



Novel kinetics model for third-liquid phase-transfer catalysis system of the “complex” carbanion: Competitive role between catalytic cycles



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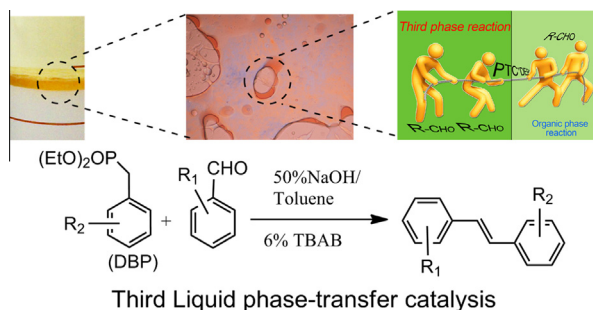
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HIGHLIGHTS

- Third phase surrounded the aqueous phase and generated PTC⁺PO⁻ was the main catalyst.
- Novel kinetics model consisted the third phase reaction and the organic phase reaction was deduced.
- High ratio of the third phase reaction was responsible for relatively high catalytic activity.
- Anion in the TLPTC system could cause the autocatalytic role or catalyst poisoning.
- Catalyst activity was dependent on the steric hindrance, lipophilicity of the cation and polarity of the third phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Kinetic model for Horner–Wadsworth–Emerson (HWE) reaction of the “complex” carbanion in the third-liquid phase-transfer catalysis (TLPTC) system was proposed and the factors that influenced the model parameters were investigated in details. The generation process and the composition of the third phase revealed that there were two catalytic cycles (the third phase reaction and the organic phase reaction) in this TLPTC system. Kinetic model which consisted of ion-exchange reaction rate constant, bond-forming reaction rate constant and the contribution ratio between each two catalytic cycle was deduced. Distribution of the carbanion ion-pair between the third phase and the organic phase caused the competitive relationship between these two catalytic cycles. Third phase was the preferred region for the bond-forming reaction, and which contribution was always 5–6 times higher than that of the organic phase reaction. Reaction rate of each catalytic cycle was also affected by lipophilicity of the anion in this TLPTC system. The steric hindrance, lipophilicity of the catalyst cation and polarity of the third phase were primary factors influencing catalyst activity.

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1. Introduction

Phase-transfer catalysis (PTC) is an extremely useful method for performing a large number of organic unit reactions in the synthesis of pharmaceuticals, flavors, dyes, perfumes, etc [1,2]. Thereinto, liquid–liquid PTC (LLPTC) system is the most conventional system

Nomenclature

$a_{TL,o}$	interfacial area provided by the third phase per unit volume of the organic phase, cm^2/cm^3 organic phase	$C_{DEBP,0}^{org}$	initial concentration of DEBP in the organic phase, mol/L of the organic phase
$C_{PTC^+X^-}^{org}$	concentration of the catalyst in the organic phase, mol/L of the organic phase	K_{1-2}	equilibrium constants
$C_{DEBP^-PTC^+}^{org}$	concentration of the ion-pair in the organic phase, mol/L of the organic phase	k_1	rate constant for the reaction of benzaldehyde with the carbanion in the third phase for the catalytic cycle II ($(\text{mol/L})^{-1} \text{min}^{-1}$)
$C_{DEBP^-PTC_{org}^+}^s$	saturation concentration of the ion-pair in the organic phase, mol/L of the organic phase	k_2	rate constant for the reaction of benzaldehyde with the carbanion in the organic phase ($(\text{mol/L})^{-1} \text{min}^{-1}$)
$C_{DEBP^-Na^+}^{int}$	concentration of the sodium salt of the carbanion in the interfacial layer, mol/L of the interfacial layer	k_3	rate constant for the reaction of benzaldehyde with the carbanion in the third phase for the catalytic cycle I ($(\text{mol/L})^{-1} \text{min}^{-1}$)
$C_{DEBP^-PTC^+}^{TL}$	concentration of the ion-pair in the third phase, mol/L of the third phase	k_{11-41}	apparent reaction rate constant
$C_{PTC^+X^-}^{TL}$	concentration of the catalyst in the third phase, mol/L of the third phase	k_{L1}	true mass-transfer coefficient on the organic phase side, (cm/s)
$C_{DEBP^-Na^+,0}^{int}$	initial concentration of the sodium salt of the carbanion in the interfacial layer, mol/L of the interfacial layer	$N_{Q,0}$	total moles of catalyst added
$C_{Stilbene}$	concentration of stilbene in the organic phase, mol/L of the organic phase	$N_{Stilbene}$	moles of stilbene
		V_{TL}	volume of the third phase (L)
		V_{org}	volume of the organic phase (L)
		Y	yield of stilbene

for a majority of PTC reaction because of the mild reaction conditions and the use of cheap solvents [3]. However, the homogenous catalyst is normally not recovered and reused and the large quantity of water is required to wash the organic phase in LLPTC system. Conversion of LLPTC system into a multiphase system is the effective method to make the process “greener”, such as, liquid–liquid–solid PTC system, third-liquid system (TLPTC) and solid–liquid–liquid system [4,5]. TLPTC is a reaction system involved a separate catalyst-philic liquid phase locating between the aqueous phase and the organic phase [6,7]. Several characteristics of TLPTC system are attractive for industrial application including enhanced reaction rate, milder reaction condition, easier catalyst recovery and reuse, increased yield and selectivity. A useful aspect of TLPTC is the ability to catalyze a wide variety of reaction types, ranging from simple substitution reaction [8–12], reduction reaction [13,14], oxide reaction [15] to hydroxide-initiated reaction [16–18].

Hydroxide-initiated PTC (HI-PTC) reaction is one of the most widespread and useful PTC methods, which uses convenient, inexpensive and relatively safe alkaline agent instead of the classic organic alkoxides, amides and hydrides [19]. For hydroxide-initiated reaction in TLPTC system, past researches were aimed at substitution and elimination reactions, for example: dehydrobromination of phenylethyl bromide or 2-bromooctane [20], brominate or oxidize of tetra-*n*-butylammonium tribromide (TBABr₃) [21], *o*-alkylation of phenolic compounds [22], alkoxylation of alcohol to produce ether [23], and dichlorocarbene reaction [24]. It should be noted that pK_a value of most substrates in these reactions was less than 23 (moderately acidic substrate) and the anion in the bond-forming reaction was oxygen anion or small carbanion. However, there is few research concerning the TLPTC system of the complex carbanion, and fundamental understanding of HI-PTC reaction of weakly acidic substrate ($pK_a > 23$) is still lacking.

Third phase (catalyst-rich) can be formed between the aqueous and organic phases containing the reactants through a proper balance of lipophilicity, hydrophilicity, interfacial tension, solubility, phase equilibria, and density [25,26]. The most common way for the conversation of LLPTC system into TLPTC system is the addition of inorganic salt or the catalyst to LLPTC system [27–29]. With the generation of the third phase, the whole reaction would have three types of reaction scheme, that is, (I) reaction occurs in the organic phase, (II) reaction occurs at the interface between the aqueous

phase and the organic phase, and (III) reaction occurs in the third phase. Generally, for TLPTC reaction, type (I) and (II) were neglected, and it was treated that the whole reaction occurred in the third phase [28–30]. However, for *n*-butoxylation reaction of sodium phenolate [30], halogen exchange reaction of benzyl bromide [31] and *n*-butoxylation reaction of *p*-chloronitrobenzene in TLPTC system [32], the whole reaction occurred both in the organic phase (type I) and the third phase (type III) because the reactant had practically no solubility in the aqueous phase and the ion-pair with the quaternary had more solubility in the organic phase as well as in the third phase than in the aqueous phase. Moreover, reactivity of the intermediate in the third phase and the organic phase was identical and relatively high catalytic activity of the third phase was attributed to the high concentration of the catalyst. However, the relationship between these two catalytic cycles and the factor influencing the contribution of these two catalytic cycles had not been investigated.

In our previous research, Horner–Wadsworth–Emerson (HWE) condensation reaction involved a bulky and weakly acidic carbanion (diethyl benzylphosphonate, DEBP, $pK_a = 28$) had been carried out in TLPTC system, and showed high yield and geometric selectivity. In this TLPTC system, the third phase was generated with less amount of the catalyst (6% equiv to the reactant), compared with the common TLPTC system (15–30% equiv to the reactant). The other product of the bond-forming reaction (diethyl phosphate anion, PO^-) was the crucial factor for the generation of the third phase and 20% of the catalyst still distributed into the organic phase with tetrabutylammonium bromide (TBAB) as the catalyst. As a corollary, in consideration of the high lipophilicity of the carbanion and the distribution of the catalyst, the whole reaction would occur both in the organic phase (type I) and the third phase (type III). The purpose of this paper was to propose the kinetics model and to quantitatively compare the contribution of each catalytic cycle. Initially, the microscopic image of the reaction mixture, distribution of the catalyst cation were explored. Subsequently, kinetics model for this TLPTC system was deduced, sensitivity for the kinetics model and effects of experiment condition parameters on each catalytic cycle were investigated in details. Furthermore, quantitative structure–activity relationship (QSAR) models for catalyst activity in this TLPTC system were evaluated. The available kinetics model for hydroxide-initiated TLPTC system of the weakly acidic substrate can provide a prototype on the

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