

Synthesis of 2,4-dichlorophenoxyacetic acid: novelties of kinetics of inverse phase transfer catalysis

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Abstract

The present work deals with the inverse liquid–liquid (L–L) phase transfer (PT) catalysed synthesis of 2,4-dichlorophenoxyacetic acid (2,4-D) by using 2,4-dichlorophenol (2,4-DCP) and chloroacetic acid (CAA), wherein the locale of the reaction is the aqueous phase. By varying the amount of NaOH used, the product can either be obtained as such in the organic phase or in the aqueous phase as sodium salt. On using stoichiometrically deficient quantity of NaOH and a low molecular weight quaternary salt, such as tetraethylammonium bromide (TEAB), the product can be obtained per se in the organic phase. The paper brings out the novelties vis-a-vis the mechanism and kinetics of inverse PT (IPT) catalysed synthesis of 2,4-D. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Inverse phase transfer catalysis (IPTC); 2,4-Dichlorophenoxyacetic acid (2,4-D); Tetraethylammonium bromide (TEAB); 2,4-Dichlorophenol (2,4-DCP); Chloroacetic acid (CAA)

1. Introduction

Phase transfer catalysis (PTC) has come of age and there are reportedly over 600 PTC processes used in the organic process industry. Most of the PTC reactions occur in the organic phase under bi-liquid phasic conditions and very few studies have been reported on the so-called “inverse” PTC (IPTC), wherein the reaction can occur in the aqueous phase.

Cyclodextrins have reportedly been used as IPTC in various reactions, such as isomerisation, reduction and epoxidation of alkenes [1–3]. Transition metals, such as platinum, palladium, rhodium, etc. form strong complexes with water soluble ligands, such as

the trisodium salt of triphenylphosphine trisulphonic acid. These complexes are completely retained in the aqueous phase but have the ability to bring organic reagents to the aqueous phase for reaction [4]. Silicon-substituted pyridines and pyridinium oxides have been patented as IPT catalysts [5]. Low molecular weight quaternary salts, such as tetramethyl- or tetraethylammonium salts which normally act as poor PT catalysts due to their lack of solubility in the organic media, have been employed as IPT catalysts to carry out highly selective carbohydrate reactions in the aqueous phase. Trimethylammonium groups attached to ion-exchange resins also act as IPT catalysts in the oxidation of benzyl alcohol by NaOCl to yield benzaldehyde [6]. The current work deals with the novelties of kinetics of IPT catalysed synthesis of 2,4-dichlorophenoxyacetic acid, commercially known as 2,4-D.

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Nomenclature

$[A]_{\text{org}}$	concentration of 2,4-D in organic phase (mol/cm^3)
$[B]_{\text{aq}}$	concentration of sodium chloroacetate in aqueous phase (mol/cm^3)
$[C]_{\text{aq}}$	concentration of HCl in aqueous phase (mol/cm^3)
$[C]_{\text{org}}$	concentration of HCl in organic phase (mol/cm^3)
k_1	rate constant for anion-exchange reaction in organic phase ($\text{cm}^3/(\text{mol s})$)
k_2	rate constant for formation of 2,4-D sodium salt in aqueous phase ($\text{cm}^3/(\text{mol s})$)
k_3	rate constant for formation of 2,4-D in aqueous phase ($\text{cm}^3/(\text{mol s})$)
K_C	distribution coefficient of HCl between aqueous and organic phase
K_P	distribution coefficient of 2,4-D between aqueous and organic phase
K_{QX}	distribution coefficient of QX between aqueous and organic phase
K_R	distribution coefficient of 2,4-dichlorophenoxy quaternary salt between aqueous and organic phase
N_{Qtotal}	total moles of catalyst added (mol)
$[P]_{\text{aq}}$	concentration of 2,4-D in aqueous phase (mol/cm^3)
$[QX]_{\text{org}}$	concentration of QX in organic phase (mol/cm^3)
$[R]_{\text{aq}}$	concentration of 2,4-dichlorophenoxy quaternary salt in aqueous phase (mol/cm^3)
$[R]_{\text{org}}$	concentration of 2,4-dichlorophenoxy quaternary salt in organic phase (mol/cm^3)
$[S]_{\text{aq}}$	concentration of 2,4-D sodium salt in aqueous phase (mol/cm^3)
V_{aq}	volume of aqueous phase (cm^3)
V_{org}	volume of organic phase (cm^3)

2,4-D is a useful herbicide and a known weed-killer, popularly accepted because of its effectiveness in low concentrations. Its selective weed-killing power without harming grains is manifested by its extensive use for weed-control on grass-like crops, such as

wheat, rice, barley, oats, etc. [7]. The condensation reaction between 2,4-dichlorophenol (2,4-DCP) and chloroacetic acid (CAA) under alkaline conditions has been widely studied. Most of the literature available for the reaction is patented. This reaction has been studied as a single phase synthesis in aqueous medium [8–10]. Chlorination of phenoxyacetic acid is another commonly used method [11]. A two-stage synthesis including preparation of phenoxyacetic acid in the first step followed by its chlorination is also reported [12]. Synthesis under triphase conditions [13], microwave irradiation [14,15] and using ultrasound [16] have been carried out. Synthesis under liquid–liquid (L–L) PTC conditions with TBAB as the PT catalyst has also been reported [17]. Most of these processes suffer due to by-product formation resulting from hydrolysis of CAA.

There is hardly any information available on kinetics of IPTC. The present work endeavours to conduct a systematic investigation of the synthesis of 2,4-D under IPTC and explore the kinetic modelling in detail.

2. Experimental procedure

All chemicals and catalysts used in this research work were obtained from firms of repute.

The reactions were studied in a 5 cm i.d. fully baffled mechanically agitated contactor of 100 cm^3 total capacity, equipped with a six-blade turbine impeller and a reflux condenser. The reactor was kept in a constant temperature bath whose temperature could be maintained at the desired value by using a temperature indicator controller. Typical runs were conducted by taking 25 cm^3 of 2.0×10^{-3} M solution of 2,4-DCP in toluene in the reactor and heating it to the desired temperature. NaOH and CAA (0.05 mol each) were then dissolved in 25 cm^3 deionised water to which an appropriate quantity of the catalyst was added and the solution was heated to the reaction temperature and thereafter added to the organic phase. All typical reactions were conducted at 90 °C.

The course of reaction was followed by NaCl estimation by Volhards method. At regular intervals, a fixed quantity of the aqueous phase was removed from the reaction mixture and diluted to a known volume. The diluted aqueous phase was then treated with excess silver nitrate solution and the excess was

estimated by titration against standardised ammonium thiocyanate solution.

3. Procedure for product recovery

Since stoichiometrically deficient quantity of NaOH was used for the reaction, all of it was consumed and the product did not come in the aqueous phase as sodium salt as in other reported reactions. The aqueous phase after 4 h of reaction was acidic in nature (pH = 3.0). The product 2,4-D was obtained in the organic phase along with the unreacted phenol. 2,4-D could be extracted from the organic phase into water as sodium salt. It was subjected to neutralisation with HCl and 2,4-D, along with excess of phenol separated out. This was treated with carbon tetrachloride to dissolve all the phenol. 2,4-D was essentially insoluble in carbon tetrachloride and could be separated. The isolated product was analysed for melting point. Its ethyl ester was prepared and tested by GC–MS.

4. Reaction mechanism and model

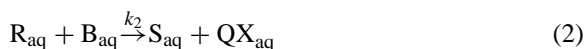
In a typical L–L PTC, the locale of the reaction is the organic phase into which the nucleophile is transferred as an ion-pair with the quaternary cation. In the current studies, it was observed that the reaction occurred in the aqueous phase into which the nucleophile was transferred as shown in Scheme 1.

Considering, **A**: 2,4-DCP; **B**: sodium chloroacetate; **C**: HCl; **R**: 2,4-dichlorophenoxy quaternary salt; **S**: 2,4-D sodium salt; **P**: 2,4-D; **D**: sodium chloride; **QX**: tetraethylammonium halide. The following steps are envisaged.

Organic phase reaction:



Aqueous phase reactions:



Mass transfer across the interface:



In Eqs. (1)–(7), k_1 , k_2 and k_3 are the reaction rate constants, while K_{QX} , K_{R} , K_{C} and K_{P} the equilibrium constants.

The rate of formation of the various species is given by the following equations:

$$\frac{d[P]_{\text{aq}}}{dt} = k_3[S]_{\text{aq}}[C]_{\text{aq}} \quad (8)$$

$$\frac{d[S]_{\text{aq}}}{dt} = k_2[R]_{\text{aq}}[B]_{\text{aq}} - k_3[S]_{\text{aq}}[C]_{\text{aq}} \approx 0, \quad \text{at steady state} \quad (9)$$

$$\begin{aligned} \frac{d[R]_{\text{org}}}{dt} V_{\text{org}} &= k_1[A]_{\text{org}}[QX]_{\text{org}} V_{\text{org}}, \\ - \frac{d[R]_{\text{aq}}}{dt} V_{\text{aq}} &= k_1[R]_{\text{aq}}[B]_{\text{aq}} V_{\text{aq}} \end{aligned} \quad (10)$$

$$\begin{aligned} k_1[A]_{\text{org}}[QX]_{\text{org}} V_{\text{org}} &= k_2[R]_{\text{aq}}[B]_{\text{aq}} V_{\text{aq}} \approx 0, \\ &\text{at steady state} \end{aligned} \quad (11)$$

$$- \frac{d[A]_{\text{org}}}{dt} = k_1[A]_{\text{org}}[QX]_{\text{org}} \quad (12)$$

From Eq. (9),

$$[S]_{\text{aq}}[C]_{\text{aq}} = \frac{k_2[R]_{\text{aq}}[B]_{\text{aq}}}{k_3} \quad (13)$$

From Eq. (11),

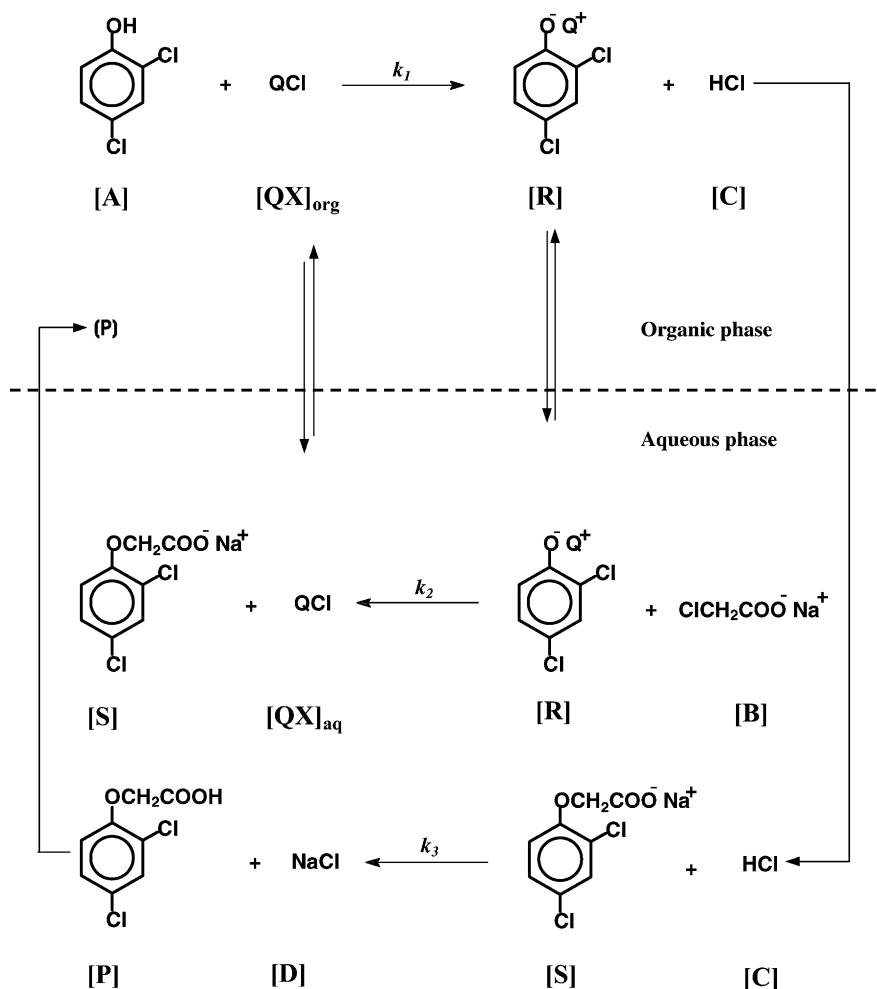
$$[R]_{\text{aq}}[B]_{\text{aq}} = \frac{k_1[A]_{\text{org}}[QX]_{\text{org}} V_{\text{org}}}{k_2 V_{\text{aq}}} \quad (14)$$

Substituting for $[R]_{\text{aq}}[B]_{\text{aq}}$ from Eq. (14), Eq. (13) can be written as,

$$[S]_{\text{aq}}[C]_{\text{aq}} = \frac{k_1[A]_{\text{org}}[QX]_{\text{org}} V_{\text{org}}}{k_3 V_{\text{aq}}} \quad (15)$$

Substituting for $[S]_{\text{aq}}[C]_{\text{aq}}$ in Eq. (8), we get

$$\frac{d[P]_{\text{aq}}}{dt} = k_1[A]_{\text{org}}[QX]_{\text{org}} \frac{V_{\text{org}}}{V_{\text{aq}}} \quad (16)$$



Scheme 1. Reaction mechanism of IPTC synthesis of 2,4-D.

From Eqs. (12) and (16):

$$\frac{d[P]_{\text{aq}}}{dt} = -\frac{d[A]_{\text{org}}}{dt} \frac{V_{\text{org}}}{V_{\text{aq}}} \quad (17)$$

The catalyst added to the bi-phasic system exists in both the phases as four different ion-pairs. Thus,

$$\begin{aligned} N_{\text{Qtotal}} &= \text{total moles of catalyst added} \\ &= \{[QX]_{\text{org}} V_{\text{org}} + [QX]_{\text{aq}} V_{\text{aq}}\} \\ &\quad + \{[R]_{\text{org}} V_{\text{org}} + [R]_{\text{aq}} V_{\text{aq}}\} \end{aligned} \quad (18)$$

But,

$$K_{\text{QX}} = \frac{[QX]_{\text{org}}}{[QX]_{\text{aq}}} \quad \text{and} \quad K_{\text{R}} = \frac{[R]_{\text{org}}}{[R]_{\text{aq}}} \quad (19)$$

$$\begin{aligned} N_{\text{Qtotal}} &= [QX]_{\text{org}} V_{\text{org}} \left[1 + \frac{1}{K_{\text{QX}}} \frac{V_{\text{aq}}}{V_{\text{org}}} \right] \\ &\quad + [R]_{\text{aq}} V_{\text{org}} \left[K_{\text{R}} + \frac{V_{\text{aq}}}{V_{\text{org}}} \right] \end{aligned} \quad (20)$$

Considering,

$$\frac{V_{\text{aq}}}{V_{\text{org}}} = \gamma \quad (21)$$

$$\begin{aligned} N_{\text{Qtotal}} &= [QX]_{\text{org}} V_{\text{org}} \left[1 + \frac{\gamma}{K_{\text{QX}}} \right] \\ &\quad + [R]_{\text{aq}} V_{\text{org}} [K_{\text{R}} + \gamma] \end{aligned} \quad (22)$$

Substituting for $[R]_{aq}$ from Eq. (14),

$$N_{Q_{total}} = [QX]_{org} V_{org} \times \left\{ \left[1 + \frac{\gamma}{K_{QX}} \right] + \frac{k_1}{k_2} \left[\frac{K_R}{\gamma} + 1 \right] \frac{[A]_{org}}{[B]_{aq}} \right\} \quad (23)$$

Considering,

$$\left[1 + \frac{\gamma}{K_{QX}} \right] = \alpha \quad \text{and} \quad \frac{k_1}{k_2} \left[\frac{K_R}{\gamma} + 1 \right] = \beta \quad (24)$$

$$[QX]_{org} = \frac{N_{Q_{total}}}{V_{org}[\alpha + \beta\{[A]_{org}/[B]_{aq}\}]} \quad (25)$$

Substituting for $[QX]_{org}$ in Eq. (16),

$$\frac{d[P]_{aq}}{dt} = \frac{k_1[A]_{org}}{V_{aq}} \frac{N_{Q_{total}}}{\alpha + \beta\{[A]_{org}/[B]_{aq}\}} \quad (26)$$

From Eqs. (17) and (26),

$$-\frac{d[A]_{org}}{dt} = \frac{k_1[A]_{org}}{V_{org}} \frac{N_{Q_{total}}}{\alpha + \beta\{[A]_{org}/[B]_{aq}\}} \quad (27)$$

Substituting for concentration of various species in terms of fractional conversion X_A and solving,

$$\frac{dX_A}{dt} = \frac{k_1 N_{Q_{total}}}{V_{org}\{(\alpha/[1 - X_A]) + \beta\gamma/(\gamma([B]_{aq-i}/[A]_{org-i}) - X_A)\}} \quad (28)$$

Considering,

$$\frac{[B]_{aq-i}}{[A]_{org-i}} = M$$

$$\frac{\alpha}{[1 - X_A]} dX_A + \frac{\beta\gamma}{[M\gamma - X_A]} dX_A = \frac{k_1 N_{Q_{total}}}{V_{org}} dt \quad (29)$$

Considering,

$$\beta\gamma = \beta' \quad \text{and} \quad M\gamma = M' \quad (30)$$

$$\left[\frac{\alpha}{[1 - X_A]} + \frac{\beta'}{[M' - X_A]} \right] dX_A = \frac{k_1 N_{Q_{total}}}{V_{org}} dt \quad (31)$$

Eq. (31) can be solved for various cases of M and γ .

Case I (For $M = \gamma = 1$). Substituting $M = \gamma = 1$ and integrating Eq. (31) between limits $0-X_A$ and $0-t$, we get

$$-\ln[1 - X_A] = \frac{k_1 N_{Q_{total}}}{V_{org}(\alpha + \beta)} t \quad (32)$$

This is the complete equation for all ratios of $M = \gamma = 1$.

Thus, for all values of $M = \gamma = 1$, a plot of $-\ln[1 - X_A]$ versus t should be linear with a slope of

$$\frac{k_1 N_{Q_{total}}}{V_{org}\{(1 + [1/K_{QX}]) + (k_1/k_2)[K_R + 1]\}} \quad (33)$$

Case II (For mole ratio study, $M \neq 1$ but $\gamma = 1$). As above, a complete solution for $M \neq 1$ and $\gamma = 1$ can be derived as:

$$\left[1 + \frac{1}{K_{QX}} \right] (-\ln[1 - X_A]) + \frac{k_1}{k_2} [K_R + 1] \ln \times \left[\frac{[B]_{aq-i}/[A]_{org-i}}{([B]_{aq-i}/[A]_{org-i}) - X_A} \right] = \frac{k_1 N_{Q_{total}}}{V_{org}} t \quad (34)$$

Eq. (34) can be solved only if k_1, k_2, K_{QX} and K_R are known.

These pseudo-constants and distribution constants can be calculated through independent experiments or can be assumed. The LHS of Eq. (34) can then be

plotted against time for various values of mole ratio M .

Case III (For phase volume ratio study, $M \neq 1$ and $\gamma \neq 1$).

$$-\ln[1 - X_A] = \frac{k_1 N_{Q_{total}}}{V_{org}\{(1 + (1)K_{QX}) + \gamma(k_1/k_2)[K_R + 1]\}} \quad (35)$$

This is a complete solution for $M \neq 1$ and $\gamma \neq 1$.

Validity of the above model was tested by conducting several experiments during which the effect of various parameters on the reaction rate was studied.

5. Kinetics of reaction

5.1. Effect of different catalysts

The effect of various catalysts on the reaction was studied by using tetrabutylammonium bromide

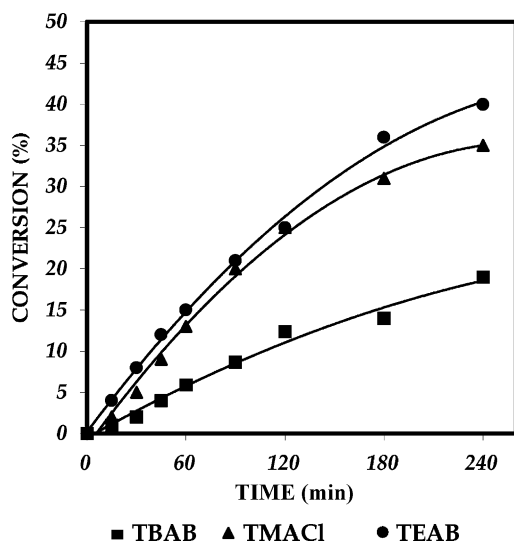


Fig. 1. Effect of different catalysts. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; catalyst: 0.005 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; temperature: 90 °C; speed of agitation: 700 rpm.

(TBAB), tetramethylammonium chloride (TMACI) and tetraethylammonium bromide (TEAB) at 700 rpm. All other experimental conditions were maintained constant. It was observed that TBAB gave low conversions, whereas, TEAB and TMACI displayed comparable catalytic activity (Fig. 1). Both TEAB and TMACI being low molecular weight, act as good IPT catalysts bringing the phenoxide ion to the aqueous phase for reaction. It is known that although TMACI is smaller in size than TEAB, the latter behaves as a better catalyst. Since TEAB gave the best results, it was used for all further reactions.

5.2. Effect of speed of agitation

To ascertain the influence of resistance to mass transfer of the reactants to the reaction phase, the speed of agitation was varied in the range of 500–1500 rpm under otherwise similar conditions. The conversion of CAA is plotted as a function of time (Fig. 2). The conversions were found to be practically the same at 500 and 700 rpm. However, as the speed of agitation was increased thereafter, the conversion was found to decrease. During the initial period, the decrease in conversion was marginal. However, the final conversion after 4 h at 1500 rpm was 32% in comparison

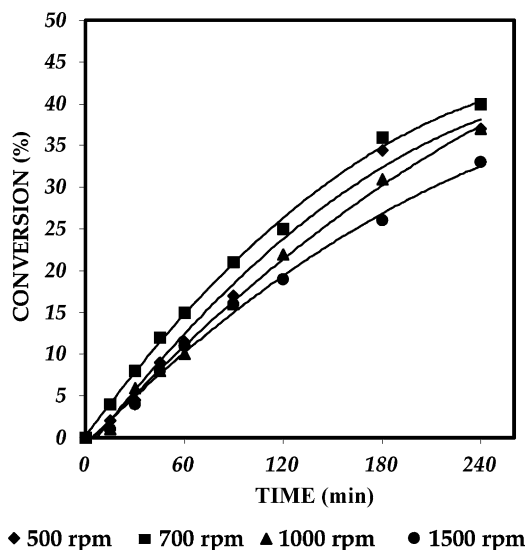


Fig. 2. Effect of speed of agitation. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; TEAB: 0.005 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; temperature: 90 °C.

with 40% at 700 rpm. Since equal volumes of aqueous and organic phases were taken, it appears that beyond 700 rpm there is a phase inversion whereby the continuous phase becomes the dispersed phase, thereby affecting interfacial area values and consequently the rates of mass transfer. Therefore, further experiments were conducted at 700 rpm.

5.3. Effect of phase volume ratio

Considering the results obtained for the effect of speed of agitation, the effect of volume ratio of organic to aqueous phase was studied. The effect was studied for 1:1, 1:2 and 2:1 ratios of organic phase to aqueous phase volumes under otherwise similar experimental conditions. When the phase ratio of organic to aqueous phase is 1:2, the best conversion values are obtained (Fig. 3), thereby suggesting that the organic phase as a dispersed phase leads to higher interfacial values that in turn enhance the mass transfer rates. However, when a phase ratio of organic to aqueous of 1:2 is used, the hydrolysis reaction of CAA becomes significant. So, further experiments were conducted by using equal volumes of the phases for which there was no by-product formation. Based on Eq. (35), a

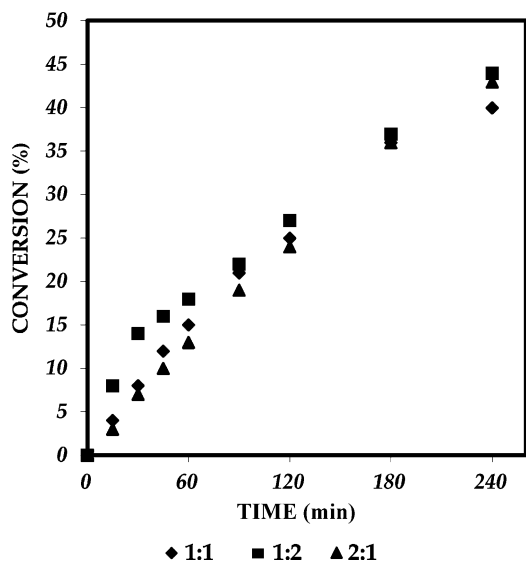


Fig. 3. Effect of phase volume ratio (org:aq). 2,4-DCP: 0.05 mol; CAA: 0.05 mol; NaOH: 0.05 mol; TEAB: 0.005 mol; temperature: 90 °C; speed of agitation: 700 rpm.

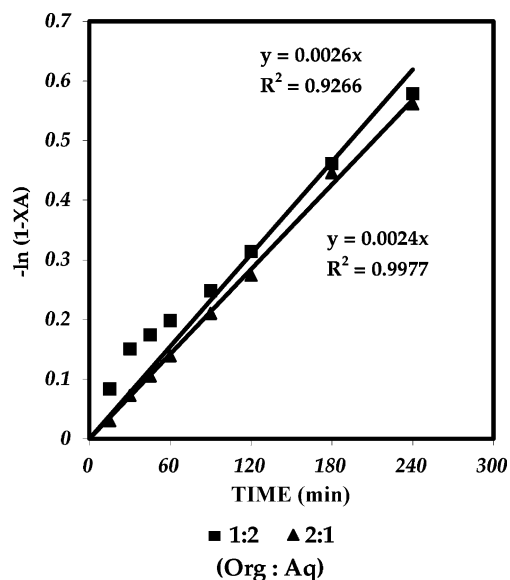


Fig. 4. Kinetic plot for phase volume ratio study. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; NaOH: 0.05 mol; TEAB: 0.005 mol; temperature: 90 °C; speed of agitation: 700 rpm.

plot of $-\ln(1 - X_A)$ versus time for varying phase volume ratio is found to validate the proposed model (Fig. 4).

5.4. Effect of catalyst loading

The concentration of catalyst (TEAB) was varied from 0.0015 to 0.0075 mol. The conversion is plotted against time for different concentration of catalyst under otherwise similar conditions (Fig. 5). As the concentration of the catalyst is increased there is an increase in the conversion, which is typical of a PTC reaction. For all the reactions a standard amount of 10 mol% of catalyst with respect to NaOH was used. A plot of $-\ln(1 - X_A)$ versus time was plotted for varying catalyst concentration (Fig. 6).

5.5. Effect of mole ratios of phenol and CAA

The experiments were conducted by taking 0.05 mol of NaOH and varying the moles of others. 2,4-DCP:CAA were varied in the mole ratios of 1:1, 1:2 and 2:1. Best results were obtained for the mole ratio of 2:1, whereas, minimum conversions were obtained for a mole ratio of 1:2 (Fig. 7). The initial rate

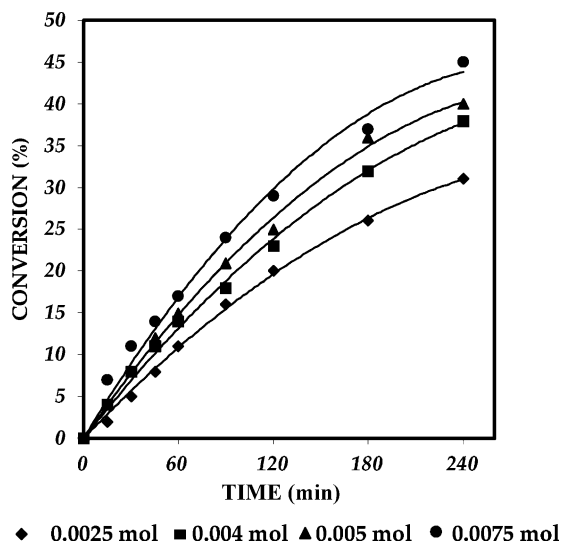
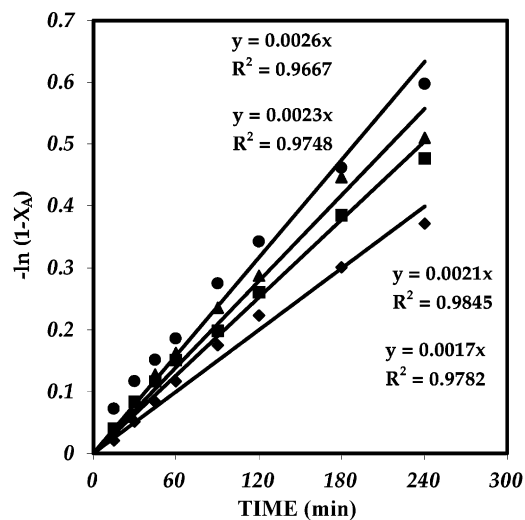


Fig. 5. Effect of catalyst loading. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; temperature: 90 °C; speed of agitation: 700 rpm.



◆ 0.0025 mol ■ 0.004 mol ▲ 0.005 mol ● 0.0075 mol

Fig. 6. Kinetic plot for the effect of catalyst loading. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; temperature: 90 °C; speed of agitation: 700 rpm.

data, however, suggests that there is marginal variation in conversions with varying mole ratio. The LHS of Eq. (34) is plotted against time for various values of mole ratio M after making the following assumptions.

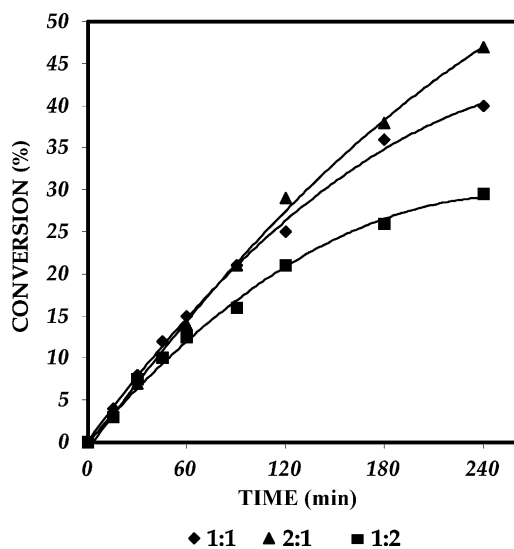
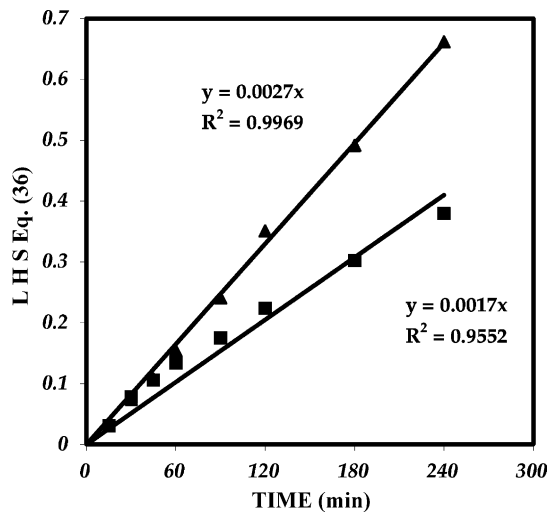


Fig. 7. Effect of mole ratio (2,4-DCP:CAA). TEAB: 0.005 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; temperature: 90 °C; speed of agitation: 700 rpm.



▲ 2:1 ■ 1:2

Mole ratio (2,4-DCP : CAA)

Fig. 8. Plot of LHS of Eq. (36) vs. time. TEAB: 0.005 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; temperature: 90 °C; speed of agitation: 700 rpm.

Eq. (34) can be written as:

$$-\ln[1 - X_A] + \frac{\beta}{\alpha} \ln \left[\frac{M}{M - X_A} \right] = \frac{k_1 N_{Q_{\text{total}}}}{\alpha V_{\text{org}}} t \quad (36)$$

LHS of Eq. (36) can be plotted against time for different values of β/α .

The values are chosen so as to cover a range of ratios. Thus, the plot was made for $\beta/\alpha = 1000, 100, 10, 1, 0.1, 0.01$ and 0.001. The best fit was obtained for $\beta/\alpha = 0.01$. A plot of $-\ln[1 - X_A] + (\beta/\alpha)(\ln[M/(M - X_A)])$ versus time for $\beta/\alpha = 0.01$ (Fig. 8).

A comment is in order as to why $\beta/\alpha = 0.01$ fits the data.

$$\frac{(k_1/k_2)[(K_R/\gamma) + 1]}{[1 + (\gamma/K_{QX})]} = 0.01$$

i.e.

$$\left[\frac{K_{QX} + 1}{K_{QX}} \right] \gg \frac{k_1}{k_2} [K_R + 1]$$

i.e. k_2 is much faster than k_1 or the aqueous phase reaction is much faster or $K_R \ll 1$.

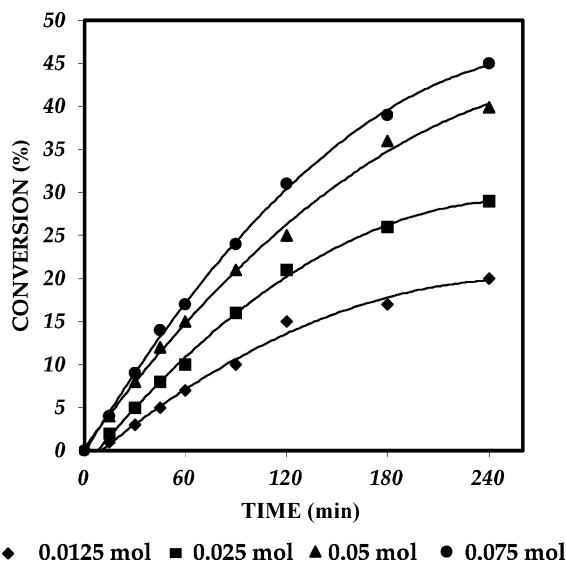


Fig. 9. Effect of NaOH concentration. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; TEAB: 0.005 mol; temperature: 90 °C; speed of agitation: 700 rpm.

Most of the quaternary salt of 2,4-DCP is in the aqueous phase. This also shows that the IPTC mechanism is appropriate.

5.6. Effect of NaOH concentration

NaOH loading was varied from 0.0125 to 0.075 mol under otherwise similar experimental conditions. The conversion was found to increase with the NaOH concentration (Fig. 9). In these experiments, phenol and CAA were each taken at 0.05 mol and the moles of NaOH were varied. In the absence of NaOH, no reaction takes place. When excess of NaOH is used the conversion increases but the system essentially becomes a single phase reaction and the formation of glycolic acid becomes significant. Therefore, it is essential to use equimolar quantities of each of the reactants and alkali. To validate the proposed model, a plot of $-\ln(1 - X_A)$ versus time for different NaOH concentrations was plotted (Fig. 10).

5.7. Effect of temperature

The reactions were studied at four different temperatures of 60, 70, 80 and 90 °C under otherwise similar

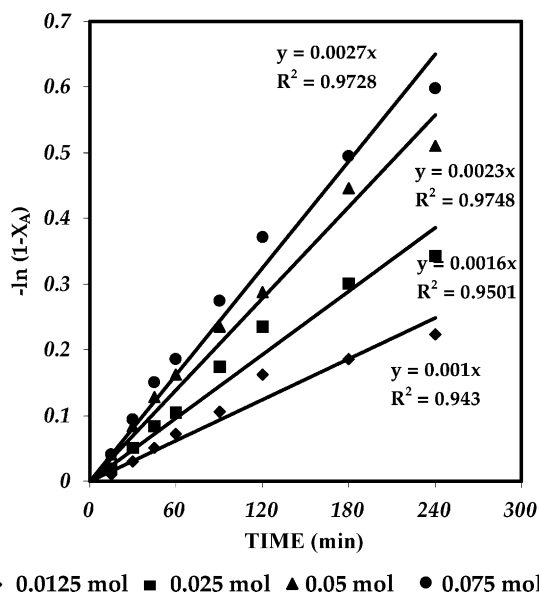


Fig. 10. Kinetic plot for the effect of NaOH concentration. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; TEAB: 0.005 mol; temperature: 90 °C; speed of agitation: 700 rpm.

experimental conditions. The conversion was found to increase with the temperature (Fig. 11). A plot of $-\ln(1 - X_A)$ versus time was plotted for varying temperatures (Fig. 12) and from the slope values the

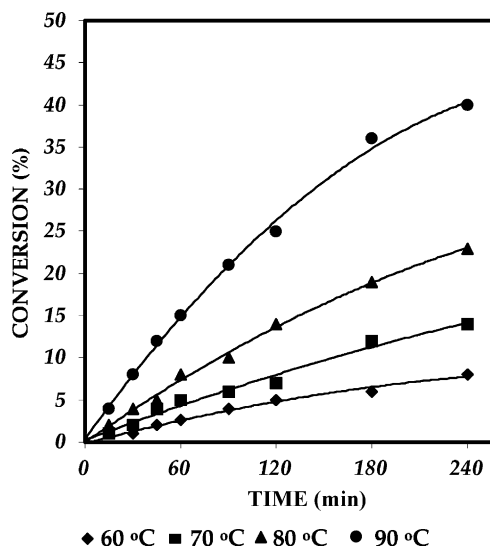


Fig. 11. Effect of temperature. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; TEAB: 0.005 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; speed of agitation: 700 rpm.

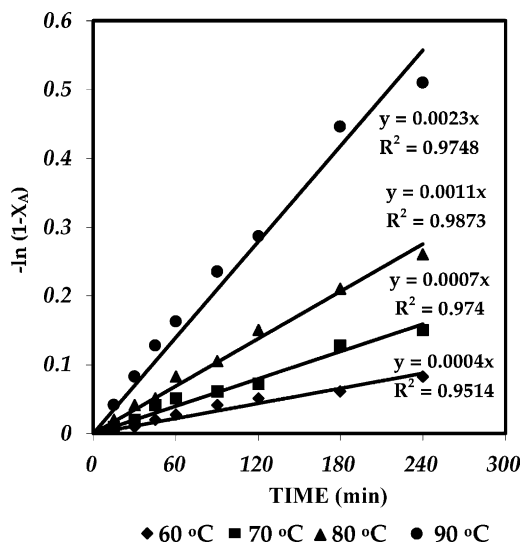


Fig. 12. Kinetic plot for the effect of temperature. 2,4-DCP: 0.05 mol; CAA: 0.05 mol; TEAB: 0.005 mol; NaOH: 0.05 mol; toluene: 25 cm³; H₂O: 25 cm³; speed of agitation: 700 rpm.

Arrhenius plot for the reaction was made (Fig. 13). The energy of activation for the reaction was calculated to be 22.837 kcal/mol. Thus, there were no mass transfer effects.

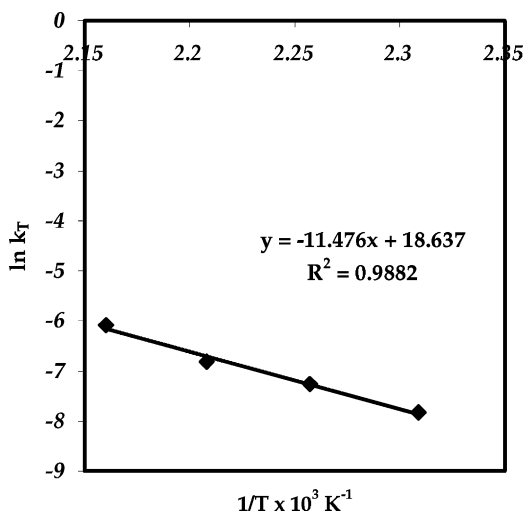


Fig. 13. Arrhenius plot.

6. Conclusions

The reaction of CAA and 2,4-DCP in the presence of NaOH in a bi-phasic system to give 2,4-D occurs according to the IPTC mechanism. TEAB was found to be the most suitable catalyst. The formation of glycolic acid is suppressed in the reaction when equal phase volume ratio is used. A model based on the mechanism of the reaction has been proposed and validated against experimental data.

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