36 *J. Phys. Chem. A* **1997,** *101,* 36−48

Mechanistic and Kinetic Investigation of Liquid−Liquid Phase Transfer Catalyzed Oxidation of Benzyl Chloride to Benzaldehyde

Ganapati D. Yadav* and Bhagyashree V. Haldavanekar

Chemical Engineering Division, University Department of Chemical Technology, University of Bombay, Matunga, Bombay/Mumbai 400 019, India

Received: June 6, 1996[⊗]

The kinetics and mechanism of liquid−liquid phase transfer catalyzed oxidation of benzyl chloride with chromate salts is investigated in great detail in a systematic way to throw light on the selectivity of the reaction to benzaldehyde. This system presents a complex case of consecutive and parallel reactions in which benzyl alcohol is formed as an intermediate which is further oxidized to benzaldehyde. The results are novel, and the experimental data fit the theoretical model very well.

1. Introduction

Phase transfer (PT) catalysis has become a pervasive and widely accepted synthetic tool, notwithstanding several limitations on its commercial exploitation. However, there is very limited information on the kinetics of multiphase PT catalysis reactions, in liquid−liquid, liquid−solid, liquid−liquid−solid (triphase) systems, particularly those involving complex mechanisms and series and/or parallel steps; for instance, the oxidation of benzyl chloride with aqueous chromate salts is such a case.

On laboratory scale, inorganic oxidizing agents have been reported for the oxidation of benzyl chloride or benzyl alcohol using solid−liquid (S−L) or liquid−liquid (L−L) systems, and some of these include hypochlorite, chromic acid, chromates, dichromates, hydrogen peroxide, etc. There is a dearth of accounts on the mechanism and the kinetics of oxidation of alkyl or aralkyl halides with chromate and dichromate ions under phase transfer catalysis. This study was therefore undertaken to investigate the liquid−liquid phase transfer catalyzed oxidation of benzyl chloride with aqueous chromate/dichromate salts.

2. Literature Review and Suggested Mechanisms

Various phase transfer catalysts, such as quaternary onium salts, crown ethers, and poly(ethylene glycol)s, have been used for oxidation of alkyl and aralkyl halides and also of alcohols. Haldavanekar[1] has reviewed the literature[2−17] on the preparation of benzaldehyde under phase transfer catalysis. A new technique of capsule membrane phase transfer catalyzed oxidation of benzaldehyde has emanated from this laboratory.[18−19]

Cardillo et al.[14] have reported the usefulness of chromate ion as a nucleophile for the crown ether catalyzed oxidation of alkyl halide to aldehyde in hexamethylphosphoric triamide (HMPT), where the reaction proceeds via S_N2 displacement of the halogen atom by chromate ion to form a chromate ester which further decomposes to the corresponding carbonyl compound.

$$R{-}CH_2X + K_2CrO_4 \xrightarrow[\text{crown ether}]{\text{HMPT}} RCH_2CrO_4K \rightarrow RCHO \tag{1}$$

Gopalan and Subbarayan[15] have, on the basis of kinetic study, proposed a mechanism for the oxidation of benzyl chloride by chromic acid in which the reaction was found to be first order in the concentration of each of benzyl chloride, oxidant, and H^+. The mechanism involves rapid formation of a chromate ester which subsequently decomposes to afford benzaldehyde and Cr(IV) species. The reaction was overall third order. Pletcher and Tait[16] have studied the oxidation of alcohols with stoichiometric quantity of dichromate in 3 M aqueous sulfuric acid using tetrabutylammonium bisulfate as the phase transfer catalyst (PTC). They have suggested that the reaction proceeds via disproportionation of chromate ester in which the proton catalyzed disproportionation of Cr(V) or Cr(IV) to Cr(VI) is important. Cr(VI) in aqueous solution exists as a pH-dependent mixture of several species as given below:

$$CrO_4^{2-} \xrightarrow{H^+} HCrO_4^- \xrightarrow{H^+} H_2CrO_4 \tag{2}$$

$$HCrO_4^- + HCrO_4^- \xrightarrow{-H_2O} Cr_2O_7^{2-} \xrightarrow{+H^+} HCr_2O_7^- \tag{3}$$

All of the above species are capable of forming ion pairs with the PTC cation which are partitioned into the organic phase. However, the different Cr(VI) species may not be equally active for alcohol oxidation. Indeed there is an evidence[16] that the first step of oxidation of alcohol is

$$HCrO_4^- + ROH \rightarrow ROCrO_3^- + H_2O \tag{4}$$

Chromate ester has a greater solubility in organic solvents than water. Hence, Pletcher and Tait[16] have suggested the following mechanism:

$$HCrO_4^- + Q^+ \rightarrow Q^+HCrO_4^- \quad \text{(in aqueous phase)} \tag{5}$$

$$[Q^+HCrO_4^-]_{aq} \xrightarrow{\text{org. solvent}} [Q^+HCrO_4^-]_{org} \tag{6}$$

$$[Q^+HCrO_4^-]_{org} + RCH_2OH \rightarrow [RCH_2OCrO_3^-Q^+]_{org} + H_2O \tag{7}$$

$$[RCH_2OCrO_3^-Q^+]_{org} \rightarrow RCHO + Cr(IV) + Q^+ + H^+ \tag{8}$$

$$3Cr(IV) \rightarrow Cr(VI) + 2Cr(III) \tag{9}$$

where the bracketed quantities denote ion pairs.

Dey and Mahanti[17] have studied the kinetics of oxidation of substituted benzyl alcohols by quinolinium dichromate in DMF

---

* To whom correspondence should be addressed. FAX: (91-22) 414 5614. E-mail: gdy@udct.ernet.in.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

S1089-5639(96)01678-7 CCC: $14.00

in the presence of an acid and found that no further oxidation of benzaldehyde occurred under their experimental conditions.

$$3PhCH_2OH + 2Cr(VI) \rightarrow 3PhCHO + 2Cr(III) + 6H^+ \quad (10)$$

The literature reveals that most of the published information is patented and very few researchers have reported details of kinetics of the oxidation of benzyl chloride under L−L PT catalysis.

3. Experimental Section

3.1. Chemicals and Catalysts. Benzyl chloride (BnCl), toluene, potassium dichromate, and sodium carbonate of AR grade were procured from M/s s.d. Fine Chemicals Pvt. Ltd., India. Tetrabutylammonium bromide (TBAB) and cetyltrimethylammonium bromide (CTMAB) were obtained from Spectrochem, India. Aliquat-336 was obtained from Aldrich.

3.2. Experimental Setup and Procedure. Reactions were studied in a 5 cm i.d. fully baffled mechanically agitated contactor of 250 mL capacity equipped with a six-bladed pitched-turbine impeller and a condenser. The reactor was kept in a thermostatic bath whose temperature was maintained at the desired value. Initially, the required amounts of BnCl and toluene were fed to the reactor and the mixture was heated to the desired temperature. A known amount of the catalyst was then added to the reactor. An aqueous solution of potassium dichromate and sodium carbonate which had already attained the reaction temperature was added to the reactor at the same temperature, and the moment of its addition was considered as the zero time. Samples were withdrawn at a definite interval of time, and the organic phase was analyzed by gas chromatography.

Preliminary experiments were conducted with 34.1 g (0.3705 mol) of toluene, 11.803 g (0.0932 mol) of BnCl, 1.5030 g of TBAB (5% mol/mol of benzyl chloride), 50 mL of 0.93 M potassium dichromate solution, and 2.4 g (0.0222 mol) of sodium bicarbonate at 100 °C for 4 h. The pH of the aqueous phase was measured after addition of sodium bicarbonate and was found to be in the range 6.65−6.75. All other experiments were done at a temperature of 100 °C with TBAB as a catalyst except when the effect of temperature on the rate of reaction was studied.

3.3. Method of Analysis. The progress of the reaction was studied by analyzing the samples with a gas chromatograph (Perkin-Elmer 8500 model) equipped with a flame ionization detector (column: 3 mm × 4 m, stainless steel; stationary phase: 5% OV-17 on chromosorb WHP). Synthetic mixtures were prepared and used for quantifying the reactant and products.

4. Results and Discussion

4.1. Mass Transfer Accompanied by Chemical Reaction and Locale of Reaction. L−L PT catalyzed reactions involve diffusion of the ion pairs back and forth between the aqueous and organic phases and the reaction between the substrate and the ion pair incorporating the nucleophile. Most of the L−L PT catalyzed reactions are known to occur in the organic phase wherein the concentration of the desired ion pair must be maximum for achieving higher reaction rates and conversions. It is thus necessary to ascertain the values of the relative rates of mass transfer and chemical reaction to deduce mechanisms and kinetics. The theory of mass transfer accompanied by chemical reaction in G−L, L−L, S−L, G−L−S (reactant), and G−L−S (catalyst) multiphasic systems is well documented, for instance, by Doraiswamy and Sharma,[20] who have classified these reactions into four regimes. The theory is presented here in brief in the context of L−L PT catalysis on the basis of a two-film model (Figure 1).

Regime 1: Very Slow Reaction (Figure 1a). The rate of mass transfer of the ion pair containing the nucleophile $[Q^+Y^-]$ into the reaction phase is far greater than the rate of its reaction with the substrate RX. The concentration of the ion pair will be uniform throughout the reaction (organic phase), and the overall rate is governed by the kinetics of the homogeneous chemical reaction. Here the speed of agitation will have no influence on the rate of chemical reaction.

Reactive 2: Slow Reaction (Figure 1b). In this regime, the rate of reaction is much greater than the rate of transfer of the ion pair $[Q^+Y^-]$ from the interface through the liquid (organic) film to the bulk liquid face. The overall rate is governed by the rate of mass transfer. There is a concentration gradient for the ion pair, and its concentration in the bulk reaction (organic phase) is zero. However, no reaction occurs in the diffusion film next to the L−L interface in the reaction phase. Here speed of agitation has a pronounced effect on the overall rate because the mass transfer coefficient and the liquid−liquid interfacial areas are dependent on the speed of agitation.

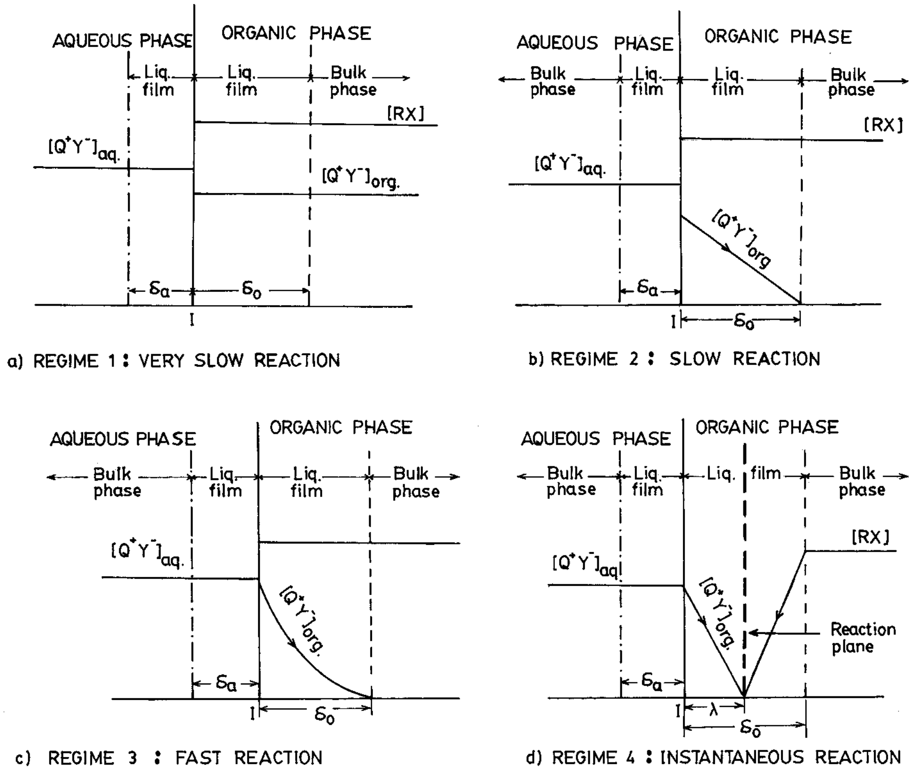
Regime 3: Fast Reaction (Figure 1c). Under certain conditions, the reaction of ion pair $[Q^+Y^-]_{org}$ and substrate RX occurs while the ion pair is diffusing through the liquid (organic) film from the interface. The chemical reaction and diffusion become steps in parallel. There is an enhancement in the rate of diffusion due to reaction.

Regime 4: Instantaneous Reaction (Figure 1d). In this case, the reaction is so fast that the ion pair $[Q^+Y^-]_{org}$ and substrate RX cannot coexist. At a certain distance λ from the L−L interface in the liquid (organic) film, a reaction plane is formed at which both the ion pair and substitute RX are consumed by the reaction. The rate of mass transfer here is controlled by the rate at which $[Q^+Y^-]_{org}$ and RX diffuse to the reaction plane.

There are also cases of overlaps between regimes 1 and 2, regimes 1, 2, and 3, and regimes 3 and 4 depending on the reaction conditions and mass transfer effects (see Doraiswamy and Sharma[20]).

The theory suggests that the mass transfer rates will be important in regimes 2 and 4, and here the speed of agitation will play a dominant role.

4.2. Effect of Speed of Agitation. The speed of agitation was varied under otherwise similar conditions from 500 to 1500 rpm (Figure 2). The conversion of BnCl remained unchanged at a particular time beyond 1000 rpm, thereby indicating absence of mass transfer resistance to the transfer of ion pairs across the interface. It is possible to calculate the rate of mass transfer at 1000 rpm from established correlations for L−L agitated systems as given by Doraiswamy and Sharma.[20] Thus for the concentration of PTC used in standard experiments it would be most appropriate to compare the relative rates of mass transfer and chemical reaction. A typical calculation is given here. The estimated value of volumetric mass transfer coefficient for the ion pair at 1000 rpm is 0.3 s^{-1} and the rate of mass transfer for the PTC concentration of 9.32×10^{-5} mol/cm^3 is 2.796×10^{-5} (mol/cm^3 of organic phase)/s, whereas the measured value of the rate of reaction is 3.13×10^{-7} (mol/cm^3 of organic phase)/s, which is almost 2 orders of magnitude lower. Thus, it is clear that the rate of organic phase reaction is very slow in comparison with the rate of mass transfer of the ion pair from the interface. The reaction belongs to the so-called regime 1 of very slow reaction free of any mass transfer effects. To be on the safe side, the speeds of reaction were always maintained at or beyond 1000 rpm in all other experiments.



a) REGIME 1 : VERY SLOW REACTION

b) REGIME 2 : SLOW REACTION

c) REGIME 3 : FAST REACTION

d) REGIME 4 : INSTANTANEOUS REACTION

Figure 1. Theory of mass transfer accompanied by chemical reaction in L−L PT calatysis: Typical concentration profiles according to the four regimes of operation. $[Q^+Y^-]_{aq}$ = ion pair of nucleophile in aqueous phase. $[Q^+Y^-]_{org}$ = ion pair of nucleophile in organic phase. RX = substrate. δ_a = thickness of aqueous phase film next to interface I. δ_o = thickness of organic phase film next to interface I. (a) Regime 1: very slow reaction. The reaction occurs in the bulk organic phase as a homogeneous reaction. Mass transfer effects are unimportant. (b) Regime 2: slow reaction. The reaction occurs in the bulk organic phase. No free concentration of ion pairs exists in the bulk organic phase. (c) Regime 3: fast reaction. Diffusion of $[Q^+Y^-]_{org}$ and its reaction with RX are steps in parallel, and the reaction occurs in the organic liquid film next to the L−L interface. (d) Regime 4: instantaneous reaction. The reaction between $[Q^+Y^-]_{org}$ and RX is so fast that they cannot coexist in the organic phase. $[Q^+Y^-]_{org}$ diffuses from the L−L interface, and RX diffuses from the bulk organic phase into the organic liquid film and react at a plane λ from the interface. No free $[Q^+Y^-]_{org}$ exists beyond distance λ, and no free RX exists beyond distance ($\delta_o - \lambda$) toward the interface. Note that for simiplicity other ion pairs are not shown.

4.3. Mechanism and Kinetics of Formation of Benzaldehyde.

4.3.1. Formation of Chromate Ester. The various ionic reactions of potassium dichromate and water are given below.

$$K_2Cr_2O_7 \rightleftarrows Cr_2O_7^{2-} + 2K^+ \qquad (11)$$

$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2HCrO_4^- \qquad (12)$$

Thus, in this case along with $HCrO_4^-$, an appreciable amount of $Cr_2O_7^{2-}$ is formed. Starks and Liotta[21] have reported that the transfer of monovalent ion from aqueous phase to organic phase is easier than that of the divalent ion. To convert $Cr_2O_7^{2-}$ into $HCrO_4^-$, it was thought worthwhile to add Na_2CO_3 to the reaction mixture.

$$Na_2CO_3 + Cr_2O_7^{2-} \rightleftarrows 2\,Na^+ + 2CrO_4^{2-} + CO_2 \qquad (13)$$

$$CrO_4^{2-} + H^+ \rightleftarrows HCrO_4^- \qquad (14)$$

Starks and Liotta[21] have given an account of chromate extraction, particularly $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, and $Cr_2O_7^{2-}$ into organic solvents by using the PTC. It is shown that $HCrO_4^-$ and $HCr_2O_7^-$ are readily phase transferred provided the aqueous phase is acidic, but almost no transfer of chromate anions occurs from alkaline aqueous solutions. The dichromate anion $Cr_2O_7^{2-}$, in contrast to $HCrO_4^-$, is reported to be difficult to transfer into an organic solution, as is typical of divalent anions.

In the current studies, the pH of the solution was such that it was always slightly acidic. Thus, formation of $[Q^+HCrO_4^-]$ is only taken into account in this work. The species $HCr_2O_7^-$ is formed in strong acid. The species $HCrO_4^-$ is the only predominant species in the pH range 6−8, which was used in the current work.

4.3.2. Reaction Paths. Since several species are involved in the reaction mixture which can possibly follow different series and parallel reactions resulting in the formation of benzyl alcohol (BnOH), benzaldehyde (PhCHO), dibenzyl ether (BnOBn), benzoic acid (BnCOOH), and benzyl benzoate (BnCOOBn), it is essential to conduct the experiments under controlled conditions limiting the byproduct formation. Some experiments were designed to trace the path of the reaction of benzyl chloride, leading to the formation of benzaldehyde, the main product.

The selectivity S of benzaldehyde, in general, is defined as

$$S = \frac{[\mathrm{PhCHO}]}{[\mathrm{BnOH}] + [\mathrm{BnOBn}] + [\mathrm{BnCOOH}] + [\mathrm{BnCOOBn}]} \qquad (15)$$

The preliminary L−L PT catalysis experiments on the chromate oxidation of benzyl chloride (BnCl) with tetrabutylammonium bromide (TBAB) as a phase transfer catalyst at 100 °C showed that the reaction led to the formation of BnOH and PhCHO only. There was no oxidation of the solvent toluene at all which was independently confirmed under otherwise similar conditions except the addition of benzyl chloride. There was no formation of dibenzyl ether or benzyl benzoate. Further, since PhCHO could be overoxidized to benzoic acid (BnCOOH), both the aqueous and organic phases were further analyzed. The

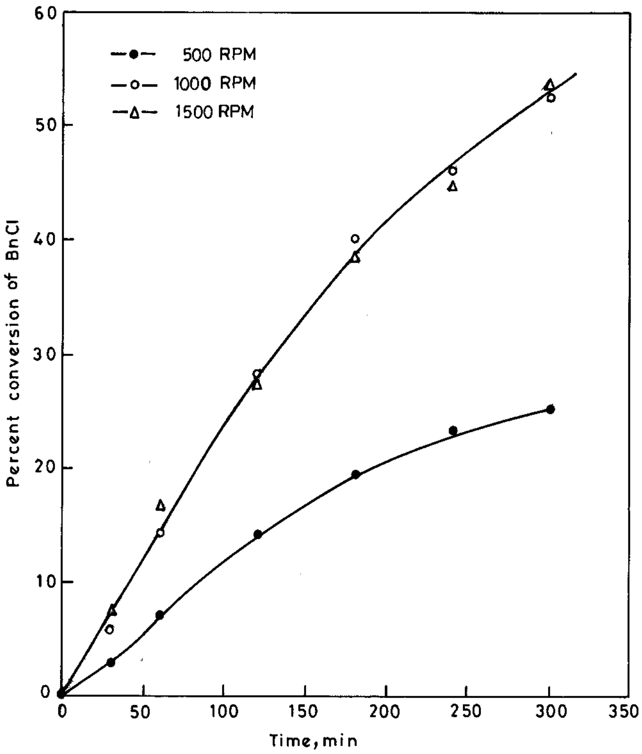


Figure 2. Effect of speed of agitation on conversion of benzyl chloride. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^{3}of organic phase. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3 of aqueous phase. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3 of aqueous phase. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

TABLE 1: Typical Selectivity Profile of Benzaldehyde in Standard Experiments[a]

time (min)	selectivity ratio [PhCHO]/[BnOH]	time (min)	selectivity ratio [PhCHO]/[BnOH]
0	0	90	0.85
15	0.21	120	0.91
30	0.24	180	1.28
45	0.38	240	2.00
60	0.45		

[a] Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^{3}of organic phase. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3 of aqueous phase. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3 of aqueous phase. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

pH−metric titration of the aqueous phase as well as extraction of the organic phase with aqueous NaOH did not detect any benzoic acid.

Thus,

$$S = \frac{[\mathrm{PhCHO}]}{[\mathrm{BnOH}]} \qquad (16)$$

Table 1 shows a typical selectivity profile of benzaldehyde, which increases with time, thereby indicating that BnOH was further oxidized to PhCHO. Thus, triangular reaction paths starting from BnCl leading to PhCHO, as depicted in Figure 3, were formulated and the hypothesis was tested by conducting different isolated experiments under otherwise similar conditions at 100 °C and in the absence of any mass transfer limitations.

The type of experiments required per these paths are as follows (see Figure 3):

1. Hydrolysis of benzyl chloride with aqueous $HCrO_4^-$ to benzyl alcohol by two paths a and b:

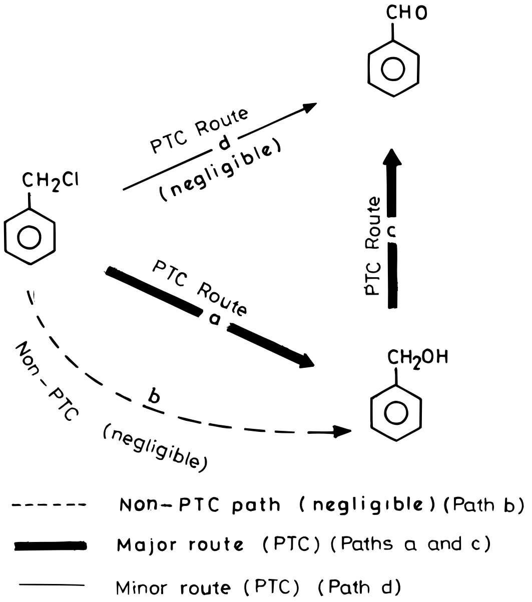


Figure 3. Triangular paths of reaction. The PT catalysis path is due to the formation of [$Q^+HCrO_4^-$]$_{org}$.

(i) **Path a**: in the presence of PTC (rate constant k_a). This path is possibly due to the formation of an intermediate chromate ester [$RCH_2OCrO_3^-H^+$], which decomposes to BnOH and CrO_3, which is immediately transformed to aqueous phase to regenerate $HCrO_4^-$ ions.

(ii) **Path b**: without a PTC (rate constant k_b). Since trace hydrolysis of BnCl is known to occur in water, it is essential to compare the relative rates of paths a and b leading to the formation of BnOH and whether the contribution due to the noncatalytic path b could be neglected.

2. **Path c**: Oxidation of benzyl alcohol, formed in situ, with aqueous $HCrO_4^-$ to benzaldehyde under PT catalysis conditions. This reaction is possible because of the formation an intermediate chromate ester [$PhCH_2OCrO_3^-Q^+$] of BnOH which further decomposes to PhCHO. The possibility of formation of PhCHO by a noncatalytic oxidation of BnOH ought to be also verified. This is not shown in Figure 3 for reasons put forward later.

3. **Path d**: Oxidation of benzyl chloride directly to benzaldehyde with aqueous $HCrO_4^-$ in the presence of a PTC.

4.4. Testing of the Hypothesis on Reaction Paths. The non-PT catalysis reactions were conducted under otherwise similar conditions to find out the contributions of these reactions to overall conversion in the absence of any phase transfer catalyst.

4.4.1. Path b: Hydrolysis of Benzyl Chloride(BnCl) with Aqueous $HCrO_4^-$ without Phase Transfer Catalyst. The hydrolysis of BnCl was carried out at 100 °C with aqueous chromate solution but without the addition of a phase transfer catalyst. It was interesting to note that the hydrolysis of BnCl took place even in the absence of phase transfer catalyst and BnOH was the sole product. However, the formation of benzaldehyde was detected only in the presence of a phase transfer catalyst. The rate of reaction can be described by a first-order kinetics.

$$-\frac{d[\mathrm{BnCl}]}{dt} = k_b[\mathrm{BnCl}] \qquad (17)$$

Upon integration eq 17 gives

$$-\ln(1 - X_A) = k_b t \qquad (18)$$

where X_A is the fractional conversion of benzyl chloride.

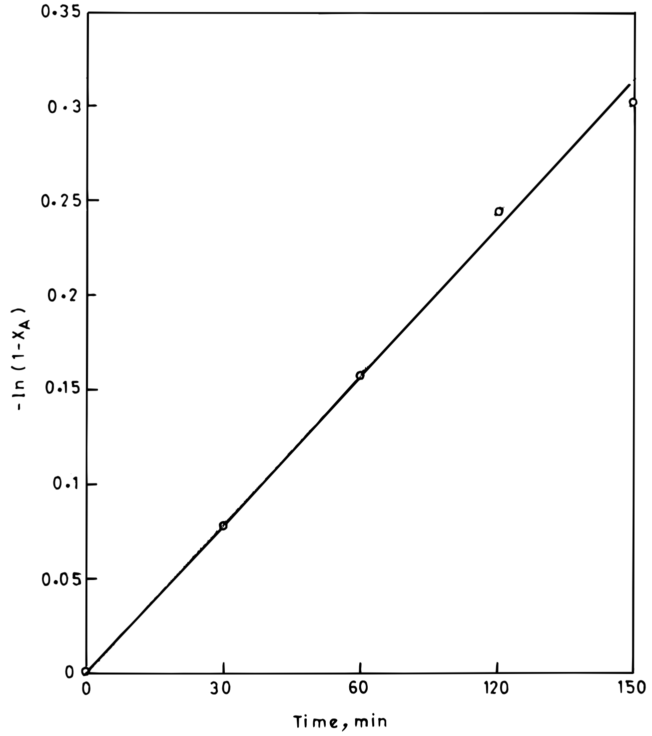


Figure 4. First-order kinetics plot for the hydrolysis of benzyl chloride in the absence of phase transfer catalyst. $[K_2CrCr_2O_7] = 9.33 \times 10^{-4}$ mol/cm^3. $Vol_{org} = Vol_{aq} = 50$ mL. $[Na_2CO_3] = 4.44 \times 10^{-4}$ mol/cm^3.

The kinetic plot of $-\ln(1 - X_A)$ vs time is shown in Figure 4. It confirms that the reaction is first order with respect to benzyl chloride. The rate constant k_b was found to be 3.47×10^{-5} s^{-1} at 100 °C.

The above experiment also demonstrated that there was no simultaneous formation of PhCHO directly from BnCl by a noncatalytic oxidation route.

To elucidate whether the presence of chromate is essential or not, another set of experiments was conducted at a pH of 6.6 between BnCl and water, both in the presence and absence of phase transfer catalyst at 100 °C. However, a very negligible amount of BnOH was noticed even after 4 h of reaction. This suggested that the species $HCrO_4^-$ was necessary for hydrolysis of BnCl.

4.4.2. Oxidation of Benzyl Alcohol (BnOH) with $HCrO_4^-$ without Phase Transfer Catalyst. To verify whether the oxidation of BnOH requires a phase transfer catalyst or not, typical experiments were conducted with BnOH and potassium dichromate without the phase transfer catalyst at 100 °C. No formation of benzaldehyde was observed even after 4 h, which suggested that the presence of phase transfer catalyst was needed for the oxidation of BnOH. Thus, further experiments were conducted in the presence of a PTC.

4.4.3. Path c: Oxidation of Benzyl Alcohol with $HCrO_4^-$ with Phase Transfer Catalyst. To examine the role of phase transfer catalyst in the oxidation of BnOH, some experiments were conducted, under otherwise similar conditions, with tetrabutylammonium bromide (TBAB) as the phase transfer catalyst at 100 °C.

There was a suspicion that dibenzyl ether might be formed from BnOH. However, the earlier literature on oxidation of alcohol to benzaldehyde under PT catalysis conditions mentioned no formation of dibenzyl ether. When samples drawn at different times were analyzed, no detectable dibenzyl ether was noticed up to 3 h or so. The concentration profile of BnOH and PhCHO given in Figure 5 shows a pseudo-first-order behavior. Further, there was no benzoic acid formed because the analysis of aqueous phase did not show any detectable benzoic acid. The kinetics of this reaction were established from the data up to 2 h.

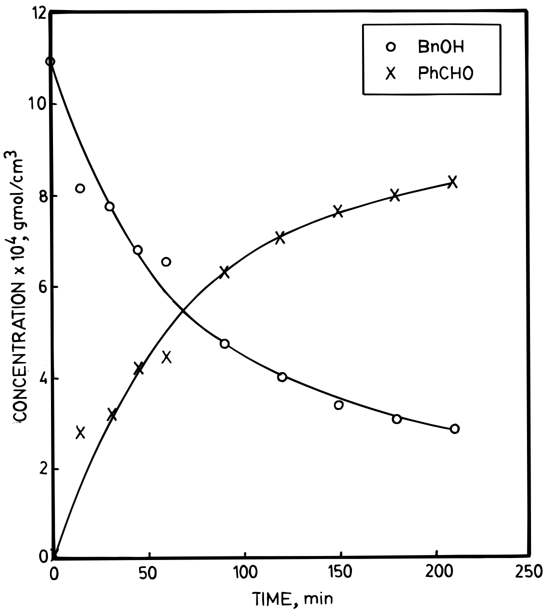


Figure 5. Oxidation of benzyl alcohol with $HCrO_4^-$ under PT catalysis conditions. Speed = 1000 rpm. Temperature = 100 °C. $[BnOH] = 1.09 \times 10^{-3}$ mol/cm^3. $[K_2CrCr_2O_7] = 9.33 \times 10^{-4}$ mol/cm^3. $Vol_{org} = Vol_{aq} = 50$ mL. $[Na_2CO_3] = 4.44 \times 10^{-4}$ mol/cm^3. $[TBAB]_{org} = 9.32 \times 10^{-5}$ mol/cm^3.

The rate of reaction of benzyl alcohol in presence of a PTC is given by

$$-\frac{d[BnOH]}{dt} = k_{c1}[BnOH] \qquad (19)$$

$$\text{where} \quad k_{c1} = k_c[PTC] \qquad (20)$$

where k_{c1} is a pseudo-first-order rate constant.

Equation 19 can be integrated, to get

$$-\ln(1 - X_B) = k_{c1}t \qquad (21)$$

where X_B is the fractional conversion of benzyl alcohol.

A plot of $-\ln(1 - X_B)$ against time t is given in Figure 6, from which the value of k_{c1} is obtained as 1.13×10^{-4} s^{-1} for the TBAB concentration of 9.32×10^{-5} mol/cm^3 (org). The value of k_c was calculated as 1.2123 cm^3/(mol s). It is thus obvious that only the phase transfer catalyzed oxidation of benzyl alcohol leads to the formation of benzaldehyde (path c).

4.4.4. Reaction of Benzyl Chloride with Aqueous $HCrO_4^-$ in the Presence of PTC: Path a or Path d or Both? It is rather tricky to verify the formation of PhCHO directly from BnCl by path d because of its parallel reaction by path a followed by path c. One of the ways is to tag some molecules of BnOH and add them in the reaction mixture. However, a simple way is to carefully analyze the progress of the reaction vis-à-vis the concentration profiles of BnCl, BnOH, and PhCHO.

To establish the correct paths for the formation of benzaldehyde, several experiments were conducted with stoichiometric amounts of benzyl chloride and $HClO_4^-$ under otherwise similar conditions, with TBAB as the PTC. Figure 7 depicts the typical

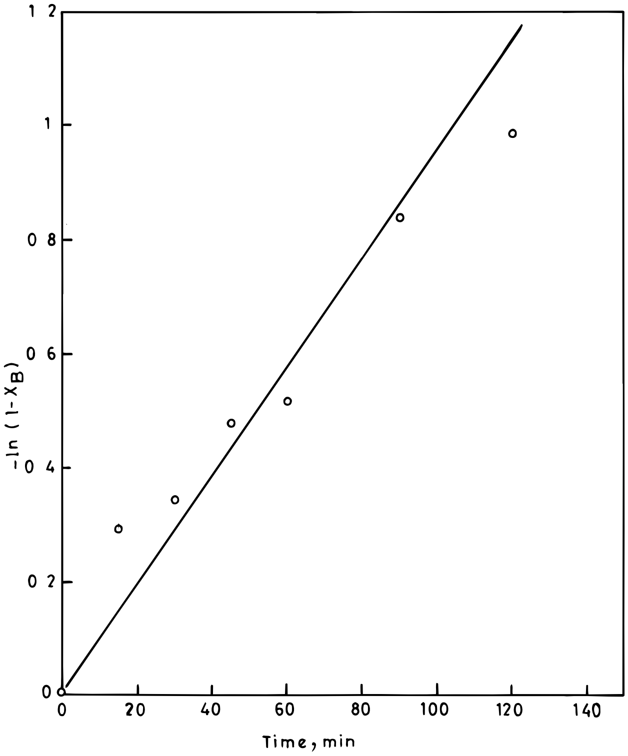


Figure 6. Kinetics of plot of oxidation of benzyl alcohol with $HCrO_4^-$ under PT catalysis conditions. Speed = 1000 rpm. Temperature = 100 °C. [BnOH] = 1.09×10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33×10^{-4} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44×10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32×10^{-5} mol/cm^3.

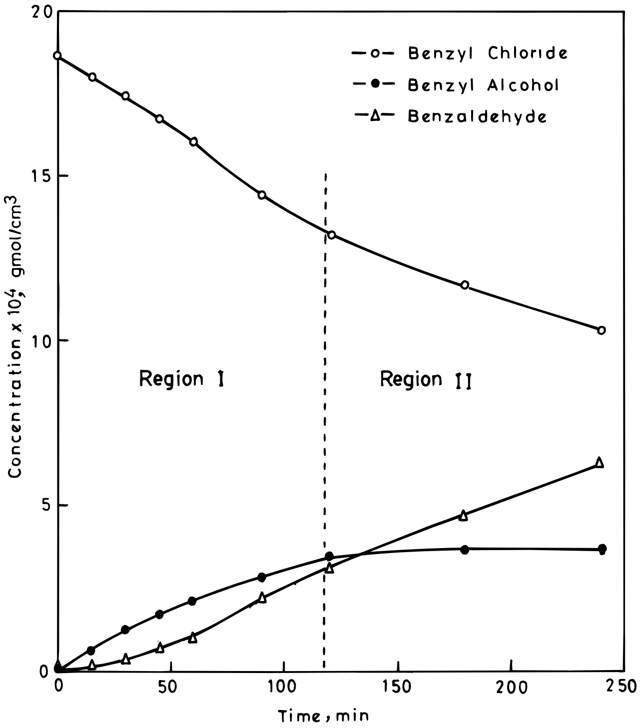


Figure 7. Reaction of benzyl chloride with aqueous $HCrO_4^-$ in the presence of PTC. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86×10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33×10^{-4} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44×10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32×10^{-5} mol/cm^3.

concentration profiles of the reactants and products, and it is divided in two regions, I (up to 2 h) and II (beyond 2 h).

It is seen that the concentration of benzyl alcohol increases in region I up to 2 h, and thereafter, it remains constant throughout in region II. The concentration of benzaldehyde is less than that of benzyl alcohol in region I, and it becomes greater in region II.

The concentration of benzyl chloride decreases continuously in both the regions. However, an interesting trend is seen in region II. The BnCl concentration drop is linear in time in that region, and simultaneously, the increase in concentration of PhCHO is also linear in time. This suggests that the rate of reaction of BnCl in region II is independent of its concentration and that of formation of PhCHO also independent of benzyl chloride concentration. Further, the slope of concentration of BnCl with time in region II is identical and opposite in sign with the slope of concentration of PhCHO in that region.

Since the concentration of BnOH is constant in region II, its net rate is zero, that is, the rate of formation of benzyl alcohol (by path a) is equal to its consumption by path c to produce benzaldehyde. It is obvious that the rate of reaction of benzyl chloride is equal to the rate of formation benzaldehyde in region II.

If both the concentrations of benzyl alcohol and benzaldehyde had increased with time, then it would have suggested that there was no oxidation of benzyl alcohol and that benzaldehyde was formed directly from benzyl chloride by path d. Under such a case, benzyl chloride would disappear by two parallel reactions, namely, one leading to the formation of benzyl alcohol and another leading to the formation of benzaldehyde. However, this supposition is contrary to the facts.

The material balance for region II of Figure 7 is as follows:

Rate of reaction of benzyl chloride

$$\frac{-\mathrm{d[BnCl]}}{\mathrm{d}t} = k_\mathrm{d}\mathrm{[PTC][BnCl]} + k_\mathrm{a}\mathrm{[PTC][BnCl]} \tag{22}$$

Net rate of formation of benzaldehyde

$$\frac{\mathrm{d[BnOH]}}{\mathrm{d}t} = k_\mathrm{a}\mathrm{[PTC][BnCl]} - k_\mathrm{c}\mathrm{[PTC][BnOH]} \tag{23}$$

$$= 0 \quad \text{in region II}$$

Net rate of formation of benzaldehyde

$$\frac{\mathrm{d[PhCHO]}}{\mathrm{d}t} = k_\mathrm{d}\mathrm{[PTC][BnCl]} + k_\mathrm{c}\mathrm{[PTC][BnOH]} \tag{24}$$

In eqs 21−23,

$$\mathrm{[PTC]} = [\mathrm{Q^+HCrO_4{}^-}]_\mathrm{org} \tag{25}$$

From eq 23, k_a[BnCl] = k_c[BnOH] in region II. Since both k_a and k_c are finite and BnOH is not overoxidized to benzoic acid, it follows that for region II

$$\frac{-\mathrm{d[BnCl]}}{\mathrm{d}t} = \frac{\mathrm{d[PhCHO]}}{\mathrm{d}t}$$

$$= k_\mathrm{a}\mathrm{[PTC][BnCl]} = \text{rate of formation of BnOH from BnCl}$$

$$= k_\mathrm{c}\mathrm{[PTC][BnOH]} = \text{rate of reaction of BnOH generated in-situ to yield PhCHO} \tag{26}$$

Therefore, $k_\mathrm{d} = 0$

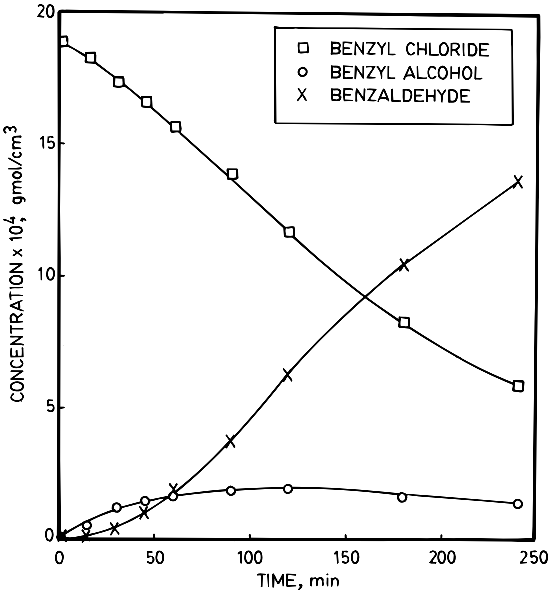


Figure 8. Concentration profiles for reaction of benzyl chloride with aqueous $HCrO_4^-$ in the presence of PTC (at higher concentration). Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86×10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33×10^{-4} mol/cm^3. $Vol_{org} = Vol_{aq}$ = 50 mL. [Na_2CO_3] = 4.44×10^{-4} mol/cm^3. $[TBAB]_{org}$ = 1.86×10^{-4} mol/cm^3.

Further proof for the existence of path a through path c for the formation of the benzaldehyde is provided in what follows. The independent experiments on the oxidation of BnOH (Figure 5 and Figure 6) show that the PT catalyzed oxidation of BnOH is first order in BnOH concentration. In region I of Figure 7, the concentration of BnOH is always higher than that of PhCHO, thereby indicating that the net rate of formation of BnOH (by path a) is higher than the net rate of formation of PhCHO by both paths c and d, up to 2 h. The initial rate of formation of BnOH and the initial rate of reaction of BnCl, as calculated from the concentration profiles in region I of Figure 7 indicate that they are practically the same and hence contribution by the path d to the formation of PhCHO could be neglected. Indeed, all experiments conducted thereafter confirmed the same. Table 1 also shows that the selectivity of benzaldeyde increases with time at the cost of benzyl alcohol.

Another mechanistic interpretation is based on the relative rates of formation of the chromate esters [$PhCH_2OCrO_3^-$ H^+] and [$PhCH_2OCrO_3^-Q^+$] from BnCl and BnOH, respectively, in the organic phase where the ion pair [$Q^+HCrO_4^-$] is preferentially partitioned. [$PhCH_2OCrO_3^-H^+$] immediately decomposes to BnOH with CrO_3 as byproduct, which goes back into the aqueous phase and is regenerated as $HCrO_4^-$, thereby indicating that it is a hydrolysis reaction (path a) and not oxidation. The decomposition of $PhCH_2OCrO_3^-H^+$ directly to PhCHO is a dehydration reaction which is not favored in the organic phase. To supplement these arguments, higher concentrations of catalyst and longer reaction times were chosen as shown in Figure 8, which depicts a continuous decline in [BnCl], [BnOH] goes through a maximum and declines slowly, and [PhCHO] increases with time accordingly.

Thus, the reaction path for the formation of benzaldehyde under L−L PT catalysis from benzyl chloride is via the formation of benzyl alcohol (path a) followed by its subsequent oxidation (path c).

4.5. Measurement of Kinetics. The L−L PT catalysis mechanism for formation of benzaldehyde from benzyl chloride can now be described:

Transfer of $HCrO_4^-$ from Aqueous Phase to Organic Phase

$$(Q^+X^-)_{aq} + HCrO_4^-{}_{aq} \rightleftharpoons (Q^+HCrO_4^-)_{aq} + X^-_{aq} \quad (27)$$

(The parentheses show the ion pair.)

Extraction of Ion Pairs into Organic Phase

$$(Q^+HCrO_4^-)_{aq} \rightleftharpoons (Q^+HCrO_4^-)_{org} \quad (28)$$

Reactions in the Organic Phase

$$PhCH_2Cl + (Q^+HCrO_4^-)_{org} \rightleftharpoons PhCH_2OCrO_3H + (Q^+Cl^-)_{org} \quad (29)$$

$$PhCH_2OCrO_3H \rightleftharpoons PhCH_2OH + CrO_3 \quad \text{(path a)} \quad (30)$$

Chromium trioxide dissolves in water with accompanying depolymerization, as given below:

$$(CrO_3)_n + nH_2O \rightarrow nH_2CrO_4(aq) \quad (31a)$$

$$H_2CrO_4 \rightarrow H^+ + HCrO_4^-(aq) \quad (31b)$$

which helps in regeneration of $HCrO_4^-$ (refer to Cainelli and Cardillo[22]). Equation 31 represents a hydrolysis reaction and not oxidation.

Now benzyl alcohol generated in situ reacts with ($Q^+HCrO_4^-$) in the organic phase.

$$PhCH_2OH + (Q^+HCrO_4^-)_{org} \rightleftharpoons (PhCH_2OCrO_3^-Q^+)_{org} + H_2O \quad (32)$$

$$(PhCH_2OCrO_3^-Q^+)_{org} \rightleftharpoons PhCHO + CrO_2 + Q^+ + H^+ \quad (33)$$

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4 \quad (34)$$

$$(Q^+Cl^-)_{org} \rightleftharpoons (Q^+Cl^-)_{aq} \quad (35)$$

Let Q_o be the amount of quaternary salt added to the organic phase at time $t = 0$. The material balance on Q_o is as follows:

$$Q_o = [Q^+HCrO_4^-]_{aq} + [Q^+HCrO_4^-]_{org} + [Q^+X^-]_{aq} + [Q^+X^-]_{org} \quad (36)$$

As the distribution coefficient of quaternary salts is generally high in organic phase than in aqueous phase,

$$Q_o = [Q^+HCrO_4^-]_{org} + [Q^+X^-]_{org} \quad (37)$$

$$\text{if} \quad [Q^+HCrO_4^-]_{aq} = [Q^+X^-]_{aq} = 0 \quad (37a)$$

The anion exchange equilibrium across the interface is

$$(\mathrm{Q^+X^-})_{\mathrm{org}} + (\mathrm{HCrO_4}^-)_{\mathrm{aq}} \overset{K}{\rightleftarrows} (\mathrm{Q^+HCrO_4}^-)_{\mathrm{org}} + \mathrm{X^-}_{\mathrm{aq}} \tag{38}$$

$$K = \frac{[\mathrm{Q^+HCrO_4}^-]_{\mathrm{org}}[\mathrm{X^-}]_{\mathrm{aq}}}{[\mathrm{Q^+X^-}]_{\mathrm{org}}[\mathrm{HCrO_4}^-]_{\mathrm{aq}}} \tag{39}$$

But, $[\mathrm{Q^+HCrO_4}^-]_{\mathrm{org}}[\mathrm{X^-}]_{\mathrm{aq}} =$

$$\mathrm{K}\{\mathrm{Q_o} - [\mathrm{Q_+HCrO_4}^-]_{\mathrm{org}}\}[\mathrm{HCrO_4}^-]_{\mathrm{aq}} \tag{40}$$

Hence, $$[\mathrm{Q^+HCrO_4}^-]_{\mathrm{org}} = \frac{KQ_{\mathrm{o}}[\ \mathrm{HCrO_4}^-]_{\mathrm{aq}}}{[\mathrm{X^-}]_{\mathrm{aq}} + K[\mathrm{HCrO_4}^-]_{\mathrm{aq}}} \tag{41}$$

Now, the net rates of reaction of BnCl and of formation BnOH and PhCHO can be written as

$$\frac{-\mathrm{d[BnCl]}}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{BnCl}]\left\{\frac{KQ_{\mathrm{o}}[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}{[\mathrm{X^-}]_{\mathrm{aq}} + K[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}\right\} \tag{42}$$

$$\frac{\mathrm{d[BnOH]}}{\mathrm{d}t} = k_{\mathrm{a}}\{[\mathrm{BnCl}] - k_{\mathrm{c}}[\mathrm{BnOH}]\}\left\{\frac{KQ_{\mathrm{o}}[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}{[\mathrm{X^-}]_{\mathrm{aq}} + K[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}\right\} \tag{43}$$

$$\frac{\mathrm{d[PhCHO]}}{\mathrm{d}t} = k_{\mathrm{c}}[\mathrm{BnOH}]\left\{\frac{KQ_{\mathrm{o}}[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}{[\mathrm{X^-}]_{\mathrm{aq}} + K[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}\right\} \tag{44}$$

The instantaneous selectivity S of PhCHO over BnOH is given by the ratio of eq 44 to 43:

$$\frac{\mathrm{d[PhCHO]}}{\mathrm{d[BnOH]}} = \frac{k_{\mathrm{c}}[\mathrm{BnOH}]}{k_{\mathrm{a}}[\mathrm{BnCl}] - k_{\mathrm{c}}[\mathrm{BnOH}]} \tag{45}$$

The left-hand side of eq 45 is the difference in concentrations in time increments t_i and t_{i+1} and is given by

$$\frac{\Delta[\mathrm{PhCHO}]}{\Delta[\mathrm{BnOH}]} = \frac{k_{\mathrm{c}}[\mathrm{BnOH}]}{k_{\mathrm{a}}\ [\mathrm{BnCl}] - k_{\mathrm{c}}\ [\mathrm{BnOH}]} \tag{46}$$

Thus, the selectivity is independent of catalyst concentration or its type.

$$\text{Let}\quad \frac{KQ_{\mathrm{o}}[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}{[\mathrm{X^-}]_{\mathrm{aq}} + K[\mathrm{HCrO_4}^-]_{\mathrm{aq}}} = \text{constant} = K_{\mathrm{cat}} \tag{47}$$

Equation 47 is the same as eq 41, and K_{cat} is the concentration of $[\mathrm{Q^+HCrO_4}^-]$ in the organic phase.

Equations 42 and 43 can be rewritten as

$$\frac{-\mathrm{d[BnCl]}}{\mathrm{d}t} = k_{\mathrm{a}}K_{\mathrm{cat}}[\mathrm{BnCl}] = k_{\mathrm{a1}}[\mathrm{BnCl}] \tag{48}$$

$$\frac{\mathrm{d[BnOH]}}{\mathrm{d}t} = \{k_{\mathrm{a}}[\mathrm{BnCl}] - k_{\mathrm{c}}[\mathrm{BnOH}]\}\{K_{\mathrm{cat}}\} \tag{49}$$

$$= k_{\mathrm{a1}}[\mathrm{BnCl}] - k_{\mathrm{c1}}[\mathrm{BnOH}] \tag{50}$$

The value of k_{c} was obtained independently from the PT catalysis oxidation of BnOH to PhCHO from the slope of $-\ln(1 - X_{\mathrm{B}})$ vs t (see section 4.4.3, Figure 6).

$$\frac{\mathrm{d[PhCHO]}}{\mathrm{d}t} = k_{\mathrm{c}}[\mathrm{BnOH}]\{K_{\mathrm{cat}}\} = k_{\mathrm{c1}}[\mathrm{BnOH}] \tag{51}$$

The above eq 51 can be analytically solved to get the following (see for instance, Levenspiel[23]), provided K_{cat} is constant.

$$[\mathrm{BnCl}] = [\mathrm{BnCl}]_{\mathrm{o}}\ \mathrm{e}^{-k_{\mathrm{a1}}t} \tag{52}$$

$$[\mathrm{BnOH}] = [\mathrm{BnCl}]_{\mathrm{o}}\{k_{\mathrm{a1}}/(k_{\mathrm{c1}} - k_{\mathrm{a1}})\}(\mathrm{e}^{-k_{\mathrm{a1}}t} - \mathrm{e}^{-k_{\mathrm{a1}}t}) \tag{53}$$

$$[\mathrm{PhCHO}] = [\mathrm{BnCl}]_{\mathrm{o}} - [\mathrm{BnCl}] - [\mathrm{BnOH}] \tag{54}$$

where the subscript represents initial concentration condition.

The time, t_{max}, when [BnOH] attains a maximum is obtained by setting the derivative of [BnOH] with respect to time as zero.

$$t_{\mathrm{max}} = \frac{\ln(k_{\mathrm{a1}}/k_{\mathrm{c1}})}{(k_{\mathrm{c1}} - k_{\mathrm{a1}})} \tag{55}$$

From eq 52,

$$[\mathrm{BnOH}]_{\mathrm{max}} = [\mathrm{BnCl}]_{\mathrm{o}}\{k_{\mathrm{a1}}/\ k_{\mathrm{c1}}\}^{k_{\mathrm{a1}}/(k_{\mathrm{a1}}-k_{\mathrm{c1}})} \tag{56}$$

$$\ln\frac{[\mathrm{BnCl}]}{[\mathrm{BnCl}]_{\mathrm{o}}} = -\ln(1 - X_{\mathrm{A}}) = k_{\mathrm{a1}}t \tag{57}$$

$$= k_{\mathrm{a}}\left\{\frac{KQ_{\mathrm{o}}[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}{[\mathrm{X^-}]_{\mathrm{aq}} + K[\mathrm{HCrO_4}^-]_{\mathrm{aq}}}\right\}t \tag{58}$$

If $K[\mathrm{HCrO_4}^-] > [\mathrm{X^-}]_{\mathrm{aq}}$, then eq 58 can be equated to $k_{\mathrm{a1}}Q_{\mathrm{o}}$, from the slope of which k_{a1} can be calculated.

From the independent oxidation of BnOH, the value of k_{c1} can be similarly found (see eqs 19 and 21). The slope will be equal to $k_{\mathrm{c}}Q_{\mathrm{o}}$.

Since k_{a1} is known and k_{c1} is also known independently as given in section 4.4.3 it is possible to calculate t_{max}, the time at which the concentration of BnOH goes to a maximum value, from eq 55 at a particular concentration Q_{o} of a PTC. This value can now be verified with that obtained from the plot of concentration vs time for the PTC catalyzed oxidation of BnCl.

Upon the basis of the above mechanistic and kinetic analysis, the effects of the various pertinent variables which appear in the final rate equation were studied to ascertain the validity of the theory.

4.6. Effect of Catalyst Concentration. As given by eq 48, the rate of reaction of benzyl chloride should be directly proportional to K_{cat}, which is a function of the effective catalyst concentration in the form of $[\mathrm{Q^+HCrO_4}^-]$ ion pair in the organic phase. In other words, it is a function of the quaternary species $\mathrm{Q^+}$ and its distribution between the organic phase and aqueous phase. Although it is most desirable to have the distribution coefficient ($[\mathrm{Q^+HCrO_4}^-]_{\mathrm{org}}/[\mathrm{Q^+Cl^-}]_{\mathrm{aq}}$) greater than 100, a conservative estimate shows that a value of above 10 or so makes the PT catalysis process very effective and the rate of reaction will be directly proportional to the catalyst concentration added initially (Q_{o}) (see Dehmlow and Dehmlow[24]).

The effect of catalyst concentration was studied for TBAB in the range 9.322×10^{-5} to 3.72×10^{-4} mol/cm^3 of organic phase, by keeping all other variables constant. The results are plotted in Figure 9, from which the initial rates of benzyl chloride were calculated. Figure 10 shows the plot of initial rate of reaction against Q_{o}. During the initial period, the

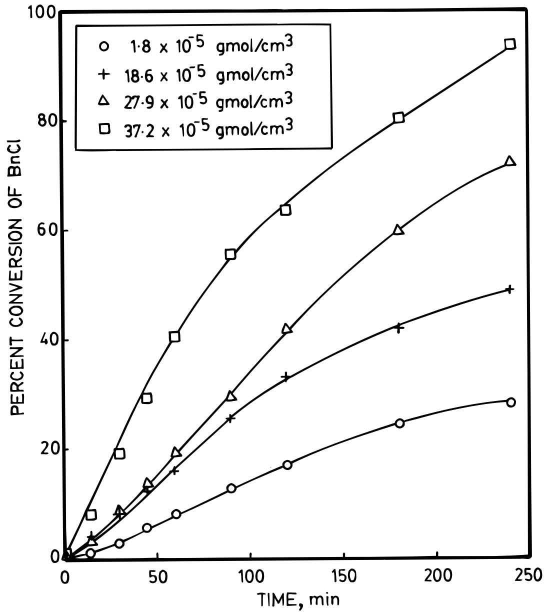


Figure 9. Effect of catalyst concentration on conversion of benzyl chloride. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. $Vol_{org} = Vol_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. $[TBAB]_{org}$ = 9.32 × 10^{-5} mol/cm^3.

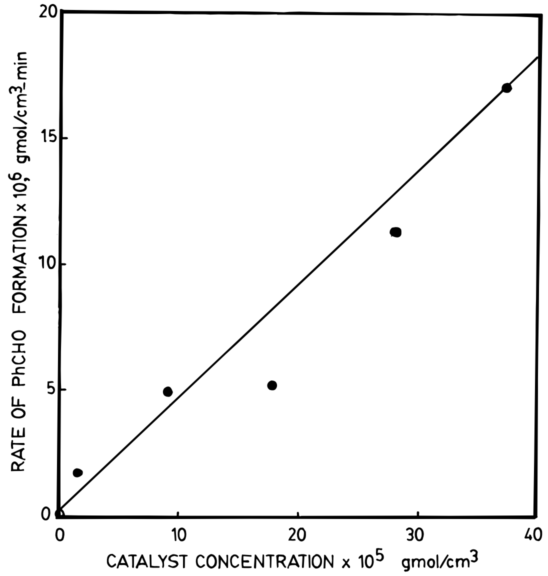


Figure 10. Plot of initial rate of reaction of benzyl chloride against concentration catalyst. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. $Vol_{org} = Vol_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. $[TBAB]_{org}$ = 9.32 × 10^{-5} mol/cm^3.

formation of BnOH is predominant and 1 mol of BnCl requires 1 mol of [$Q^+HCrO_4^-$].

The best fit shows that the rate of reaction BnCl, expressed as (mol/cm^3 of organic phase)/min, is linearly proportional to the catalyst concentration Q_o. This also suggests that the equilibrium constant K is quiet high and most of the catalyst is in the organic phase as [$Q^+HCrO_4^-$]. The reasons for plotting initial rates is that the contribution of X^-_{aq} in the denominator of the eq 47 for K_{cat} is very small because the leaving species Cl^- has less concentration in the aqueous phase.

The linear dependence of the rate of reaction on the catalyst concentration is truely characteristic of PT catalysis. Thus, the oxidation of BnCl to BnOH and PhCHO is a PT catalysis reaction. The catalyst concentration in the organic phase is taken equal to the amount of catalyst added initially divided by the volume of the organic phase.

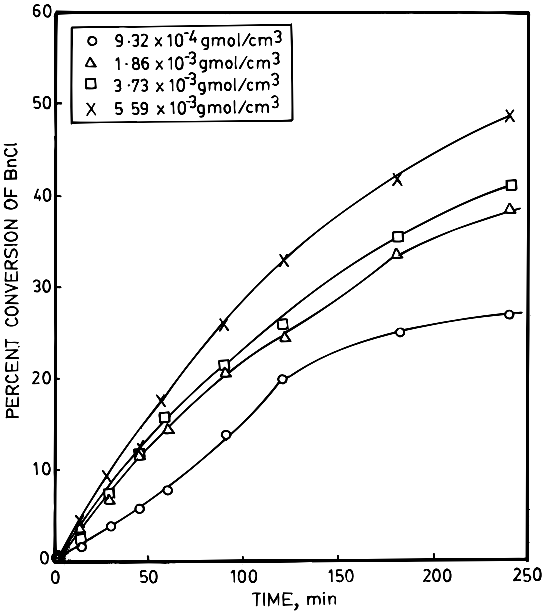


Figure 11. Effect of concentration of benzyl chloride on conversion. Speed = 1000 rpm, Temperature = 100 °C. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. $Vol_{org} = Vol_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. $[TBAB]_{org}$ = 9.32 × 10^{-5} mol/cm^3.

TABLE 2: Effect of Catalyst Concentration on Selectivity of Benzaldehyde after 4 h

catalyst concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]	catalyst concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]
1.864 × 10^{-5}	0.56	2.793 × 10^{-4}	8.63
1.864 × 10^{-4}	4.17	3.729 × 10^{-4}	11.70

Table 2 demonstrates the effect of concentration of catalyst on the selectivity of benzaldehyde (after 4 h). It can be seen that the selectivity improves with an increase in the concentration of catalyst. This is due to the fact that the pseudo rate constant k_{c1} increases, leading to higher rates of oxidation of BnOH formed in situ.

4.7. Effect of Concentration of Benzyl Chloride and Benzyl Alcohol. Figure 11 shows typical plots of benzyl chloride conversion against time under otherwise similar conditions, from which the initial rates were calculated. A plot of initial rate of reaction of BnCl against its initial concentration is shown in Figure 12, which demonstrates a linear relationship. The reaction is first order in BnCl concentration.

To study the effect of concentration of benzyl chloride on selectivity, the selectivity of benzaldehyde after 4 h was calculated for each run (Table 3). The selectivity of benzaldehyde was found to increase with an increase in the concentration of benzyl chloride.

4.8. Effect of Concentration of Nucleophile, $HCrO_4^-$. Since the pH was maintained at 6.6−6.7, only $HCrO_4^-$ was the predominant oxidizing species present. The amount of $K_2CrCr_2O_7$ added to the aqueous phase was varied from 4.66 × 10^{-4} to 1.87 × 10^{-3} mol/cm^3 of the aqueous phase by keeping Na_2CO_3 constant at 4.44 × 10^{-4} mol/cm^3 under otherwise similar conditions. Figure 13 shows the conversion of BnCl against time. The conversions are practically the same because the concentration of the species $Q^+CrO_4^-$ is constant in the organic phase. This further lends credence to the argument proposed in section 4.4 that K_{cat} is constant for a given Q_o and thus, from eq 47, Q_o = [$Q^+HCrO_4^-$], for the $K_2CrCr_2O_7$ concentration used.

TABLE 3: Effect of BnCl Concentration on Selectivity of Benzaldehyde after 4 h

BnCl concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]	BnCl concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]
0.932 × 10^{-3}	1.44	3.732 × 10^{-3}	6.50
1.866 × 10^{-3}	1.83	5.596 × 10^{-3}	8.38

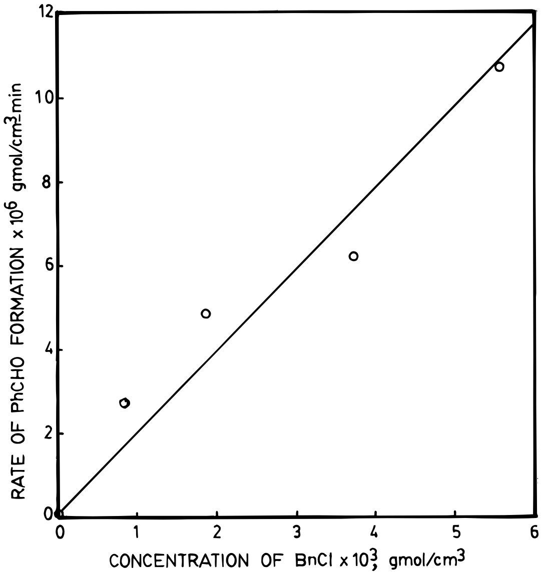


Figure 12. Plot of initial rate of reaction against conversion of BnCl. Speed = 1000 rpm. Temperature = 100 °C. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

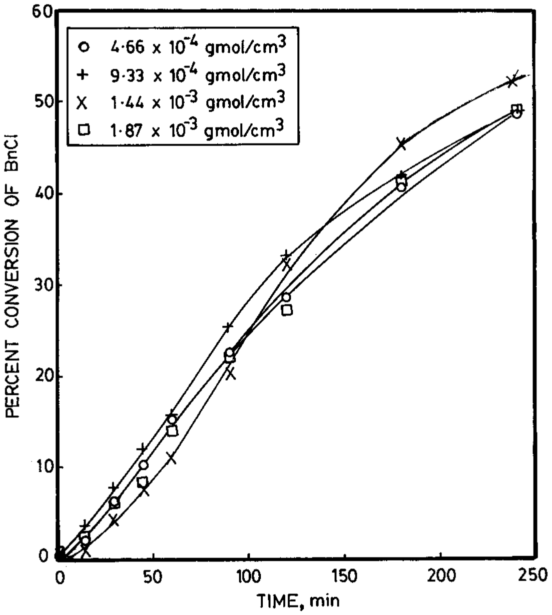


Figure 13. Effect of concentration of nucleophile $HCrO_4^-$ on rate of reaction of benzyl chloride. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

The effect of concentration of nucleophile on the initial rate of reaction is presented in Figure 14. Table 4 shows that the selectivity is practically the same.

4.9. Effect of Sodium Carbonate, Na_2CO_3. Since sodium carbonate was added to the aqueous solution of potassium dichromate to maintain a pH of 6.6, the effect of sodium carbonate on the rate of consumption of BnCl was found by carrying out the reaction with different amounts of sodium carbonate under otherwise identical reaction conditions, including an experiment without sodium carbonate. The pH determines the existence of the oxidizing species in a particular form. Figure 15 demonstrates the effect of the amount of sodium carbonate on the conversion of BnCl.

The quantity of Na_2CO_3 added to vary the pH resulted in the four experiments resulted in pHs of 2.92, 6.6, 7.04, and 9. When no Na_2CO_3 was added, the pH was 2.92, at which the species $Cr_2O_7^-$ predominantly exists and is difficult to extract as $Q_2Cr_2O_7$ in organic phase (Starks and Liotta[21]), and therefore, rates

TABLE 4: Effect of the Concentration of $K_2Cr_2O_7$ on the Selectivity of Benzaldehyde after 4 h

$K_2CrCr_2O_7$ concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]	$K_2CrCr_2O_7$ concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]
0.466 × 10^{-3}	1.96	1.44 × 10^{-3}	2.18
0.933 × 10^{-3}	2.00	1.87 × 10^{-3}	2.22

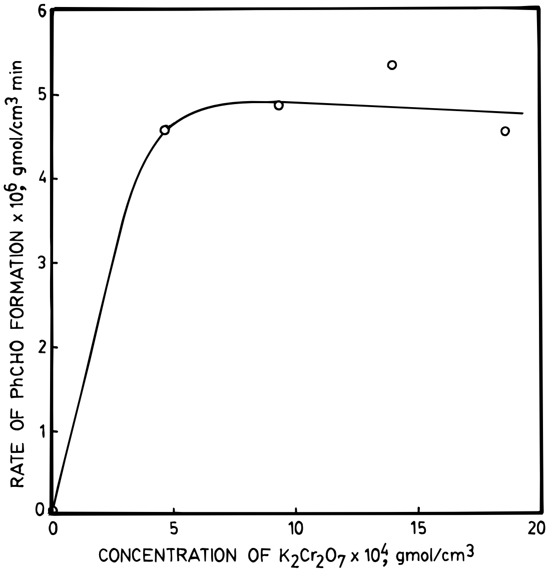


Figure 14. Effect of concentration of nucleophile on the rate of formation of benzaldehyde. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

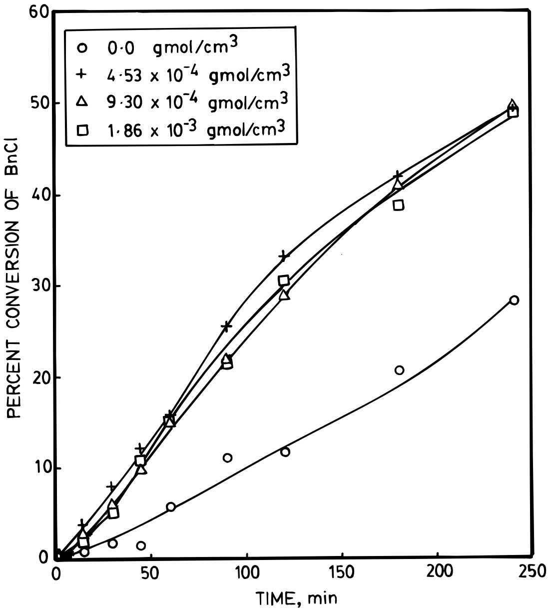


Figure 15. Effect of addition of sodium carbonate on conversion of benzyl chloride. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

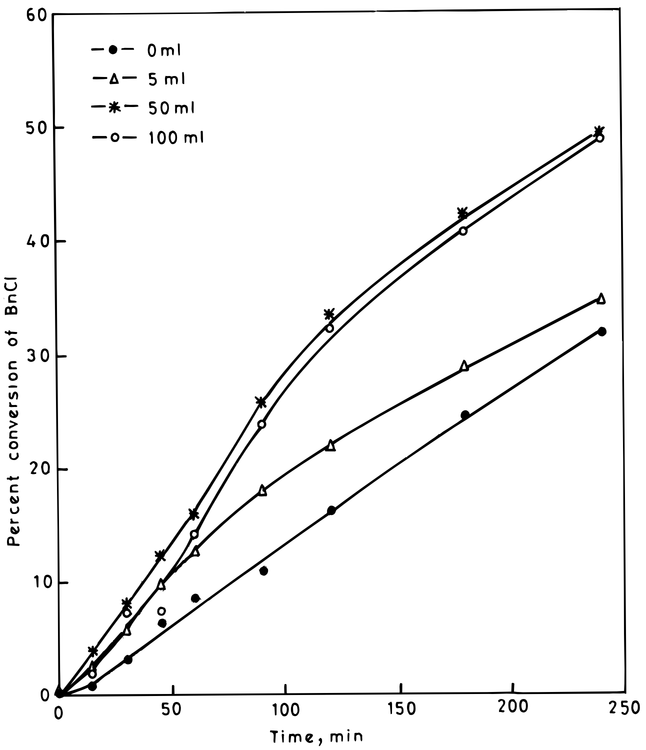


Figure 16. Effect of amount of water on conversion of benzyl chloride. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. $[K_2CrCr_2O_7]$ = 9.33 × 10^{-4} mol/cm^3. Vol_{org} = 50 mL. $[Na_2CO_3]$ = 4.44 × 10^{-4} mol/cm^3. $[TBAB]_{org}$ = 9.32 × 10^{-5} mol/cm^3.

TABLE 5: Effect of the Concentration of Na_2CO_3 on the Selectivity of Benzaldehyde after 4 h

Na_2CO_3 concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]	Na_2CO_3 concn (mol/cm^3)	selectivity [PhCHO]/[BnOH]
0	165.66	1.865 × 10^{-3}	2.26
0.453 × 10^{-3}	2.00	2.794 × 10^{-3}	1.30
0.930 × 10^{-3}	2.65		

were found to be low. The conversion was maximum at a pH of 6.6 because the species $Q^+HCrO_4^-$ is easily extracted in the organic phase.

Chromium exists as $HCrO_4^-$ species in the pH range 6−8, which being an univalent ion can get extracted easily in the organic phase, and therefore, the rate of reaction was found to increase. When the pH is 9, chromium exists as CrO_4^{2-}, which being a divalent ion cannot be extracted easily, and hence, the rate of reaction was found to slightly decrease.

The effect of the amount of sodium carbonate on the selectivity of PhCHO is given in Table 5. The selectivity of PhCHO was found to decrease with increase in the amount of Na_2CO_3.

When no Na_2CO_3 was added, the pH was more acidic (i.e., 2.6) and the oxidizing species was $Cr_2O_7^{2-}$. Since $Q_2Cr_2O_7$ ion pairs are difficult to extract, the rates of reaction were low but the BnOH formed in situ got oxidized to PhCHO and thus the selectivity was highly favored. Here selectivity was found to increase at the cost of conversion of BnCl.

4.10. Effect of the Amount of Water. The effect of the amount of water was studied by varying the amount of water from 0 to 150 cm^3 under otherwise similar conditions. When no water was added to the reaction mixture, conversion of benzyl chloride was low because the $HCrO_4^-$ species was not formed initially (Figure 16). Chromium exits in other forms which are not so extractable. The selectivity for benzaldehyde was almost complete (Table 6). The conversion of benzyl chloride was found to enhance until the amount of water was increased to 50 cm^3, and then conversion practically remains constant upon further addition of water up to 100 cm^3. The rates were lower where 150 cm^3 of water was used because the distribution coefficient of $Q^+HCrO_4^-$ is low and the pH is more than 8. The selectivity for benzaldehyde decreases with an increase in the amount of water as the formation of benzyl alcohol takes place with water even without catalyst.

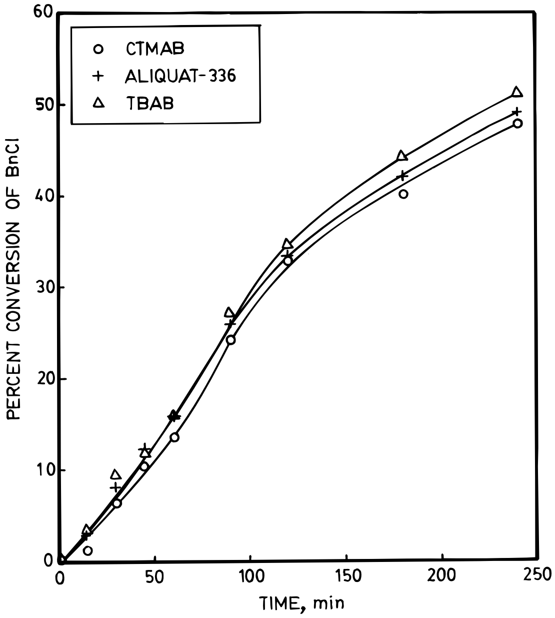


Figure 17. Effect of type of catalyst. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. $[K_2CrCr_2O_7]$ = 9.33 × 10^{-4} mol/cm^3. Vol_{org} = Vol_{aq} = 50 mL. $[Na_2CO_3]$ = 4.44 × 10^{-4} mol/cm^3. $[TBAB]_{org}$ = 9.32 × 10^{-5} mol/cm^3.

TABLE 6: Effect of the Quantity of Water on the Selectivity of Benzaldehyde after 4 h

amount of water (cm^3)	selectivity [PhCHO]/[BnOH]	amount of water (cm^3)	selectivity [PhCHO]/[BnOH]
0	79.32	50	1.82
5	10.95	100	1.60

4.11. Effect of Type of Catalyst. Besides TBAB, two other catalysts were tried. Figure 18 shows plots of conversion against time. It is seen that practically no change in conversion is obtained because for all the catalysts the *K* values are quite high, rendering the $[Q^+HCrO_4^-]$ species concentration in the organic phase about the same as Q_o, the added quantity. The selectivity for benzaldehyde was practically the same in consonance with the theory (see eq 46) that it should be independent of catalyst type.

4.12. Kinetics of the Reaction. The effect of various parameters on the rate of reaction established that the oxidation of benzyl chloride is a true phase transfer catalyzed consecutive reaction which follows the path a through path c to form benzaldehyde. The mechanism and mathematics developed earlier are thus valid (see Figure 18).

Now, as mentioned earlier, the values of k_a and k_c can be calculated and are 5 × 10^{-5} and 3.4 × 10^{-4} s^{-1} at 100 °C for TBAB as catalyst. When back-checked, the value of t_{max} obtained by using eq 55 is 6610 s whereas the experimental T_{max} is 7200 s (see Figure 6). There is deviation of 8.2% which is indeed in good agreement.

4.13. Effect of Temperature. The temperature of the reaction was varied from 80 to 100 °C in order to elucidate the effect of temperature on the rate of consumption of BnCl. The conversion of BnCl was found to increase with an increase in

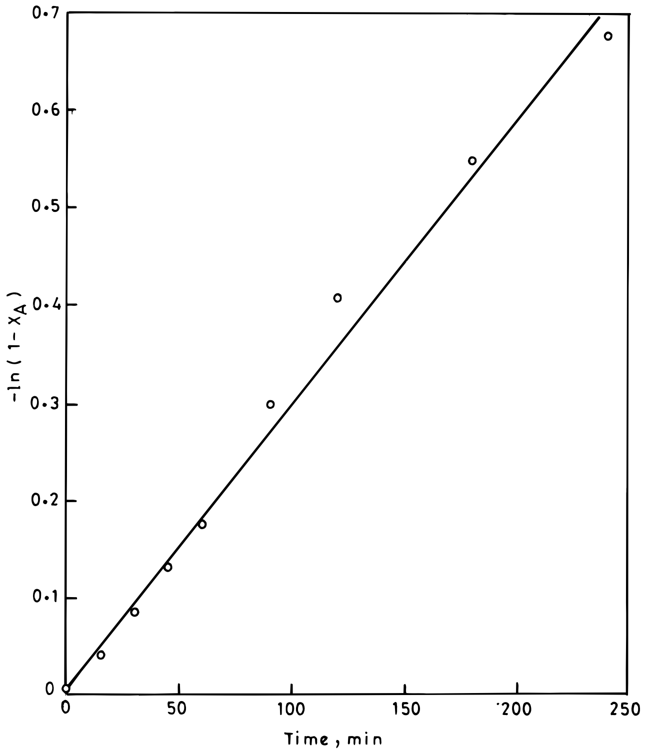


Figure 18. First-order kinetics plot. Speed = 1000 rpm. Temperature = 100 °C. [BnCl] = 1.86 × 10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

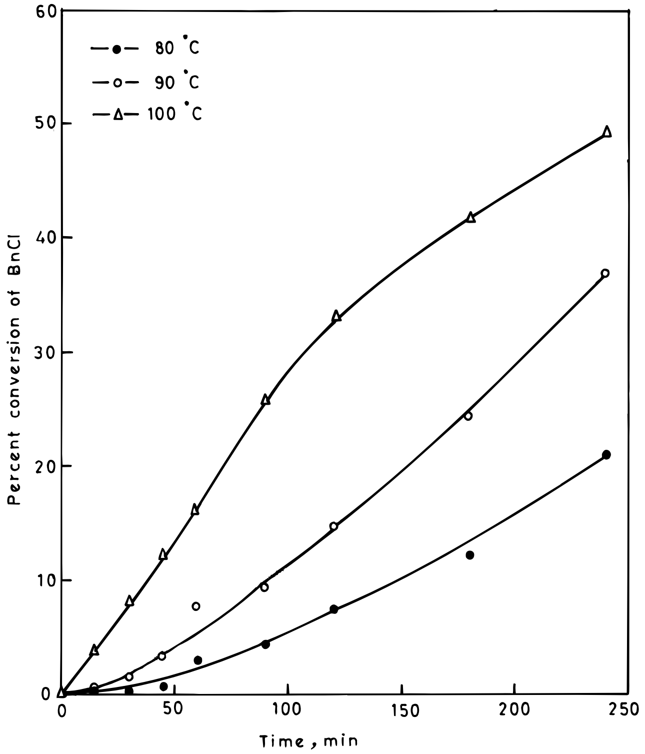


Figure 19. Effect of temperature. Speed = 1000 rpm. [BnCl] = 1.86 × 10^{-3} mol/cm^3. [$K_2CrCr_2O_7$] = 9.33 × 10^{-4} mol/cm^3. Vol$_{org}$ = Vol$_{aq}$ = 50 mL. [Na_2CO_3] = 4.44 × 10^{-4} mol/cm^3. [TBAB]$_{org}$ = 9.32 × 10^{-5} mol/cm^3.

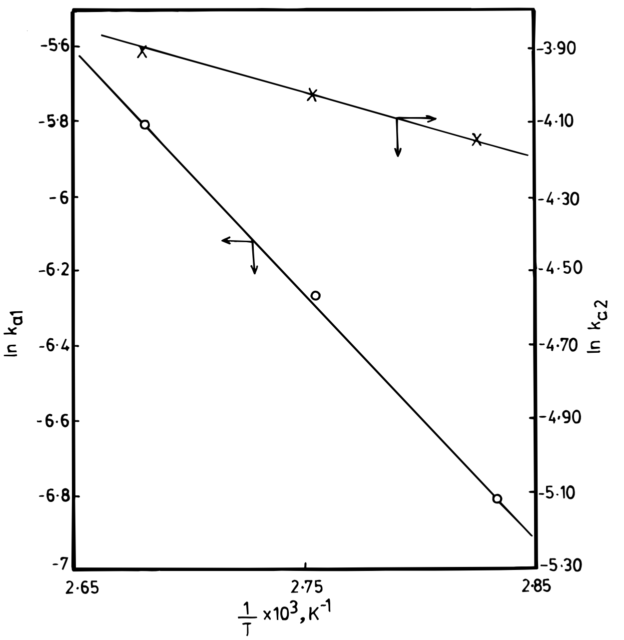


Figure 20. Arrhenius Plots: (1) Hydrolysis of benzyl chloride to benzyl alcohol (path a, k_{a1}). (2) Oxidation of benzyl alcohol to benzaldehyde (path c, k_{c1}). k_{a1} and k_{c1} include [$Q^+HCrO_4^-$]$_{org}$ and are expressed in min^{-1}.

TABLE 7: Effect of Temperature on Selectivity of Benzaldehyde after 4 h

temperature (°C)	selectivity [PhCHO]/[BnOH]	temperature (°C)	selectivity [PhCHO]/[BnOH]
80	2.07	100	2.00
90	1.95		

the temperature (Figure 19). The effect of temperature on selectivity of PhCHO (after 4 h) is presented in Table 7. It can be seen that the selectivity of PhCHO almost remains constant even if the temperature is increased from 80 to 100 °C. This proves that the rate constants for both of the reactions increase proportionately with an increase in temperature and the activation energy values are on the same order of magnitude or about the same.

Typical Arrhenius plots are shown in Figure 20, from which the activation energies for the path a and path c are formed as 13.13 and 5.67 kcal/mol, respectively, thereby proving that the reactions are kinetically controlled.

5. Conclusions

A thorough and systematic analysis of the mechanism and kinetics of the oxidation of benzyl chloride by dichromate in L–L PT catalysis has been provided to throw light on the course of reaction.

The rate of reaction depends on the pH of the aqueous phase in view of the fact that chromium exists as dichromate, perchromate, or chromate depending on the pH. It was observed that $Q^+HCrO_4^-$ was the active species for oxidation. The reaction proceeds via the formation of benzyl alcohol, which is oxidized to benzaldehyde.

Acknowledgment. G.D.Y. gratefully acknowledge the award of the Herdillia Chemicals UDCT Diamond Jubilee Distinguished Fellowship, which allowed him to write this paper.

References and Notes

(1) Haldavanekar, B. V. Supported Catalysis: Phase Transfer and Acid Catalysis. Ph.D. (Science) Thesis, University of Bombay, Mumbai, September 1993.

(2) Dehmlow, E.; Dehmlow Fisher, T.; Dowd, W. *U.S. Patent* 4,174,-352, 1979; *Chem. Abstr.* **1980**, *92*, 41600p.

(3) Hanessian, S.; Wong, D. H.; Therian, M. *Synth. Commun.* **1981**, 394.

(4) Huang, X.; Chan, C. C. *Synth. Commun.* **1982**, 1091.

(5) Hutchins, R. O.; Natale, N. R.; Cook, W. J.; Ohr, J. *Tetrahedron Lett.* **1977**, *48*, 4167.

(6) Igarashi, T.; Sakurai, M.; Suzaki, M. *Kanagawa Daigaku Kogakabu Kenkyu Hokoku* **1979**, *17*, 34; *Chem. Abstr.* **1979**, *91*, 91301s.

(7) Kumph, W.; Martinetz, D. *Z. Chem.* **1984**, *24* (5), 182; *Chem. Abstr.* **1985**, *102*, 5633t.

(8) Landini, D.; Rolla F. *Chem. Ind. (London)* **1979**, *6*, 213.

(9) Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, *20*, 1641.

(10) Ma, J.; Su, W.; Zhang, S.; Wu, Y. *Fenzi Cuihua* **1992**, *6* (1), 62; *Chem. Abstr.* **1992**, *117*, 26010n.

(11) Ma, J.; Su, W.; Zhang, S.; Ye, X.; Wu, Y. *Shiyou Huagong* **1992**, *21* (4), 228; *Chem. Abstr.* **1993**, *118*, 24065f.

(12) Ma, J.; Ye, X.; Wang, Y.; Zhang, S.; Wu, Y. *Catal. Lett.* **1992**, *15*, 275.

(13) Suyama, S.; Ishigaki, H. *Japan Kokai Tokkyo Koho* **1974**, 74,133,-345; *Chem. Abstr.* **1980**, *92*, 139687n.

(14) Cardillo, G.; Orena, M.; Sandri, S. (a) *J. Chem. Soc., Chem. Commun.* **1976**, 190; (b) *Tetrahedron Lett.* **1976**, *44*, 3985.

(15) Gopalan, R.; Subbarayan, K. *J. Indian Chem. Soc.* **1979**, *56* (7), 664.

(16) Pletcher, D.; Tait, S. J. D. *Tetrahedron Lett.* **1978,** *18*, 1601.

(17) Dey, D.; Mahanti, M. *J. Org. Chem.* **1990**, *55*, 5848.

(18) Yadav, G. D.; Mehta, P. H.; Haldavanekar, B. W. In *Heterogeneous Catalysis and Fine Chemicals III; Studies in Surface Science and Catalysis series*; Guinet, N., et al., Eds.; Elsevier: Amsterdam, 1993; Vol. 78, p 503.

(19) Yadav, G. D.; Mistry, C. K. *J. Mol. Catal. A: Chem.* **1995**, *102*, 67.

(20) Doraiswamy, L. K.; Sharma, M. M. *Heterogeneous Reactions: Analysis, Examples, and Reactor Design*; Wiley-Interscience: New York, 1984; Vol. 2.

(21) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis*; Academic Press: New York, 1978.

(22) Cainelli, R.; Cardillo, G. *Chromium Oxidation in Organic Chemistry*; Springer-Verlag: Berlin, 1984.

(23) Levenspiel, O. *Chemical Reaction Engineering*; Wiley: New York, 1972.

(24) Dehmlow, E. V.; Dehmlow, S. *Phase Transfer Catalysis*; VCH: Weinheim, Germany, 1993.

JP961678X