organic phase of the chlorobenzene/NaOH aqueous system with or without adding HOCH$_2$CF$_3$ (Table 3). From the reaction mechanism it is clear that either the catalyst QOR or QX may stay within the organic phase or the aqueous phase. We attribute the competition of QOR with QX to stay within the organic phase is due to the addition of HOCH$_2$CF$_3$. It is obvious that the addition of the organophilic substance will make the quaternary cation move into the organic phase.

As a consequence, the preferential extraction of $-OCH_2CF_3$ into the organic phase by the quaternary cation catalyst is responsible for the efficiency of the reaction. The apparent extraction constant, E_{app}, is thus an index for reflecting the mass transfer effect. Thus, a larger value of E_{app} implies that the two-phase reaction is dominated by the effects of mass transfer.

Influence of solvents on the rate of the reaction was examined by employing seven different solvents under PTC conditions (Table 3). The order of relative activities of the solvents is dichloroethane > chlorobenzene > dichloromethane > benzene > toluene > chloroform > hexane. Higher values of $k_{0.5/2}$ imply a significant influence of the mass transfer on the reaction rate.

From the Arrhenius plot of $k_{0,app}$ of $vs.$ $1/T$ for different initial concentration ratios of NaOH and $HOCH_2CF_3$, the activation energy, E_a, was obtained and presented in Table 4. Thus, the effects of mass transfer and chemical reaction kinetics on the conversion depend highly on the reactant concentrations of NaOH and $HOCH_2CF_3$.

$HOCH_2CF_3$ (g)	NaOH (g)	E_a (kcal/mol)
14	2.5	11.4
7	7	19.0
7	3	7.1

Table 4. Energy of activation at various amounts of NaOH and $HOCH_2CF_3$. (Adapted from Ref. [56], by permission).
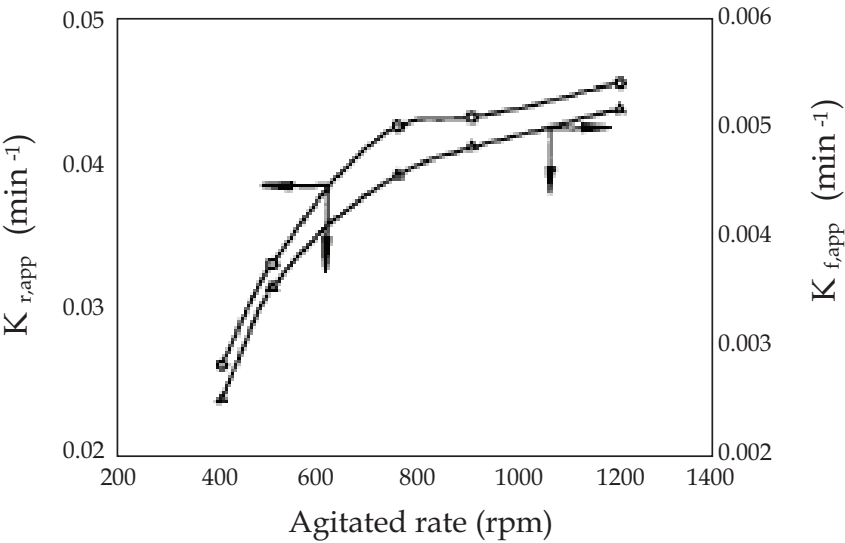

Fig. 5. Dependence of the apparent reaction rate constants $k_{r,app}$ and $k_{f,app}$ on the agitated rate; 7 g of $HOCH_2CF_3$, 0.0059 mol of $(NPCl_2)_3$, 3 g of NaOH, 20 mL of H_2O, 0.175 mequiv of catalyst, 50 mL of chlorobenzene, 20 °C. (Adapted from Ref. [59], by permission)

Further, the kinetics and the mass transfer behaviors of synthesizing polytrifluoroethoxycyclotriphosphazene from the reaction of 2,2,2-trifluoroethanol with hexachlorocyclotriphosphazene by triphase catalysis in an organic solvent / alkaline solution were studied [59]. In general, the reaction mechanism of the triphase catalysis is: (1) mass transfer of reactants from the bulk solution to the surface of the catalyst pellet,

(2) surface or intrinsic reaction of reactants with active sites, and (3) diffusion of reactants to the interior of the catalyst pellet (active sites) through pores. It was found that the diffusional limitation involves both ion diffusion and organic reactant diffusion within the catalyst pellet. The mass transfer limitation influences the triphase reaction rate. The displacement reaction rate of $(NPCl_2)_3$ in the organic phase was limited by the particle diffusion and the intrinsic reactivity together. The film diffusion of the aqueous phase in the ion-exchange step is the main rate limiting factor. The mass transport of the ion-exchange step in the aqueous phase was not improved by increasing the concentration of $NaOCH_2CF_3$. The effect of the agitation speed on the conversion of hexachlorocyclotriphosphazene is shown in Figure 5. The reaction follows a pseudofirst-first-order rate law. Rate constants increased with the agitation rate up to 750 rpm and increased only slightly up to 1200 rpm.

2.3 C-Alkylation

The essential condition for a reaction to occur is the effective collision of reactant molecules, even in the phase transfer catalysis system. Recently, Vivekanand and Blakrishnan [29] investigated the effect of varying stirring speed on the rate of the reaction of C-alkylation of dimedone by dibromoethane in the range 200–800 rpm under PTC conditions (Scheme 2). The experimental results show that the rate constants increase with the increase of stirring speed from 200 to 600 rpm. Further increase in the speed of agitation had practically no effect on the rate of reaction (Fig. 6). This is because the interfacial area per unit volume of dispersion increased linearly with increasing the stirring speed till 600 rpm is reached and there after there is no significant increase in the interfacial area per unit volume of dispersion with the corresponding increases in the speed. Consequently, increasing the stirring speed changes the particle size in the dispersed phase. At stirring speeds of 700 and 800 rpm, nearly constant rate constant values were observed. This is not because the process is necessarily reaction rate-limited, but because the mass transfer has reached a constant value. Thus, Fig. 6 is indicative of an interfacial mechanism rather than Starks' extraction mechanism. Chiellini et al. [60] observed a continuous increase in the rate of ethylation of PAN, even up to stirring speeds of 1950 rpm, for which an interfacial mechanism was proposed. Similar observations were made under various phase transfer catalytic reactions and an interfacial mechanism was proposed [41,61–64].
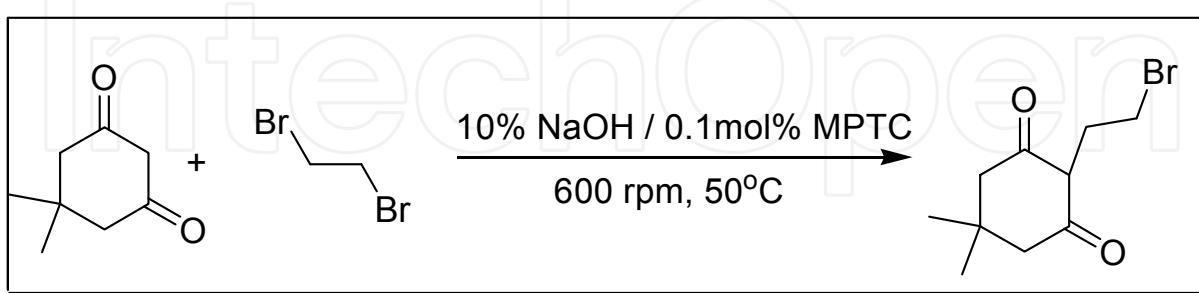
Scheme 2. C-Alkylation of dmedone under PTC conditions

2.4 N-Alkylation

The synthesis of 1-(3-phenylpropyl)-pyrrolidine-2,5-dione was successfully carried out [23] from the reaction of succinimide with 1-bromo-3-phenylpropane in a small amount of KOH and organic solvent solid–liquid phase medium under phase-transfer catalysis (PTC)

almost water-free conditions (Scheme 3). For a solid-liquid phase reaction system, agitation increases the kinetic energy of the system and tends to speed up the reaction until a limiting factor is reached. After this the reaction rate is not affected by increasing stirring rates. Therefore, the effect of the agitation speed on the conversion and the reaction rate was studied in the range of 0-1200 rpm. As shown in Figure 7, the experimental data of the reaction kinetics follows the pseudo-first-order rate law and passes the origin point of a straight line for each experimental run. The apparent rate constants (k_{app}) were obtained from the slope of the straight lines. There was a significant increase in the apparent rate constant values from 0 to 200 rpm, but it remained at an almost constant value from 200 to 1200 rpm. This phenomenon indicated less influence of the external mass transfer resistance on the reaction beyond 200 rpm. Thus, the organic-phase reaction is obviously a rate determining step at 200-1200 rpm. All subsequent reactions were set at 1200 rpm to assess the effect of various factors on the rate of reaction.
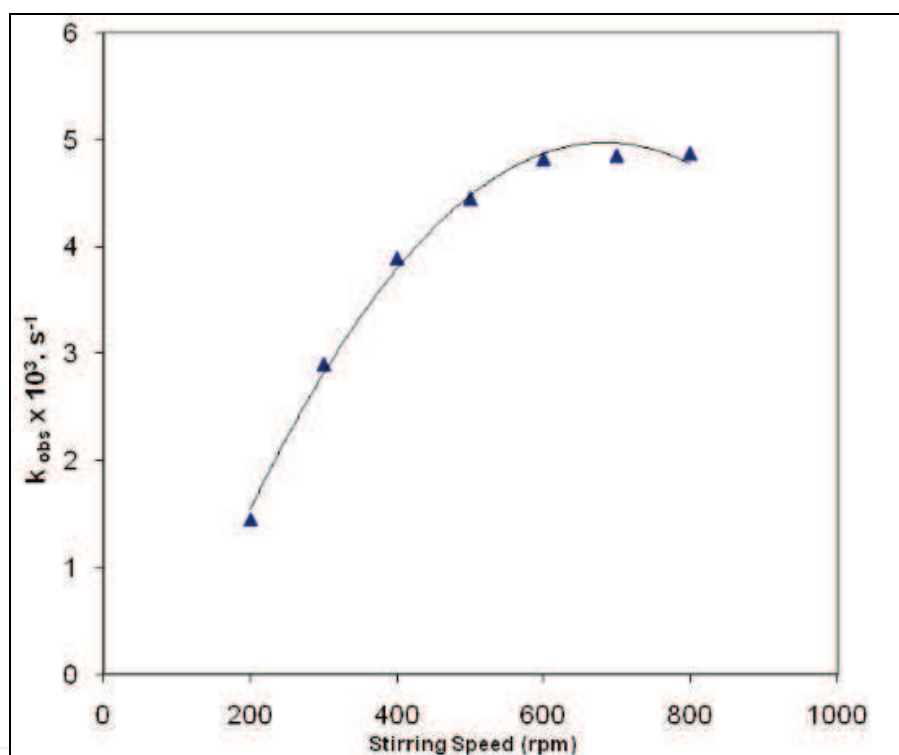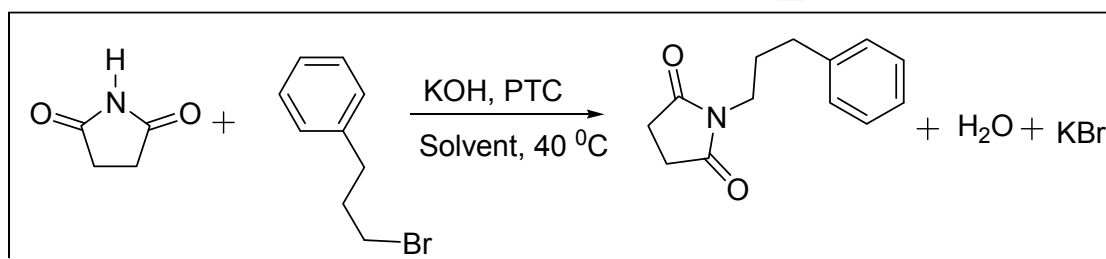

Fig. 6. Dependence of k_{obs} on stirring speed in the C-alkylation of dimedone. (Adapted from Ref. [29], by permission)

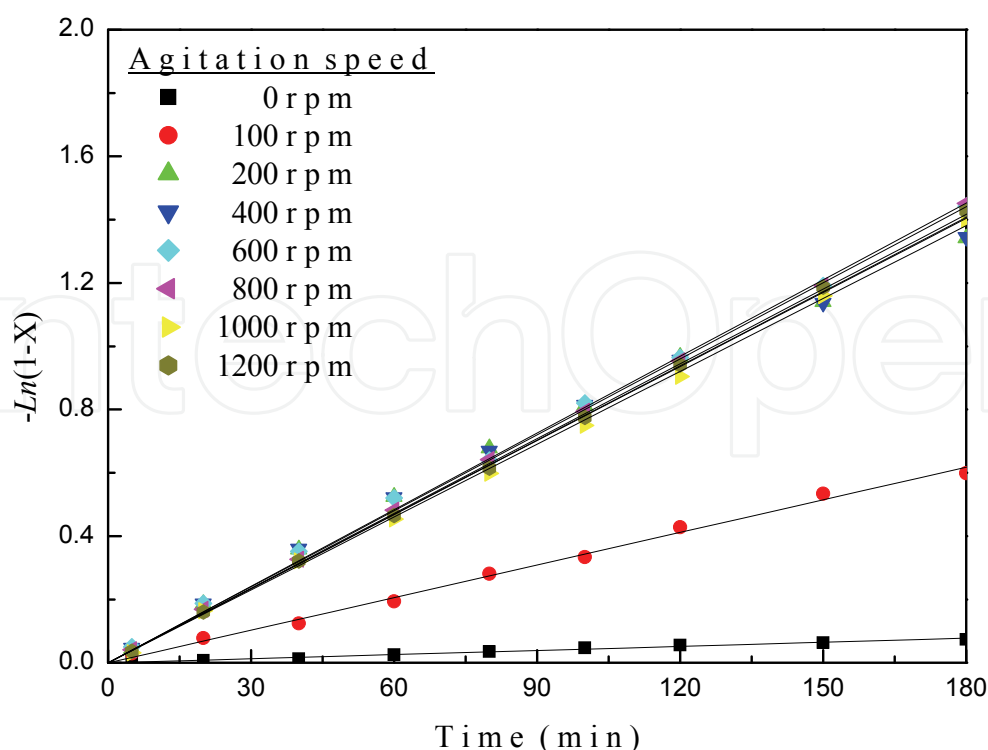Scheme 3. *N*-alkylation of Succinimide with 1-bromo-3-phenylpropane under S-L-PTC conditions

Fig. 7. Plot of -ln(1 - X) of 1-bromo-3-phenylpropane versus time with various agitation speeds; 9.0×10^{-2} mol of succinimide, 1 g of KOH, 0.4 g of TOAB, 6.0×10^{-3} mol of 1-bromo-3-phenyl-propane, 50 mL of cyclohexanone, 0.3 g of internal standard (naphthalene), 40 °C. (Adapted from Ref. [23], by permission)

2.5 S-Alkylation

The reaction between sodium sulfide and *n*-bromobutane to synthesize di-*n*-butyl sulfide was carried out for in an organic solvent/alkaline solution two-phase medium under phase transfer catalysis (PTC) conditions [65]. The overall reaction is presented in Scheme 4. In the two-phase reaction, mass transfer resistance is an important factor in affecting the reaction rate. In general, either the organic or the aqueous solution can be dispersed in smaller droplet size by agitating the two-phase solution, so, the contact area of two phases is increased with higher agitation speed. The flux of the two-phase mass transfer is also highly dependent on the flow condition (e.g. agitation speed). Fig. 8 shows the dependence of the apparent rate constant ($k_{app,1}$) on the agitation speed. For agitation speeds less than 350 rpm, both mass transfer and reaction resistance are important in determining the overall reaction rate. In this work, the reaction rate does not significantly change for agitation speeds larger than 350 rpm, and the mass transfer resistances of the active catalyst between the two phases are the same for agitation speed over 350 rpm. Hence, it is obvious that the reaction in organic phase is the rate-controlling step for agitation speed larger than 350 rpm under the standard reaction conditions. Below 50 rpm, the reaction rate is quite low because the two-phase solutions do not mix well and layering is clearly observed. Over 100 rpm, the ivory-white dispersion phase occurs. However, the phenomenon of constancy of the reaction rate constant over a certain agitation speed widely exists in PTC reactions, which are formulated based on an extraction model. Wang and Tseng [66], Jayachandran et al. [67], Park et al. [68], Wang and Wu [69] and Do and Chou [70], proposed the agitation speeds

from 200 to 800 rpm. This threshold value changes with changes in the reaction parameters, e.g. the two-phase surface tension will be changed using different organic solvents or adding cationic surfactants, so the maximum two-phase mass transfer rate will be changed under different agitation speeds.

$$2RBr + 2Na_2S \xrightarrow{\text{PTC}} R_2S + 2NaBr$$

Scheme 4. Thioether synthesis under phase-transfer catalysis conditions
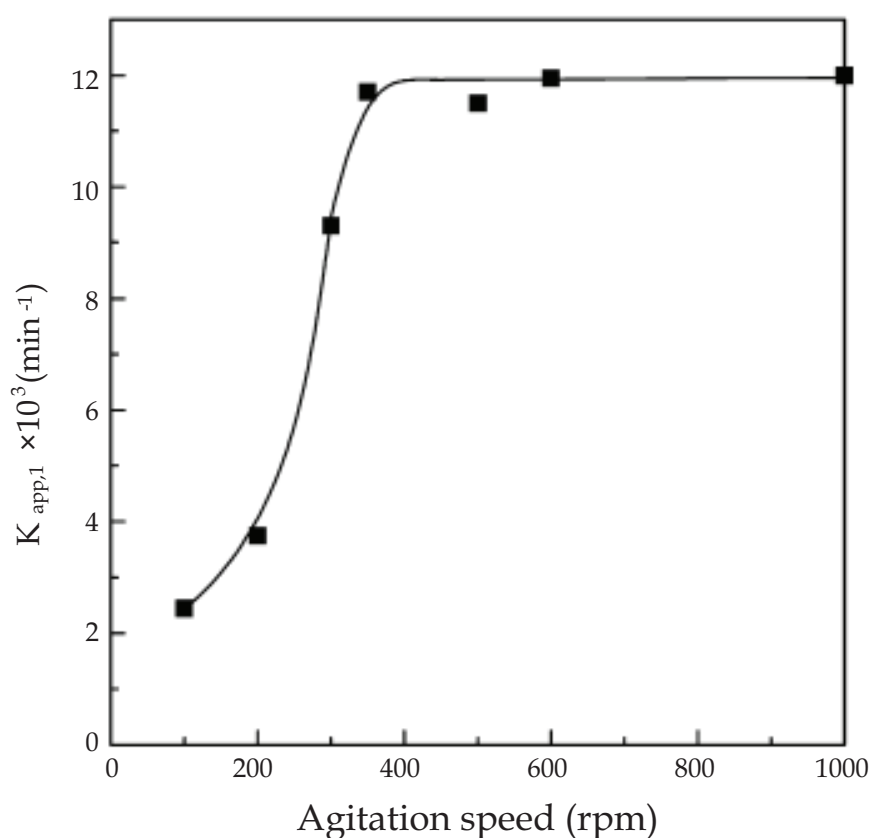
Fig. 8. Effect of the agitation speed on the apparent rate constant ($k_{app,1}$) in the organic phase; 7 g of sodium sulfide, 10 ml of water, 0.15 mmol of TBAB, 4 mmol of n-bromobutane, 40 ml of n-hexane, 40 °C. (Adapted from Ref. [65], by permission)

2.6 Dichlorocyclopropanation

Mass transfer between two phases in a phase-transfer catalysis system is important in affecting the conversion or the reaction rate. From the point of kinetics, changing the agitation speed can influence both the mass transfer rate, which relates to the mass transfer coefficient and the interfacial area between two phases, and the reaction rate. Increasing the agitation speed leads to increase both the mass transfer coefficient and the interfacial area, thus enhancing the mass transfer rate. The effects of varying stirring on the rate constants of the dichlorocarbene addition reactions were documented in the literature [40, 71-73].

The kinetics of dichlorocarbene addition to 1,7-octadiene have been studied under phase transfer catalytic conditions [74] using aqueous sodium hydroxide as the base and tetrabutylammonium chloride as a phase transfer catalyst (Scheme 5). In this work, the effect of agitation speed on the conversion for the reaction carried out at low alkaline concentration (30% NaOH) is shown in Fig. 9. No other byproducts were obtained during or after the reaction. The conversion is highly dependent on agitation speeds less than 800 rpm, above which the conversion is not influenced by increasing the agitation speed. The corresponding rate constant values with various agitation speeds are given in Table 5. Increasing the agitation speed leads to increase both the mass transfer coefficient and the interfacial area, thus enhancing the mass transfer rate. A similar trend was observed by Vivekanand and Balakrishnan [75] in the kinetic study of dicholorocarbene addition to indene catalyzed by triphase catalyst, where the rates were found to be independent of stirring speed >400 rpm.
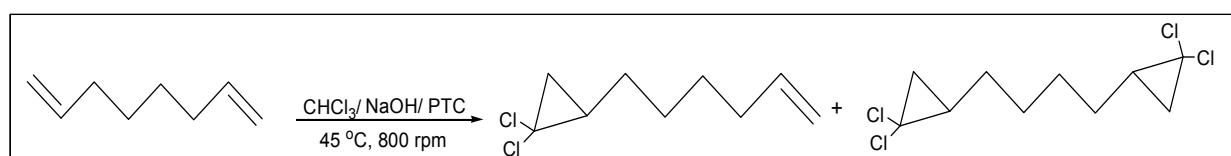
Scheme 5. Dichlorocarbene addition to 1,7-octadiene under PTC conditions

Agitation speed (rpm)	$k_{app\ 3} \times 10$ $(min^{-1}\,M^{-2})$
200	0.26
400	0.88
600	1.90
700	2.58
800	3.29
100	3.41

Table 5. Effect of the agitation speed on the $k_{app,3}$ value at low NaOH concentration: 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 40 °C. (Adapted from Ref. [74], by permission)

2.7 Esterfication

Dutta *et.al.* [76] reported kinetics of esterification of phenol derivatives *viz.*, phenol, *m*-cresol and resorcinol in alkaline solution catalyzed by polystyrene supported tri-*n*-butyl phosphonium ion under pseudo-first order conditions (Scheme 6). Kinetic results presented are interpreted in terms of three rate processes *i.e.* mass transfer of benzoyl chloride (organic substrate) to the catalyst surface, diffusion of the substrate through the polymer matrix and intrinsic reactivity at the active sites. The reaction engineering aspects have been addressed from experimentally observed rate determining phenomena as complimented by the theory of diffusive mass transfer in porous catalyst.

The order of reactivity of different phenol derivatives: resorcinol< *m*-cresol< phenol. Apparent rate constants were found to increase up-to 800-1000 rpm (stirring speed) for different phenols, beyond which the k_{app} values were found to be remain constant. They reported that catalysts with particle size lower than 70µm do not enhance the rate. This is

attributed to low mass transfer of reactants from the bulk phase to the particle surface and hence the reaction rate is reduced. However the reaction rate is better than the uncatalyzed reaction. In presence of highly active catalyst, mass transfer from the bulk phase to the surface of the catalyst particle can be rate controlling step. They reported that the mass transfer of benzoyl chloride from the bulk organic phase to the surface of the catalysts depends on the contact between the polymer particles and organic droplets, both of which are suspended in a continuous phase of aqueous sodium phenolate. Authors interpreted the kinetic results in terms of three aspects *viz.,* i) mass transfer of benzoyl chloride to the catalyst surface, ii) diffusion of benzoyl chloride through polymer matrix, and iii) intrinsic reactivity at the active sites.
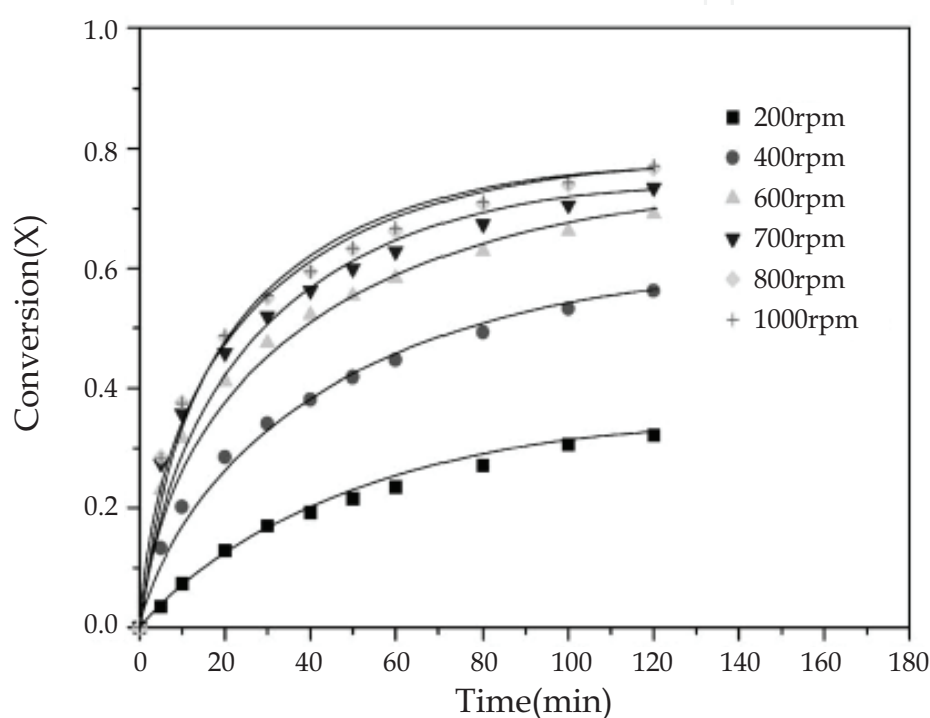

Fig. 9. Effect of the agitation speed on the conversion of 1,7-octadiene at low alkaline concentration (30% NaOH): 10 mmol of 1,7-octadiene, 20 ml of chloroform, 0.2 mmol of tetrabutylammonium chloride (TBAC), 6 g of NaOH, 14 ml of water, 40 °C. (Adapted from Ref. [74], by permission)

Esterifcation of benzyl chloride with sodium acetate to form benzyl acetate and sodium chloride were carried out under tri-phase conditions using polymer supported tributylmethylammonium chloride as the phase transfer catalyst [77]. The investigation focused on the determination of external mass transfer coefficient from the liquid bulk phases to the surface of the catalyst in tri-phase catalytic systems. Special emphasis was placed on the equipment (rotating disk contactor, RDC) which has been conceived and designed for this purpose. Determination of mass transfer coefficient involves an analysis of the various regimes of solid-liquid systems with the solid not soluble in the liquid phase. Esterfication was found to be mass transfer controlled at low agitation speeds and it was found to be characterized by considerable non-catalytic reaction and effects due to dispersion associated with the catalyst. Nevertheless, it was possible to determine the external mass transfer coefficient as a function of the bulk agitation speed. The mass transfer

coefficient increases with the increasing agitation rate indicated the dependence of the mass transfer coefficient on the agitation rate.
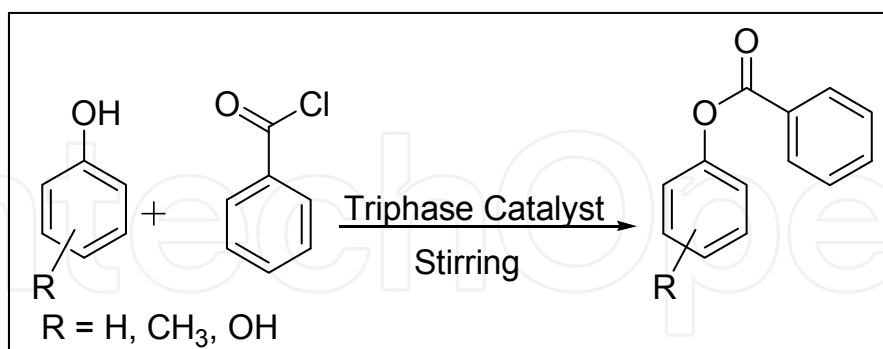
Scheme 6. Esterfication of substituted phenols under PTC conditions

3. Conclusion

Conventional technologies for multiphase organic reactions were largely uneconomical and polluting and hence were commercially not feasible. In recent years, several new techniques have emerged that use homogeneous or heterogeneous catalysts such as phase transfer catalysts, supported metal catalysts, biocatalysts etc. Among various types of catalysts, phase transfer catalysts have attracted more and more attention. It facilitates inter-phase transfer of species, making reactions between reagents in two immiscible phases possible.

Many organic synthetic applications based on PTC have shown great success. The present chapter has hence concentrated on the PTC reactions, *viz.*, alkylation reactions, esterfication reactions, dichlorocarbene addition reactions etc., using both soluble and immobilized forms of the catalyst. By its very nature, PTC involves interphase transport of species, neglecting which can grossly over predict the conversion of a PTC mediated reaction. Hence, greater emphasis has been given to present the role of mass transfer in PTC-assisted reactions. Nevertheless, there are definitely numerous catalytic reactions still waiting to be discovered and hence, opportunity for major discovery will remain vibrant for a very long time indeed. The new designs for microwaves and ultrasound assisted PTC reactions and the relevant mass transfer data is most essential to understand the design and scale-up of these emerging technologies in industries. It is hoped that this chapter will spur further research in this area, whose applications in the manufacture of organic intermediates and fine chemicals seems almost unlimited.

4. Acknowledgments

5. Nomenclature

A   = Mass-transfer area between organic and aqueous phase, cm^2/cm^3

X   = Conversion of allyl bromide

C_{ArOQ}^{org} = Concentration of ArOQ in organic phase, M

C_{ArOQ}^{aq} = Concentration of ArOQ in aqueous phase, M

C_{QBr}^{aq} = Concentration of QBr in aqueous phase, M

C_{QBr}^{org} = Concentration of QBr in organic phase, M

C_{ArOK}^{aq} = Concentration of ArOK in aqueous phase, M

C_{ArOR}^{org} = Concentration of ArOR in organic phase, M

C_{RBr}^{org} = Concentration of RBr in organic phase, M

E_o = Initial moles of 2,4,6-tribromophenol

f = V_o / V_a

K_{aq} = Reaction rate constant of the aqueous phase, M^{-1} min^{-1}

K_{org} = Reaction rate constant of the organic phase, M^{-1} min^{-1}

K_{ArOQ} = Mass-transfer coefficient of ArOQ from aqueous to

K_{QBr} = Mass-transfer coefficient of QBr from organic phase

m_{QBr} = Distribution coefficient of QBr $\left(\dfrac{C_{QBr}^{org(s)}}{C_{QBr}^{aq(s)}} \right)$

m_{ArOQr} = Distribution coefficient of ArOQ $\left(\dfrac{C_{ArOQ}^{org(s)}}{C_{ArOQ}^{aq(s)}} \right)$

V_a = volume of aqueous phase, L

V_o = Volume of organic phase, L

t   = Time in minutes

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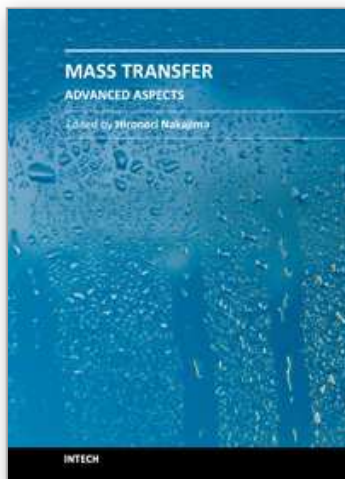
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Our knowledge of mass transfer processes has been extended and applied to various fields of science and engineering including industrial and manufacturing processes in recent years. Since mass transfer is a primordial phenomenon, it plays a key role in the scientific researches and fields of mechanical, energy, environmental, materials, bio, and chemical engineering. In this book, energetic authors provide present advances in scientific findings and technologies, and develop new theoretical models concerning mass transfer. This book brings valuable references for researchers and engineers working in the variety of mass transfer sciences and related fields. Since the constitutive topics cover the advances in broad research areas, the topics will be mutually stimulus and informative to the researchers and engineers in different areas.

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