Kinetics of Reaction of Benzyl Chloride with Sodium Acetate/Benzoate: Phase Transfer Catalysis in Solid–Liquid System

Ganapati D. Yadav and Man Mohan Sharma*

Department of Chemical Technology, University of Bombay, Bombay 400019, India

Kinetics of the reaction of benzyl chloride with solid sodium acetate/benzoate, catalyzed by a variety of tertiary amines and quaternary ammonium salts as phase transfer catalysts, was studied at 101 °C in a 10 cm i.d. mechanically agitated contactor. The diffusional resistance was unimportant beyond a speed of 1000 rev/min. The reaction was found to occur in the organic phase and was first order in the concentrations of the substrate and the catalyst. Cetyldimethylbenzylammonium chloride was the most efficient catalyst among those studied. The effect of temperature on the reaction of benzyl chloride with solid sodium acetate was studied in the ranges of 90 to 110 °C and 101 to 139 °C for toluene and benzyl acetate as solvents, respectively. The apparent value of the activation energy was estimated as 14.5 kcal/g-mol.

Introduction

Benzyl esters are manufactured by the reaction of benzyl chloride with solid sodium carboxylate (e.g., acetate/benzoate) catalyzed by tertiary amines such as triethylamine (German Patent, 1913; Hennis and co-workers, 1967, 1968). In recent years a large number of papers on phase transfer catalysis (PTC) have appeared which indicate that instead of amines such as trimethylamine or triethylamine, use of certain quaternary ammonium/phosphonium salts, crown ethers, cryptates, diamines, polyamines, etc. may be far more beneficial (Starks, 1971, 1980; Dehmlow, 1974; Yadav, 1975; Weber and Gokel, 1977; Starks and Liotta, 1979). These types of phase transfer catalysts bound to insoluble resins such as cross-linked polystyrene, known as triphase catalysts, are also likely to be attractive (Regen, 1979). This solid–liquid reaction is of considerable importance and catalysts superior to triethylamine would merit attention. Further, kinetics of such reactions, which have certain unique features, also deserves attention. There is scanty information on the kinetics of solid–liquid phase transfer catalysis (S–L PTC) although some information is available on liquid–liquid phase transfer catalysis (L–L PTC) Starks and Owens, 1973; Weber and Gokel, 1977; Starks and Liotta, 1979). It was, therefore, thought desirable to study systematically the various aspects of the kinetics of a S–L PTC reaction of benzyl chloride with sodium acetate/benzoate and also to make a comparative study of catalysis due to tertiary amines and quaternary ammonium salts, which may be commercially attractive. It was also considered worthwhile to study the effect of water as a third phase on the S–L PTC reaction.

Literature Review

Many tertiary amines, quaternary ammonium salts, crown ethers, cryptates, open-chain polyethers (glymes, polypodes), diamines, and polyamines are used as S–L PT catalysts (Hennis and co-workers, 1967, 1968; Knöchel et al., 1975; Normant et al., 1975; Dehmlow, 1977).

An early German patent (1913) describes the use of triethylamine as a catalyst for the reaction of benzyl chloride with potassium benzoate. A number of investigators have studied the reaction of benzyl chloride with potassium acetate/benzoate. Hennis and co-workers (1967, 1968) have used methyl ethyl ketone as a solvent and a variety of tertiary amines as catalysts where the quaternary salts were generated in situ. Further, NaI was used as a

cocatalyst in this reaction to convert benzyl chloride to benzyl iodide and the latter was alkylated by a tertiary amine. Normant et al. (1975) have reported that phosphoramidates, diamines, and polyamines are better catalysts than quaternary ammonium salts. However, Gokel and Garcia (1978) have found that tetramethylenediamine (TMDA)—a typical catalyst used by Normant et al.—was less effective than triethylbenzylammonium chloride (TEBAC) for the same reaction. Liotta et al. (1974) have found that 18-crown-6 catalyzed reaction of benzyl bromide with potassium acetate in acetonitrile results in 100% benzyl acetate at 25 °C in less than 2 h.

Further, Zwain and Hartner (1978) have shown that Aliquat 336 (tricaprylylmethylammonium chloride) was equivalent to and in many cases markedly superior to both crown ether and TMDA, under otherwise similar conditions, for the solid–liquid phase transfer catalyzed reactions of acetate, fluoride, and adeninyl anions. However, the cyanide anion was found to react at least 100 times faster when catalyzed by crown ether relative to Aliquat 336. Knöchel et al. (1975) have investigated the effect of a wide variety of macrocyclic polydentate ligands on the reaction of benzyl chloride with solid potassium acetate in acetonitrile. The characteristics of the ligand, which influence the reaction rate, were shown to be the stability of the metal–ligand complex, the lipophilicity of the ligand, the rigidity of the ligand, and the reactivity of the ligand toward the substrate (the aza crowns).

Toke and Szabo' (1977) and Lehmkuhl et al. (1977) have used polyethylene glycol ether as a catalyst for the reaction of benzyl chloride with potassium/sodium acetate in acetonitrile. Dehmlow and Slopianka (1980) have reported that the reaction of benzyl bromide with aqueous potassium acetate was catalyzed by tetrabutylammonium bromide (TBAB). Recently, Garcia et al. (1980) have used tertiary amine oxides such as *N,N*-dimethyloctadecylamine oxide as catalysts for the reaction of solid potassium acetate with benzyl chloride in acetonitrile.

The evaluation of various catalysts has been done by Herriot and Picker (1975) for the alkylation of thiophenol with 1-bromooctane. Dou et al. (1977) have studied the behavior and stability of some phase transfer catalysts for the alkylation of thio reagents by alkyl halides of low reactivity under biphase and triphase conditions where one of the phases was an aqueous phase, and have shown that the catalyst can degrade in the aqueous phase to the

corresponding tertiary amine depending on the type of nucleophile and structure of the quaternary salt, although in most cases it is only a secondary reaction.

Experimental Section

All the amines used in this work are commercially available. The quaternary salts were prepared by the standard method of refluxing the relevant tertiary amine with an excess of alkyl halide in ethanol. All the quaternary salts were recrystallized from ethanol and dried in a vacuum desiccator. Benzyl chloride was doubly distilled under vacuum. Toluene, benzyl acetate, and benzyl benzoate was redistilled. Anhydrous AR grade sodium acetate and sodium benzoate were dried at 100 °C before use; AR grade NaCl was used. The particle size of solid sodium acetate as well as sodium benzoate was below 5 μm.

The experimental setup consisted of a 10 cm i.d. four necked 1-L capacity glass reactor equipped with four stainless steel baffles, cooling coil, thermometer pocket, sampling device with G-4 type sintered glass end, and a reflux condenser connected to a CaCl$_2$ trap. There was also a provision to introduce nitrogen in the reactor for flushing it before commencement of a run. A 4 cm diameter disk turbine impeller with six blades, located at a height of 2 cm from the bottom of the reactor, was used. Three reactors of this type were placed in a polyethylene glycol bath whose temperature could be controlled to within ±0.5 °C. 1,2,4-Trichlorobenzene was used as a coolant to control the temperatures of the reaction mixture.

In a typical run, the slurry of sodium acetate in toluene was charged to the reactor and was well agitated at the reaction temperature for 1 h. Benzyl chloride containing an appropriate amount of catalyst was taken from the stock solution maintained at the same temperature and was charged to the sodium acetate slurry in such an amount that the mole ratio of sodium acetate to benzyl chloride was 2. The total volume of the organic phase was 400 cm^3. The reactor was flushed with nitrogen for some time and then the agitation was started. A sample at zero time was withdrawn. Preliminary experiments had indicated that a very good control of reaction temperature, especially in the initial stages, was needed to reproduce the kinetics within 5%. The samples of organic phase (3–5 mL) were withdrawn at regular intervals and were immediately quenched. A small amount of water was added to the sample and the aqueous layer was saturated with NaCl. After separation of the phases, the organic phase was analyzed by gas–liquid chromatography using a 3 m × 4 mm stainless steel column packed with 20% SE-30 and partially esterified sorbitol oleate (as a tailing reducing agent) on Chromosorb W/AW (AIMIL G.C., FID, 170 °C, N$_2$ as carrier gas (30 cm^3/min)). Synthetic mixtures of nearly the same composition were prepared and analyzed simultaneously. From the appropriate calibration, concentrations of BzCl and BzOAc in the reaction mixture were obtained. A similar column with 1.5 m length was used for the analysis of benzyl benzoate. The reaction was followed up to 50% conversion of BzCl in most of the cases and above 90% in a few cases. The rate constants were based on the disappearance of BzCl as well as on the rate of formation of the ester. The results agreed well to within 3%. A material balance for NaCl was also found to be accurate to within 4%. The rate constants were calculated using the least-square technique and involved a minimum of six samplings and gave a correlation coefficient of at least 0.98.

Results and Discussion

Some preliminary experiments at a speed of 1000 rev/min and in the absence of catalyst showed that practically no reaction occurred at 101 °C over a period of 3 h. However, when a catalyst (0.02 g-mol/g-mol of BzCl) was added to the reaction mixture, quantitative conversions were realized with 100% yield of BzOAc within 2–4 h depending on the type of catalyst. The rate of reaction was found to vary with the catalyst concentration. Plots of concentrations of BzCl against time on a semilog scale, at a particular catalyst concentration, were linear with a correlation coefficient of at least 0.98. The slopes of these plots were directly proportional to the catalyst concentration only, thereby showing a pseudo-first-order kinetic behavior. Therefore, the following mechanism and the kinetic model based on it were developed and experimentally verified.

Mechanism

The mechanism for S–L PTC is illustrated by the SN$_2$ type of reaction of the substrate RX with the nucleophile Y$^-$ of the solid reactant MY. M$^+$ is the inorganic (metallic) counterion of the nucleophile Y$^-$. The overall reaction is

$$RX(org) + MY(s) + (Q^+X^-)(org) \xrightarrow{k_{obsd}}$$
$$RY(org) + MX(s) + (Q^+X^-)(org) \quad (1)$$
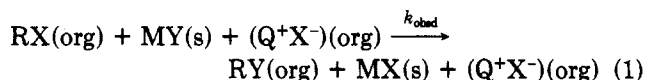
In the case of tertiary amine (R$_3$'N) added to the organic phase the amine quaternizes with the substrate, RX, according to

$$R_3'N + RX \xrightarrow{k_Q} (R_3'RN^+X^-) \quad (2)$$
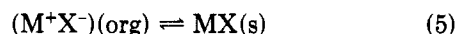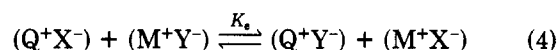$$(\equiv Q^+X^-)$$
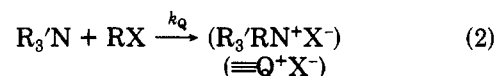
where Q$^+$ is the quaternary cation of the catalyst. (Q$^+$X$^-$) is a *"loosely"* bound ion pair. Parentheses are used to show ion pairs.

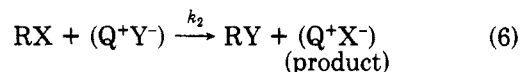The solid reactant is in equilibrium with its dissolved part in the organic phase.

$$MY(s) \rightleftharpoons (M^+Y^-)(org) \quad (3)$$
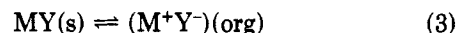
The quaternary salt (Q$^+$X$^-$) reacts with the dissolved nucleophile according to

$$(Q^+X^-) + (M^+Y^-) \xrightleftharpoons{K_e} (Q^+Y^-) + (M^+X^-) \quad (4)$$

$$(M^+X^-)(org) \rightleftharpoons MX(s) \quad (5)$$

The substrate RX reacts with (Q$^+$Y$^-$) according to

$$RX + (Q^+Y^-) \xrightarrow{k_2} RY + (Q^+X^-) \quad (6)$$
$$(product)$$

The quaternary salt is thus generated repeatedly to catalyze the reaction. However, there is no transfer of the catalyst across the interface as is normally observed in the case of liquid–liquid phase transfer process.

The rate of quaternization of reaction 2 is given by

$$\frac{d[Q^+X^-]}{dt} = k_Q[RX][R_3'N] \quad (7)$$

The equilibrium constant for reaction 4 is given by

$$K_e = \frac{[Q^+Y^-][M^+X^-]}{[Q^+X^-][M^+Y^-]} \quad (8)$$

The rate of reaction 6 is given by

$$-\frac{d[RX]}{dt} = k_2[RX][Q^+Y^-] \quad (9)$$

$$= k_2 K_e \frac{[M^+Y^-]}{[M^+X^-]}[RX][Q^+X^-] \quad (10)$$

Table I. Reaction of Benzyl Chloride with Solid Sodium Acetate[a,b]

no.	catalyst	cat. abbrev.	$[Q_0] \times 10^5$ g-mol/cm^3	$k_1 \times 10^5$ s^{-1}	k_2, cm^3/ g-mol s	rel reactivity with respect to TEA
1	none	-	-	0.130	0.045	0.14
2	trimethylamine	TMA	18.30	2.9016	0.1585	0.50
3	triethylamine	TEA	8.30	2.6433	0.3185	1.00
4	tri-n-butylamine	TBA	2.267	1.0303	0.4546	1.46
5	cetyldimethylamine	CDMA	4.55	36.536	8.0301	25.27
6	tetra-n-butylammonium bromide	TBAB	5.364	26.283	4.90	15.38
7	cetyltrimethylammonium chloride	CTMAC	2.23	5.4033	2.416	7.58
8	cetyltrimethylammonium bromide	CTMAB	2.54	11.070	4.353	13.67
9	lauryldimethylbenzylam- monium chloride	LDMBAC	4.55	27.083	5.952	18.68
10	cetyldimethylbenzylam- monium chloride	CDMBAC	4.55	36.780	8.705	27.37

[a] Solvent, toluene; temperature, 101 ± 0.5 °C; speed of agitation, >1000 rev/min. [b] Benzyl acetate yield = 100% (Yields based on concentration of benzyl acetate/total conversion of benzyl chloride).

Table II. Reaction of Pure Benzyl Chloride with Solid Sodium Acetate[a,b]

no.	catalyst	$[Q_0] \times 10^5$ g-mol/cm^3	k_1, s^{-1}	k_2, cm^3/ g-mol s	rel rate with respect to TEA
1	none	-	2.926×10^{-6}	0.045	0.068
2	TEA	23.2	1.52×10^{-4}	0.655	1
3	TBA	17.34	1.686×10^{-4}	0.9723	1.48
4	CDMA	8.023	1.198×10^{-3}	14.933	22.80
5	CTMAC	5.08	2.475×10^{-4}	4.875	7.448
6	CDMBAC	7.36	1.147×10^{-3}	15.583	23.80

[a] Temperature, 101 ± 0.5 °C; speed of agitation, >1000 rev/min. [b] Benzyl acetate yield = 100%.

Table III. Reaction of Benzyl Chloride with Solid Sodium Benzoate[a,b]

no.	catalyst	$[Q_0] \times 10^5$ g-mol/cm^3	k_1, s^{-1}	k_2, cm^3/ g-mol s	rel rate with respect to TEA
1	TEA	10.71	8.956×10^{-5}	0.8366	1
2	TBA	10.71	1.2475×10^{-4}	1.1646	1.39
3	CDMA	5.94	7.50×10^{-4}	12.628	15.09
4	LDMBAC	5.55	4.90×10^{-4}	8.838	10.56
5	CDMBAC	5.55	7.296×10^{-4}	13.136	15.70

[a] Solvent, toluene; temperature, 101 ± 0.5 °C; speed of agitation, >1000 rev/min. [b] Benzyl benzoate yield $\approx$ 100%.

if $[M^+Y^-]/[M^+X^-] = r$, a constant. For a quaternary salt catalysis, eq 9 becomes

$$-\frac{d[RX]}{dt} = k_1[RX] \tag{11}$$

where

$$k_1 = k_2 \cdot K_e \cdot r \cdot [Q^+X^-] \tag{12}$$

Equations 7 and 10 should be simultaneously integrated for a tertiary amine catalysis and eq 10 or 11 should be solved for a quaternary salt catalysis. Equations 7 and 10 cannot be easily simultaneously integrated, unless some simplifying assumptions are made. However, they can be numerically solved.

Integration of eq 11 yields the equation

$$\ln ([RX]/[RX]_0) = -k_1 t \tag{13}$$

with the boundary condition

$$\text{at } t = 0: \quad [RX] = [RX]_0 \tag{14}$$

Here, k_1 is a constant for a particular concentration of the catalyst, $[Q_0]$ added to the system. Thus, a plot of log $([RX]/[RX]_0)$ against t will give a slope of $-k_1/2.303$. The value of this slope can be changed by varying the catalyst concentration.

Tables I, II, and III present data on various systems studied. The effect of different variables on the rate of

reaction was studied with cetyldimethylbenzylammonium chloride (CDMBAC) as a catalyst, because preliminary experiments indicated that under otherwise similar conditions it was the most efficient catalyst among those studied. In addition, a few experiments were conducted, for each variable, in the presence of tertiary amines to verify the general findings.

Effect of Speed of Agitation. Figure 1 shows that the speed of agitation has no effect on the rate of reaction in the range of 1000–2100 rev/min at a solid loading of 19.1% w/w. The rate was slightly lower (by <8%) at 480 rev/min than that in the range 1000–2100 rev/min. Therefore, speeds of agitation in the range of 1000–1500 rev/min were employed for assessing the effect of other variables on the rate of reaction.

Effect of Solid Loading. Figure 2 shows that the rate of reaction was independent of the solid loading. At a loading of 7% w/w, the rate of reaction was marginally less (<4%) than that in the range of 10–33.1% w/w. The solid reactant was taken 100% in excess over the theoretically required for complete conversion of BzCl. The particle surface area (a_p) at a loading of 19.1% w/w was around 1120 and 560 cm^2/cm^3 of organic phase at the beginning and the end of the reaction, respectively $(\rho_p = 1.65$ g/cm^3, $d_p = 5 \times 10^{-4}$ cm). The value of solid–liquid mass transfer coefficient, k_{SL}, by assuming the Sherwood number to be
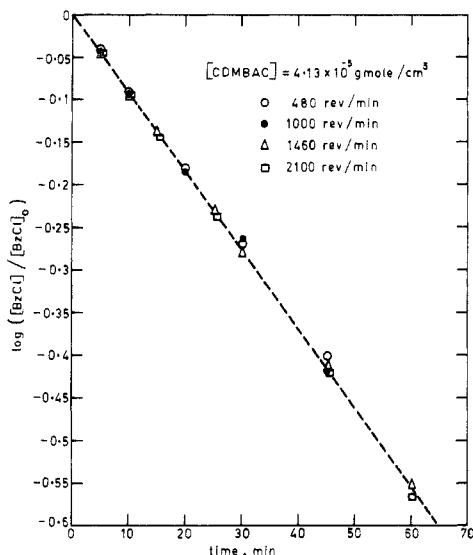
Figure 1. Effect of speed of agitation on rate of reaction of benzyl chloride with sodium acetate: solvent, toluene; temperature, 101 ± 0.5 °C.
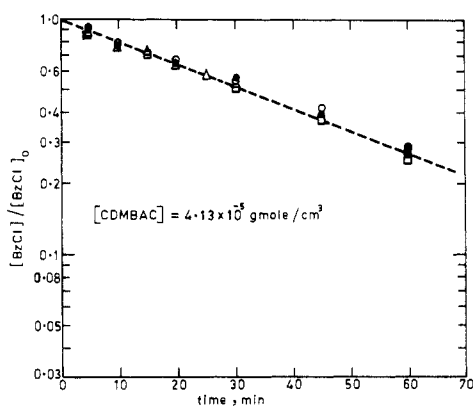

Figure 2. Effect of loading of solid sodium acetate on rate of reaction with benzyl chloride: solvent, toluene; temperature, 101 ± 0.5 °C; speed of agitation, 1000 rev/min. Symbol and solid loading, % w/w: O, 7.0; ●, 10.0; △, 19.10; □, 33.15.

equal to 2 is 0.14 cm/s ($D \approx 3.5 \times 10^{-5}$ cm²/s at 101 °C). Thus, the rate of solid dissolution represented by $k_{SL}a_p$ is very much greater than the rate of reaction (k_1) (see Table II). Thus, it is clear that the diffusional resistance was unimportant.

Effect of Catalyst Concentration. Figure 3 shows that the rate of reaction (pseudo-first-order constant) varies linearly with the catalyst concentration in the range 1.96×10^{-6} to 4.92×10^{-5} g-mol/cm³ for CDMBAC. A similar observation was made in the case of catalysis by tertiary amines (e.g., triethylamine (TEA), tributylamine (TBA), and cetyldimethylamine (CDMA) as well as other quaternary ammonium salts (e.g., CTMAC).

Although CDMBAC is a cationic surfactant having a rod-like molecular structure and is known to form molecular aggregation/micelles in nonpolar solvents, the catalysis in our studies was due to PTC and not due to micellar catalysis (MC), because the rate of reaction is directly proportional to catalyst concentration over a wide range as against the micellar catalysis where the rate of reaction is generally found to be proportional to higher powers (4–5) of the catalyst concentration. There is a typical discontinuous behavior in micellar catalysis, where substantial enhancement in rate of reaction is shown near critical micelle concentration (CMC) followed by a constant or decreasing rate at higher concentrations (Herriot and
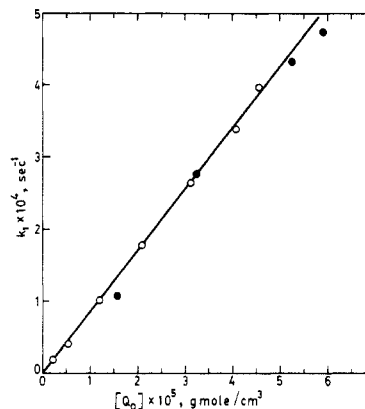

Figure 3. Effect of catalyst concentration on pseudo-first-order rate constant for reaction of benzyl chloride with solid sodium acetate: solvent, toluene; temperature, 101 ± 0.5 °C; symbol: O, CDMBAC; ●, CDMA.

Picker, 1975; Fendler and Fendler, 1977; Starks and Liotta, 1979). [Critical micelle concentration (*CMC*) is the narrow range of concentration at which the micelles (molecular aggregates) first become detectable.] Moreover, the concentrations of catalyst employed in this work are low, which are likely to be well below the *CMC*.

Rate of Solid Dissolution in the Presence of Catalyst. The rate of solid dissolution in the presence of a PT catalyst may be affected due to complex formation. Therefore, the solubilities of NaOAc and NaCl in toluene at 101 °C were estimated by titrimetric methods and were found to be 3.85×10^{-5} and 3.24×10^{-5} g-mol/cm³, respectively. In the presence of CDMBAC with a concentration of 2.19×10^{-5} g-mol/cm³, the total chloride and acetate concentrations were found to be 6.25×10^{-5} and 5.6×10^{-5} g-mol/cm³, respectively. The solubility measurements are accurate to within 10%. These data indicate that the increase in the chloride concentration was due to both NaCl and that from reacted CDMBAC and in the acetate concentration due to both NaOAc and cetyldimethylbenzylammonium acetate. That is, the organic phase was always saturated with the nucleophile and almost all the catalyst was in the (Q^+Y^-) form. For tertiary amine catalysis also the catalyst will be in (Q^+Y^-) form, if the quaternization process is very fast. Starks and Liotta (1979) have also reported about such kind of behavior.

Effect of Presence of NaCl in the Beginning of the Reaction. It was found that there was practically no effect of the presence of NaCl on the rate of reaction, when a few typical experiments were repeated, under otherwise similar conditions, in the presence of 0.25 and 0.50 g-mol of NaCl/g-mol of NaOAc at the beginning of the reaction. Thus, it is clear that the equilibrium in eq 4 shifts entirely toward the right and the catalyst (Q^+X^-) is almost exclusively in the (Q^+Y^-) form in the organic phase. Thus, the process of exchange of X^- (leaving group) by Y^- (nucleophile) by the quaternary ammonium ion (Q^+) is a very fast reaction and the ion-pairs are "*loosely*" bound to allow so.

Quaternization Reaction. Figure 3 and the tables show that the values of k_1 or k_2 and hence the rates of reaction are nearly the same in the presence of CDMA and CDMBAC, under otherwise similar conditions. This indicates that quaternization of CDMA with benzyl chloride is relatively a very fast reaction at the reaction temperature and the catalysis of CDMA appears to be due to CDMBAC generated in situ. Further, the rate of reaction was proportional to the amine concentration—for instance, CDMA, TEA, TBA.

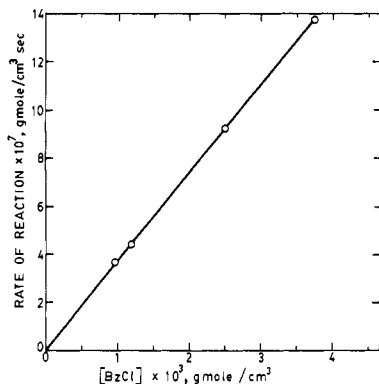**Effect of Initial Concentration of BzCl.** The rate of reaction was found to be proportional to the initial

Figure 4. Effect of initial concentration of benzyl chloride on rate of reaction with solid sodium acetate: solvent, toluene; temperature, 101 ± 0.5 °C; [CDMBAC], 4.54 × 10^{-5} g-mol/cm^3.

concentration of BzCl in the organic phase in the range of 9.2 × 10^{-4} to 3.75 × 10^{-3} g-mol/cm^3 (Figure 4).

Effect of Type of Catalyst. Tables I, II, and III show the same order in the catalytic activity of the various amines and quaternary salts covered in this work. The different catalytic activities are mainly due to the different solubilities of the ion pair (M^+Y^-) in the presence of catalysts in the organic phase, which in turn can be attributed to the nature and bulkiness of the cation Q^+ and the polarity of the medium. In the case of symmetrical amines, the catalytic efficiency increases as the chain length increases. The efficacy of tertiary amines, which are present as quaternary salts of benzyl chloride, is as follows: TMA (≡TMBAC) < TEA (≡TEBAC) < TBA (≡TBBAC) < CDMA (≡CDMBAC). CTMAB is more efficient than CTMAC because Br^- is more reactive than Cl^-. Tetra-n-butylammonium bromide (TBAB) is much more powerful than TBA, which is present as TBBAC (tributylbenzyl-ammonium chloride) due to the fact that TBBAC is less bulky than TBAB, is unsymmetrical, and has less reactive Cl^- anion. TBAB is a better catalyst than CTMAC but comparable to CTMAB. It seems that symmetrical molecules with the same number of C atoms or bulkiness distribute the charges more evenly and are, therefore, more reactive than unsymmetrical molecules. LDMBAC (lauryldimethylbenzylammonium chloride) is a better catalyst than TBAB, due to an increase in the chain length. It is also slightly more efficient than CTMAB, due to a larger number of C atoms as well as an increase in molecular weight. CDMBAC is the most efficient catalyst among those studied, although it cannot be considered as substantially efficient than LDMBAC.

Makosza's catalyst TEBAC, generated in situ from TEA, was not found to be very effective as compared to CDMBAC (see Tables I, II, and III). Herriot and Picker (1975) have also found that TEBAC is not an efficient catalyst for the L–L PT catalyzed reaction of thiophen-oxide with 1-bromooctane in benzene. This is mainly due to the poor solubility of [M^+Y^-] in the presence of TEBAC in the organic phase as compared to the rest of the catalysts employed in our study.

Effect of Medium. The rates of reaction were found to increase as the polarity of the medium increased. Thus, the rates of reaction were found to be in the descending order in the media: toluene ≪ pure BzCl < BzOAc/ BzOBz. It is difficult to assess the exact value of the dielectric constant of the reaction medium at 101 °C. In the case of toluene as the medium, the concentrations of BzCl were low. When the reaction goes to completion, there might be some marginal gain in polarity of the reaction mixture due to BzOAc. It was difficult to observe
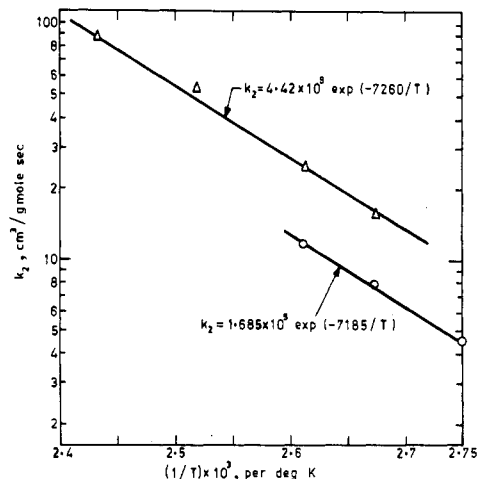

Figure 5. Arrhenius plot for reaction of benzyl chloride with solid sodium acetate. Symbol: O, toluene as solvent; E = 14.37 kcal/g-mol; Δ, BzOAc as solvent; E = 14.52 kcal/g-mol.
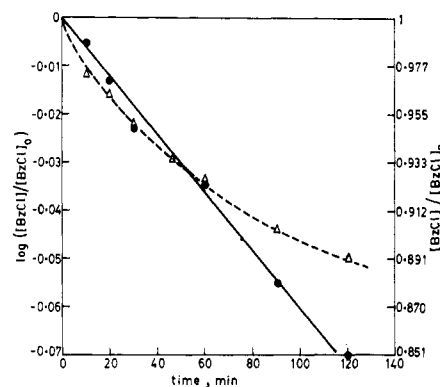

Figure 6. Effect of presence of water on rate of S–L PTC reaction of benzyl chloride with solid sodium acetate: solvent, toluene; temperature, 101 ± 0.5 °C; speed of agitation, 1500 rev/min; BzCl, 0.5 g-mol; CDMBAC = 0.02083 g-mol; NaOAc, 1.75 g-mol; NaCl = 0.583 g-mol; ●, 4 g-mol of water; O, 2 g-mol of water; volume of organic phase, 400 cm^3.

any significant effect on the rate of reaction because the reaction was followed up to 50% conversion levels in such cases.

Effect of Temperature. Figure 5 shows the Arrhenius plots for the reaction of BzCl with NaOAc. The energy of activation for the reaction in toluene and in BzOAc was nearly the same (14.5 kcal/g-mol).

Effect of Water on S–L PTC. The effect of the presence of water as a third phase on S–L PTC was studied by conducting two typical experiments, under otherwise similar conditions, where 2 and 4 g-mol of water (run A and B) per 1.75 g-mol of NaOAc and 0.583 g-mol of NaCl, were employed. In general, the rate of reaction in the presence of water was found to be less than that in the absence of water. This is contrary to the expectation that the solvation of the ion pair by water, which creates a local liquid–liquid interface, might overcome the lattice energy of the solid and a normal L–L PTC would then intercede (Weber and Gokel, 1977). It can be seen from Figure 6 that the reaction under the conditions of run A did not exactly follow a pseudo-first-order kinetic behavior (shown by the dotted curve) and the rate of reaction was higher up to a period of 1 h followed by a decrease, as compared to the rate of reaction under the conditions of run B. For run B, exact pseudo-first-order kinetic behavior can be seen from Figure 6, in which case the data were analyzed on the basis of equations developed for L–L PTC (Starks and Liotta, 1979) and the values of second-order rate constant,

k_2, and the anion partitioning equilibrium coefficient, K_A, were estimated as 2.57 cm^3/g-mol s and 0.1072, respectively. It appears that in the case of run A, the reaction conformed to a transition regime between S–L PTC and L–L PTC, for which the values of k_2 and K_A were roughly estimated as 4.34 cm^3/g-mol s and 0.062, respectively. Independent experiments were also performed for the liquid–liquid phase transfer catalysis under otherwise similar conditions to evaluate k_2 and K_A as 2.78 cm^3/g-mol s and 0.095, respectively. The estimation of K_A, the anion partitioning equilibrium coefficient, was done experimentally as 0.12 (details are reported by Yadav, 1980). This clearly indicates that run B conformed to the L–L PTC. The change in the reactivity of S–L PTC and L–L PTC can be mainly explained via the unfavorable values of K_A in the case of L–L PTC. K_A indicates the ease with which anions are preferentially transferred into the organic (reaction) phase and it also shows the proportion of the catalyst that will be in the active form as (Q^+Y^-) in the organic phase (Starks and Liotta, 1979)

$$(Q^+Y^-)_{org} = K_A[Q_0]/K_A + \frac{[X^-]_{aq}}{[Y^-]_{aq}} \qquad (15)$$

Thus, at $K_A = 0.1072$, depending on the ratio $[X^-]/[Y^-]$ in the aqueous phase, $(Q^+Y^-)_{org}$ will vary and will always be less than $[Q_0]$. Further, this reactivity change may be partly attributed to the possible catalyst degradation to the tertiary amine by CH_3COO^- (the nucleophile) in the aqueous phase. The effect of presence of water on the kinetics of S–L PTC, especially at low temperatures ($\sim$30 °C), needs further investigation.

Conclusions

For the reaction of benzyl chloride with solid sodium acetate/benzoate, the diffusional resistance was found to be unimportant. The rate of reaction was found to be first order in both the concentrations of the catalyst and the substrate. The catalysis by amines was due to quaternization in situ. Cetyldimethylbenzylammonium chloride was found to be the most efficient catalyst among those studied. The rate data could be correlated on a rational basis.

Nomenclature

a_p = particle surface area, cm^2/cm^3 organic phase
D = diffusivity of dissolved solid reactant in organic phase, cm^2/s
$k_1 = k_2 \cdot K_e \cdot r \cdot [Q^+X^-]$, pseudo-first-order rate constant, s^{-1}
k_2 = second-order rate constant for reaction 6, cm^3/g-mol s
k_{obsd} = observed second-order rate constant of the overall reaction 1, cm^3/g-mol s
K_Q = second-order rate constant for quaternization reaction 2, cm^3/g-mol s
k_{SL} = solid–liquid mass transfer coefficient, cm/s
K_A = anion partitioning equilibrium coefficient, dimensionless
K_e = equilibrium constant for reaction 4, dimensionless
M = metallic (inorganic) counterpart of leaving group, X as well as nucleophile, Y
MX = inorganic salt of leaving group, X
MY = inorganic salt of nucleophile, Y

Q = quaternary cationic part of leaving group, X as well as nucleophile, Y
QX = quaternary ammonium salt of leaving group, X; or $R_3'RN^+X^-$, in the case of tertiary amine, $R_3'N$
QY = quaternary ammonium salt of nucleophile, Y
$r = [M^+Y^-]/[M^+X^-]$, ratio of concentrations of dissolved salts of nucleophile and leaving group
R = alkyl or aralkyl group of substrate, RX
RX = substrate
RY = product
R' = alkyl or aralkyl group of tertiary amine
X = leaving group
Y = nucleophile

Greek Letter

ρ_p = density of solid reactant, MY, g/cm^3

Abbreviations for Catalysts

Aliquat 336 = tricaprylmethylammonium chloride
CDMA = cetyldimethylamine
CDMBAC = cetyldimethylbenzylammonium chloride
CTMAB = cetyltrimethylammonium bromide
CTMAC = cetyltrimethylammonium chloride
LDMBAC = lauryldimethylbenzylammonium chloride
TBA = tri(n-butyl)amine
TBAB = tetrabutylammonium bromide
TBBAC = tributylbenzylammonium chloride
TEA = triethylamine
TEBAC = triethylbenzylammonium chloride (Makosza's catalyst)
TMA = trimethylamine
TMBAC = trimethylbenzylammonium chloride
TMDA = tetramethylenediamine

Literature Cited

Dehmlow, E. V. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 170.
Dehmlow, E. V. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 493.
Dehmlow, E. V.; Slopianka, M. Unpublished data, **1980**; as cited in Dehmlow, E.; Dehmlow, S. "Phase Transfer Catalysis", 1st. ed.; Verlag-Chemie: New York, 1980.
Dou, H. J. M.; Gallo, R.; Hassanaly, P.; Metzger, J. *J. Org. Chem.* **1977**, *42*, 4275.
Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems", 1st ed.; Academic Press: New York, 1975; Chapters 10 and 11.
Garcia, B. J.; Leopold, A.; Gokel, G. W. *Tetrahedron Lett.* **1980**, 2115.
German Patent (to BASF) 268 261, Dec 22, 1913.
Gokel, G. W.; Garcia, B. J. *Tetrahedron Lett.* **1978**, 1743.
Hennis, H. E.; Easterly, J. P.; Collins, L. R.; Thompson, L. R. *Ind. Eng. Chem. Prod. Res. Dev.* **1967**, *6*, 193.
Hennis, H. E.; Thompson, L. R.; Long, J. P. *Ind. Eng. Chem. Prod. Res. Dev.* **1968**, *7*, 96.
Herriot, A. W.; Picker, D. *J. Am. Chem. Soc.* **1975**, *97*, 2345.
Knöchel, A.; Oehler, J.; Rudolph, G. *Tetrahedron Lett.* **1975**, 3167.
Lehmkuhl, H.; Rabet, F.; Hauschild, K. *Synthesis* **1977**, 184.
Liotta, C. L.; Harris, H. P.; McDermott, M.; Gonzalez, T.; Smith, K. *Tetrahedron Lett.* **1974**, 2417.
Normant, J.; Cuvigny, N. T.; Savignac, P. *Synthesis* **1975**, 805.
Regen, S. L. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 421.
Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.
Starks, C. M. *CHEMTECH* **1980**, *10*, 110.
Starks, C. M.; Liotta, C. "Phase Transfer Catalysis", 1st ed.; Academic Press: New York, 1979.
Starks, C. M.; Owens, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 3613.
Toke, L.; Szabo, G. T. *Acta Chim. Acad. Sci. Hung.* **1977**, *93*, 421.
Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis", 1st ed.; Springer-Verlag: New York, 1977.
Yadav, G. D. *Chem. Ind. Dev.* **1975**, *9*(6), 16.
Yadav, G. D. Ph.D. (Tech.) Thesis, University of Bombay, Bombay, 1980, Chapter 6.
Zwain, M. C. V.; Hartner, F. W. *J. Org. Chem.* **1978**, 2655.