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Kinetics of the Oxidation of Benzyl Alcohol by Hypochlorite Ion in the Presence of Phase-Transfer Catalyst

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The kinetics of the oxidation of benzyl alcohol by hypochlorite ion in the presence of tetrabutylammonium chloride as phase-transfer catalyst was studied. The results show that the oxidation of benzyl alcohol in two immiscible aqueous/dichloromethane systems was reaction controlled and occurred in the organic phase when the stirring rate was larger than 500 rpm. The experimental results also reveal that the reaction orders of both tetrabutylammonium ion pair and benzyl alcohol in the organic phase are both equal to one. The activation energy of the oxidation of benzyl alcohol is 10.4 kcal/mol. The extraction constant of tetrabutylammonium hypochlorite ion pair was obtained. The equilibrium constants, K_1 - K_4 , are evaluated to be equal to 0.05 M⁻¹, 17.4, 0.004 M⁻¹, and 87.7, respectively.

Introduction

Inorganic cations and anions are frequently used as catalysts (Davies, 1970; Chou and Lin, 1983), oxidants (Stevens et al., 1980; Nwaukwa and Keehn, 1982a-c; Do and Chou, 1989; Mehrotra and Amis, 1974; Sala et al., 1977; Jow and Chou, 1988), and reducing agents (Mandal et al., 1987, 1988; Ward et al., 1988) in processes for producing organic chemicals. Usually, the solubility of inorganic cations, such as metal ions, and anions, such as ClO⁻, in most organic solvents and solutions is very small. Reactions between the inorganic species and organic substances located in two immiscible phases, respectively, of a mixture are often inhibited because of the inability of reagents to meet. There are several methods to improve the solubility of inorganic ions in nonpolar organic solvents (Chou and Lee, 1985; Hwang and Chou, 1987; Kuo and Chou, 1987a,b; Starks and Liotta, 1978; Dehmlow and Dehmlow, 1980). Metal ions, for example, are immobilized or exchanged on solid polymer supports (Chou and Lee, 1985; Hwang and Chou, 1987; Kuo and Chou, 1987a,b). Theoretically, the solubility of the immobilized metal ions on the solid particles in the organic solvent can be very large. Phase-transfer catalysts have been widely applied to overcome the heterogeneity problem—many inorganic oxidants also can be transferred into an organic phase by a phase-transfer catalyst (Dehmlow, 1977; Dockx, 1973; Starks,

1987). Reaction rates, for example, oxidation, can be much improved (Starks and Liotta, 1978; Dehmlow and Dehmlow, 1980). However, the mechanism and kinetics of two-phase systems in the presence of phase-transfer catalysts are still unclear (Bar et al., 1984a,b).

Permanganate employed as an oxidant to oxidize benzyl alcohol in the presence of a phase-transfer catalyst produced a 92% yield of benzoic acid (Herriott and Picker, 1974). No benzaldehyde was observed in this system. Aqueous sodium hypochlorite under phase-transfer-catalysis conditions was employed to promote the oxidation of hydroquinone and catechols (Ishii and Kishi, 1980). Using inorganic hypochlorite as oxidant in the presence of a phase-transfer catalyst was reported to proceed the oxidation of some polycyclic aromatic compounds to arene oxide (Krishnan et al., 1977). Oxidation of alcohols in the presence of phase-transfer catalysis by hypochlorite ion was reported by several research groups (Pletcher and Tait, 1978; Tabushi and Koga, 1979; Abramovici et al., 1985; Do and Chou, 1989). Several investigators (Regen, 1976; Schneider et al., 1982) reported using a triphase catalyst for the oxidation of primary and secondary alcohols. The reaction rate was very slow, and the yield of benzaldehyde was lower than that in the homogeneous phase-transfer-catalysis system. In our previous work (Do and Chou, 1989), the oxidation of benzyl alcohol by hypochlorite anion, which was regenerated by anodic oxidation in the presence of quaternary ammonium salts as a phase-transfer catalyst, was reported. The quaternary ammonium salts

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were used as a carrier to shuttle the inorganic anion between the aqueous phase and the organic phase. Lee and Freedman (1976, 1985) demonstrated that hypochlorite anion can be transferred into the organic phase by quaternary ammonium cation for the oxidation of benzyl alcohol; the main product was benzaldehyde. For the extraction of hypochlorite anion from the aqueous phase into the organic phase, the intrinsic reaction orders and reaction rate constants and the factors affecting the rate of the oxidation of benzyl alcohol in the presence of the phase-transfer catalyst were not reported. An investigation of such issues would be very helpful for organic synthesis, because the hypochlorite ion is found to be a mild and effective oxidizing agent for the organic oxidation (Stevens et al., 1980; Nwaukwa and Keehn, 1982a-c).

A systematic study on both the extraction of hypochlorite ion from the aqueous phase to the organic phase and the two-phase oxidation of hydrocarbon in the presence of phase-transfer catalyst was carried out. Benzyl alcohol was selected as a model compound. The factors that affect the rate of the two-phase oxidation in the presence of the phase-transfer catalyst were explored. The kinetics of the extraction of hypochlorite ion from the aqueous phase into the organic phase and the two-phase oxidation under phase-transfer catalysis were also analyzed and discussed.

Experimental Section

Extraction of Tetrabutylammonium Hypochlorite Ion Pair from the Aqueous Phase into the Organic Phase. The extraction of hypochlorite anion with tetrabutylammonium cation from the aqueous phase into a dichloromethane phase is carried out in a 50-mL Erlenmeyer flask with a magnetic stirrer. On the top of the extractor, there is a reflux condenser that vents to the atmosphere and is maintained at $-15\text{ }^{\circ}\text{C}$ by a refrigeration system. The temperature of the extractor is controlled within $\pm 0.1\text{ }^{\circ}\text{C}$ by immersing the whole system in a constant-temperature bath. The concentration of hypochlorite anion is determined by an automatic potential titrator (MCI GT-05) using the iodometry titration method.

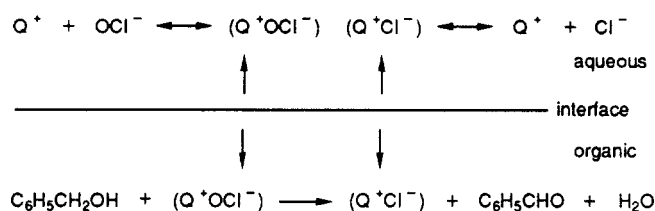
All the chemicals used are reagent grade. The aqueous solution is prepared by dissolving calcium hypochlorite in distilled water and filtrating the undissolved residue. The concentrations of hypochlorite and chloride anions are determined by iodometry titration and titration by 0.1 N AgNO_3 solution. The desired concentration of chloride and the pH value are adjusted by 5.0 N NaCl and 1.0 N HCl solutions. The organic solution is prepared by mixing the desired amounts of tetrabutylammonium chloride (phase-transfer catalyst) in dichloromethane.

At the beginning of a run, equal volumes of aqueous and organic solutions are fed into the flask, which is kept at constant temperature. A desired stirring rate is applied to the reaction system. The concentration of the tetrabutylammonium hypochlorite ion pair is periodically analyzed until a steady-state concentration is reached.

Oxidation of Benzyl Alcohol. The oxidation of benzyl alcohol with hypochlorite anion in the presence of the phase-transfer catalyst is carried out in a cylindrical glass reactor 80 mm in height and 55 mm in diameter. The motorized stirrer is used to agitate the two immiscible phases. The organic vapor is condensed by a cryostat cooling system. The entire reactor system is immersed in a water bath, and the temperature is controlled within $\pm 0.1\text{ }^{\circ}\text{C}$.

The aqueous and organic solutions are prepared as in the method described above. At the beginning of a run, the desired volumes of aqueous and organic solutions are

Scheme I



fed into the reactor, which is kept at the desired temperature. The desired stirring rate is applied to the reaction system. After about 10 min, when the ion pair equilibrium is achieved, the required amount of benzyl alcohol is introduced into the reactor. The reaction time is recorded as soon as benzyl alcohol is fed. Samples are periodically taken from the reactor by the use of a hypodermic syringe. The reactant and products are analyzed by capillary GLC (J & W Scientific, Inc., DB-1).

Theoretical Analysis

The reaction mechanism of the oxidation of benzyl alcohol by hypochlorite ion in the presence of a phase-transfer catalyst is described in Scheme I.

As shown in Scheme I, Q^+ is a tetrabutylammonium cation that shuttles between aqueous and organic phases, i.e., Q^+ cation migrates with the oxidant OCl^- from the aqueous phase into the organic phase, where the weakly solvated ion pair is formed and undergoes fast oxidation reaction. Q^+ also migrates to and from the aqueous phase again with the anion Cl^- .

I. Extraction of the Anion from the Aqueous Phase into the Organic Phase. If the dissociation of the ion pairs in the organic phase is insignificant (Gustavii and Schill, 1967), then the equilibrium equations among the cation Q^+ and anions OCl^- and Cl^- are

$$(\text{Q}^+)_{\text{aq}} + (\text{OCl}^-)_{\text{aq}} \xrightleftharpoons{K_1} (\text{Q}^+\text{OCl}^-)_{\text{aq}} \quad (1)$$

$$(\text{Q}^+\text{OCl}^-)_{\text{aq}} \xrightleftharpoons{K_2} (\text{Q}^+\text{OCl}^-)_{\text{org}} \quad (2)$$

$$(\text{Q}^+)_{\text{aq}} + (\text{Cl}^-)_{\text{aq}} \xrightleftharpoons{K_3} (\text{Q}^+\text{Cl}^-)_{\text{aq}} \quad (3)$$

$$(\text{Q}^+\text{Cl}^-)_{\text{aq}} \xrightleftharpoons{K_4} (\text{Q}^+\text{Cl}^-)_{\text{org}} \quad (4)$$

where aq and org indicate the aqueous and organic phases, respectively.

The concentrations of Q^+OCl^- and Q^+Cl^- ion pairs in the aqueous and the organic phase can be expressed as follow:

$$[\text{Q}^+\text{OCl}^-]_{\text{aq}} = K_1[\text{Q}^+]_{\text{aq}}[\text{OCl}^-]_{\text{aq}} \quad (5)$$

$$[\text{Q}^+\text{OCl}^-]_{\text{org}} = K_1K_2[\text{Q}^+]_{\text{aq}}[\text{OCl}^-]_{\text{aq}} \quad (6)$$

$$[\text{Q}^+\text{Cl}^-]_{\text{aq}} = K_3[\text{Q}^+]_{\text{aq}}[\text{Cl}^-]_{\text{aq}} \quad (7)$$

$$[\text{Q}^+\text{Cl}^-]_{\text{org}} = K_3K_4[\text{Q}^+]_{\text{aq}}[\text{Cl}^-]_{\text{aq}} \quad (8)$$

On the basis of the material balance, the total initial moles of the phase-transfer catalyst is the summation of the moles of the cation ion Q^+ and the ion pairs expressed in eqs 5-8. The result is

$$V_{\text{aq}}([\text{Q}^+]_{\text{aq}} + [\text{Q}^+\text{Cl}^-]_{\text{aq}} + [\text{Q}^+\text{OCl}^-]_{\text{aq}}) + V_{\text{org}}([\text{Q}^+\text{Cl}^-]_{\text{org}} + [\text{Q}^+\text{OCl}^-]_{\text{org}}) = N_0 \quad (9)$$

where N_0 is the total moles of the phase-transfer catalyst and V_{aq} and V_{org} are the volumes of aqueous phase and organic phase, respectively.

Substituting eqs 5-8 into eq 9, we obtain

$$[Q^+]_{aq} = [(1 + V_r)[Q]_0] / [1 + K_3(1 + K_4 V_r)[Cl^-]_{aq} + K_1(1 + K_2 V_r)[OCl^-]_{aq}] \quad (10)$$

where $[Q]_0 = N_0/V_t$, $V_r = V_{org}/V_{aq}$, and $V_t = V_{aq} + V_{org}$.

By substituting eq 10 into eq 6, the concentration of the Q^+OCl^- ion pair is obtained,

$$[Q^+OCl^-]_{org} = [K_1 K_2 (1 + V_r) [Q]_0 [OCl^-]_{aq}] / [1 + K_3(1 + K_4 V_r) [Cl^-]_{aq} + K_1(1 + K_2 V_r) [OCl^-]_{aq}] \quad (11)$$

If $V_r = 1$, then the reciprocal of $[Q^+OCl^-]_{org}$ is

$$\frac{1}{[Q^+OCl^-]_{org}} = \frac{1 + K_2}{2K_2[Q]_0} + S \frac{1}{[OCl^-]_{aq}} \quad (12)$$

where

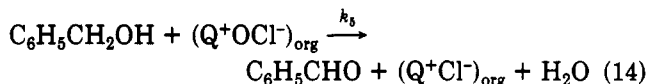
$$S = \frac{1}{2K_1 K_2 [Q]_0} + \frac{K_3(1 + K_4)}{2K_1 K_2 [Q]_0} [Cl^-]_{aq} \quad (13)$$

and S is a constant if $[Q]_0$ and $[Cl^-]_{aq}$ are given.

Equation 12 indicates that, when S is constant, the reciprocal of the concentration of Q^+OCl^- ion pair in the organic phase shows a linear relationship with the reciprocal of the concentration of hypochlorite ion in the aqueous phase.

II. Kinetics of the Oxidation of Benzyl Alcohol.

The hypochlorite ion is transferred from the aqueous phase into the organic phase by the phase transfer catalyst. In the organic phase the ion pair reacts with benzyl alcohol,



The reaction rate of eq 14 is

$$r = -d[C_6H_5CH_2OH]/dt = k_5 [Q^+OCl^-]_{org}^m [C_6H_5CH_2OH]_{org}^n \quad (15)$$

where m and n are the reaction orders of Q^+OCl^- ion pair and benzyl alcohol, respectively, in the organic phase. If both of the reaction orders of $C_6H_5CH_2OH$ and $(Q^+OCl^-)_{org}$ are equal to one, then the reaction rate can be expressed as

$$r = k_5 [C_6H_5CH_2OH]_{org} [Q^+OCl^-]_{org} \quad (16)$$

If the mass-transfer rate between the two phases is sufficiently fast, the reaction is controlled by the reaction rate in the organic phase. Substituting the concentration of Q^+OCl^- ion pair in the organic phase, i.e., eq 11 into eq 16, yields the following expression:

$$-d[C_6H_5CH_2OH]/dt = \frac{[k_5 K_1 K_2 (1 + V_r) [Q]_0 [C_6H_5CH_2OH]_{org} [OCl^-]_{aq}] / [1 + K_1(1 + K_2 V_r) [OCl^-]_{aq} + K_3(1 + K_4 V_r) [Cl^-]_{aq}]} \quad (17)$$

Rearranging eq 17, we obtain

$$dx/dt = [k_5 K_1 K_2 (1 + V_r) [Q]_0 [C_6H_5CH_2OH]_{org}^0 (1 - x) \times (\Theta_b - V_r x)] / [1 + K_1(1 + K_2 V_r) [C_6H_5CH_2OH]_{org}^0 (\Theta_b - V_r x) + K_3(1 + K_4 V_r) [C_6H_5CH_2OH]_{org}^0 (\Theta_c + V_r x)] \quad (18)$$

where x is the conversion of benzyl alcohol,

$$x = 1 - [C_6H_5CH_2OH]_{org} / [C_6H_5CH_2OH]_{org}^0 \quad (18a)$$

$[C_6H_5CH_2OH]_{org}^0$ is the initial concentration of benzyl alcohol in the organic phase, and Θ_b and Θ_c are defined as

$$\Theta_b = [OCl^-]_{aq}^0 / [C_6H_5CH_2OH]_{org}^0 \quad (19)$$

$$\Theta_c = [Cl^-]_{aq}^0 / [C_6H_5CH_2OH]_{org}^0 \quad (20)$$

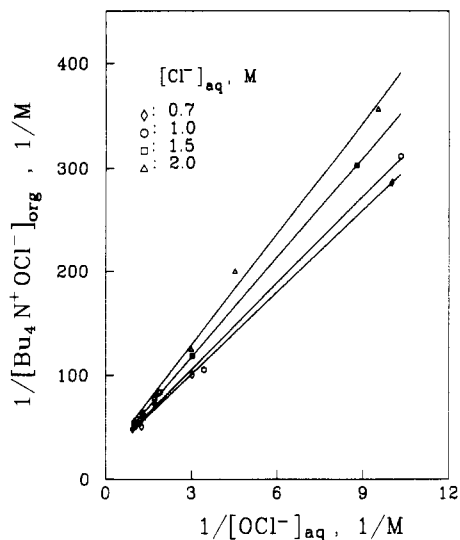


Figure 1. Equilibrium plot of $1/[Bu_4N^+OCl^-]_{org}$ versus $1/[OCl^-]_{aq}$ with the concentration of chloride ion as the parameter. Temperature = 20 °C; $V_{org}/V_{aq} = 1.0$; organic solvent, CH_2Cl_2 ; $[Q]_0 = 0.025$ M; pH = 9.0; stirring rate = 600 rpm.

where $[OCl^-]_{aq}^0$ and $[Cl^-]_{aq}^0$ are the initial concentrations of OCl^- and Cl^- ions, respectively, in the aqueous phase.

By integrating eq 18, the relationship of the conversion of benzyl alcohol and time is obtained,

$$\frac{1 + K_3(1 + K_4 V_r) [C_6H_5CH_2OH]_{org}^0 (\Theta_b + \Theta_c)}{\Theta_b - V_r} \ln(1 - x V_r / \Theta_b) - \left\{ \frac{K_1(1 + K_2 V_r) [C_6H_5CH_2OH]_{org}^0 + 1 + K_3(1 + K_4 V_r) [C_6H_5CH_2OH]_{org}^0 (\Theta_c + V_r)}{\Theta_b - V_r} \right\} \ln(1 - x) = k_5 K_1 K_2 (1 + V_r) [Q]_0 [C_6H_5CH_2OH]_{org}^0 t \quad (21)$$

Results and Discussion

Extraction of Hypochlorite Ion. The theory of the extraction of the quaternary ammonium hypochlorite ion pair from the aqueous phase into the organic phase was developed in the Theoretical Analysis section. The final result predicts that the concentration of the tetrabutylammonium hypochlorite ion pair in the organic phase is affected by the volume ratio of the organic and the aqueous phases, the initial concentration of tetrabutylammonium cation, and the concentrations of both the chloride and hypochlorite ions in the aqueous phase.

According to eq 12, the reciprocal of the concentration of the tetrabutylammonium hypochlorite ion pair in the organic phase is proportional to the reciprocal of the concentration of hypochlorite ion in the aqueous phase when the concentration of chloride ion and the initial concentration of tetrabutylammonium cation are kept constant. As shown in Figure 1, the reciprocal of the concentration of the tetrabutylammonium hypochlorite ion pair in the dichloromethane organic phase, when plotted against the reciprocal of the concentration of hypochlorite ion in the aqueous phase, presents a linear relationship at a given chloride ion concentration in the aqueous phase. The experimental results show a good agreement with the theoretical analysis. With increasing chloride ion concentration in the aqueous phase from 0.7 to 2.0 M, the slope of the straight lines increases from 26.5 to 35.9, while the intercept is almost a constant value, 21.2 M^{-1} , as il-

Table I. Effect of the Temperature and the Concentration of Chloride Ion on the Extraction of Hypochlorite Ion^a

[Cl ⁻] _{aq} , M	temp, °C	$[1 + K_3(1 + K_4)[Cl^-]_{aq}] / [2K_1K_2[Q]_0]$	$(1 + K_2) / (2K_2[Q]_0), M^{-1}$	K_2
0.70	20	26.5	21.2	17.2
1.00	20	28.0	21.1	17.9
1.50	20	32.2	20.3	
2.00	20	35.9	21.2	17.0
0.70	0	44.5	23.0	6.8
0.70	5	40.3	22.4	8.3
0.70	10	36.6	22.0	10.2
0.70	15	30.9	21.4	14.0
0.70	25	21.6	20.8	26.0

^a $V_{org}/V_{aq} = 1.0$; organic solvent, CH₂Cl₂; [Q]₀ = 0.025 M; pH = 9.0; stirring rate = 600 rpm.

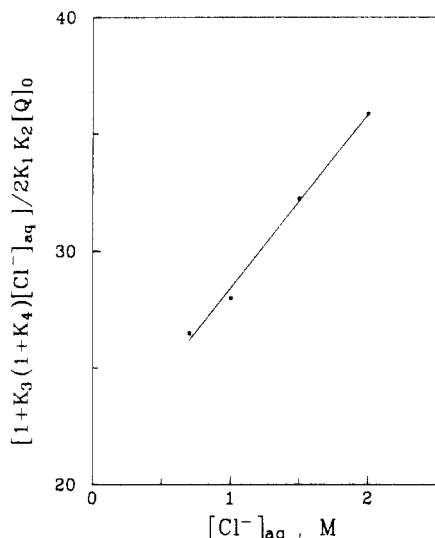


Figure 2. Effect of the concentration of chloride ion in the aqueous phase on the term $[1 + K_3(1 + K_4)] / 2K_1K_2[Q]_0$. Temperature = 20 °C; $V_{org}/V_{aq} = 1.0$; organic solvent, CH₂Cl₂; [Q]₀ = 0.025 M; pH = 9.0; stirring rate = 600 rpm.

illustrated in Table I. Comparing the experimental results with those obtained from eq 12, the intercept is expressed as

$$(1 + K_2) / (2K_2[Q]_0) = 21.2 \quad (22)$$

By substituting the value of [Q]₀ (0.025 M) into eq 22, K_2 is calculated to be equal to 17.4, which is the distribution ratio of tetrabutylammonium hypochlorite ion pair between the dichloromethane and the aqueous phase at 20 °C.

A plot of S in eq 13 against the concentration of chloride ion in the aqueous phase yields a straight line, as shown in Figure 2. The intercept and the slope of the straight line are 21.0 and 7.43 M⁻¹, respectively. Accordingly,

$$1 / (2K_1K_2[Q]_0) = 21.0 \quad (23)$$

$$K_3(1 + K_4) / (2K_1K_2[Q]_0) = 7.43 \quad (24)$$

Inserting the values of K_2 and [Q]₀ into eq 23, we calculate that K_1 is equal to 0.05 M⁻¹, the association constant of tetrabutylammonium cation ion and hypochlorite anion in the aqueous phase.

Substituting eq 23 into eq 24, the term $K_3(1 + K_4)$ is equal to 0.354 M⁻¹. The extraction constant, K_3K_4 , of the tetrabutylammonium chloride ion pair between water and dichloromethane is, therefore,

$$E_{QCl} = K_3K_4 = [Q^+Cl^-]_{org} / ([Q^+]_{aq}[Cl^-]_{aq}) \quad (25)$$

where E_{QCl} is equal to 0.35 at 20 °C (Gustavii and Schill,

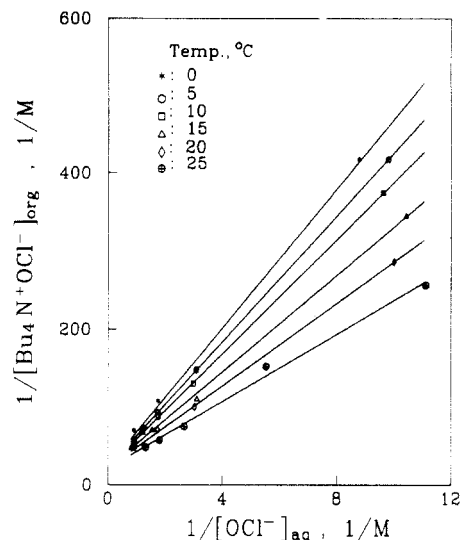


Figure 3. Plot of $1/[Bu_4N^+OCl^-]_{org}$ versus $1/[OCl^-]_{aq}$ with the temperature as the parameter. [Cl⁻]_{aq}⁰ = 0.70 M; $V_{org}/V_{aq} = 1.0$; organic solvent, CH₂Cl₂; [Q]₀ = 0.025 M; pH = 9.0; stirring rate = 600 rpm.

1967). Substituting the value of E_{QCl} into $K_3(1 + K_4)$, the association constants of tetrabutylammonium cation and chloride ion in the aqueous phase, K_3 , and the distribution ratio of tetrabutylammonium chloride ion pair between the dichloromethane and the aqueous phases, K_4 , are evaluated as 0.004 M⁻¹ and 87.7, respectively. The small value of K_3 and large value of K_4 reveal that the concentration of tetrabutylammonium chloride ion pair in the aqueous phase is very small.

Similarly, the extraction constant of the tetrabutylammonium hypochlorite ion pair can be evaluated from the values of K_1 and K_2 ,

$$E_{QOCl} = K_1K_2 = [Q^+OCl^-]_{org} / ([Q^+]_{aq}[OCl^-]_{aq}) = 0.87 \quad (26)$$

By using the extraction constants of tetrabutylammonium hypochlorite and tetrabutylammonium chloride ion pairs, the ion-exchange selectivity coefficient, $K_{OCl/Cl}$, is given by

$$K_{OCl/Cl} = \frac{[Cl^-]_{aq}[Q^+OCl^-]_{org}}{[OCl^-]_{aq}[Q^+Cl^-]_{org}} = E_{QOCl} / E_{QCl} = 2.48 \quad (27)$$

This result reveals that the tetrabutylammonium hypochlorite ion pair can be extracted from the aqueous phase into the dichloromethane phase more efficiently than the tetrabutylammonium chloride ion pair.

Effect of Temperature on the Extraction of Hypochlorite Ion at a Constant Concentration of Chloride Ion. The plots of the reciprocal of the concentration of the tetrabutylammonium hypochlorite ion pair in dichloromethane against the reciprocal of the concentration of hypochlorite ion in the aqueous phase at different temperatures results in linear relationships, as shown in Figure 3. The results correlate well with those obtained from eq 12. The slopes and intercepts of the straight lines illustrated in Table I reveal that both the slope and intercept decrease from 44.5 to 21.6 M⁻¹ and 23.0 to 20.8, respectively, when the temperature increases from 0 to 25 °C. Substituting the initial concentration of the tetrabutylammonium cation into the first term of eq 12, K_2 is evaluated as shown in the last column of Table I. The distribution ratio, K_2 , increases with the increase of temperature, and the free energy was found to be 8.60 kcal/mol. The results indicate that increasing the temperature has a favorable effect on the extraction of tetrabutyl-

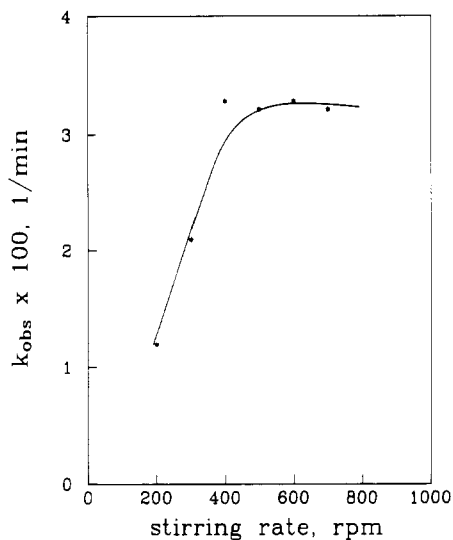


Figure 4. Effect of stirring rate on the observed reaction rate constant. Temperature = 0 °C; $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{Q}]_0 = 0.025 \text{ M}$; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0.

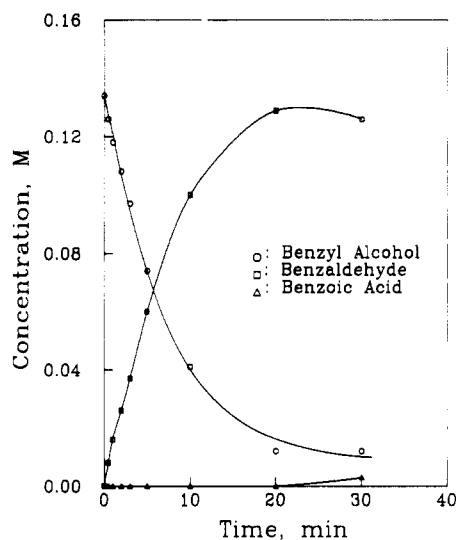


Figure 5. Concentration of reactant and products of a typical run. Temperature = 20 °C; $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{Q}]_0 = 0.025 \text{ M}$; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

ammonium hypochlorite ion pair from the aqueous phase into the organic phase.

Effect of the Stirring Rate. Based on eq 16, the reaction rate can be expressed as follow:

$$r = k_{\text{obs}}[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} \quad (28)$$

where $k_{\text{obs}} = k_5[\text{Q}^+\text{OCl}^-]_{\text{org}}$.

The experimental results show that the observed reaction rate increases linearly with the increase of the stirring rate from 200 to 400 rpm as shown in Figure 4. Further increasing the agitation rate does not increase the reaction rate. The reaction kinetics is controlled by the chemical reaction in the organic phase for stirring rates greater than 500 rpm. On the other hand, the interfacial mass-transfer rate of the reacting ion pair is a key step of the reaction system when the agitation rate is less than 400 rpm. Similar results have been reported by several investigators (Stark and Liotta, 1978; Lee and Freedman, 1985; Rabinovitz et al., 1986).

Product Compositions and Yields. The product compositions of a typical run are shown in Figure 5. The

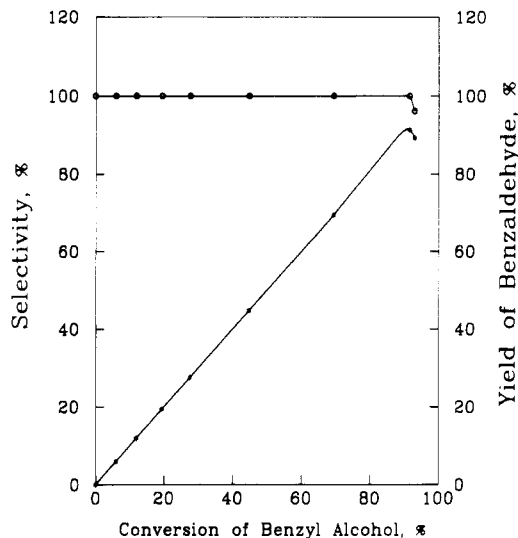


Figure 6. Yield and selectivity of benzaldehyde against conversion of benzyl alcohol. Temperature = 20 °C; $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{Q}]_0 = 0.025 \text{ M}$; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

concentration of benzyl alcohol decreases sharply in the initial stage of the run, and no induction period is found. This observation indicates that the mass transfer of tetrabutylammonium hypochlorite ion pair does not affect the reaction rate even at the beginning of the run.

The concentration of benzaldehyde increased significantly for the first 10 min of the run, as shown in Figure 5. After 10 min from the beginning of the run, the increase of benzaldehyde concentration and the decrease of benzyl alcohol concentration obviously slowed down. As shown in Figure 5, the concentration of benzaldehyde decreased very slowly; a small amount of benzoic acid was detected after 30 min of the run. The oxidation of benzaldehyde is slow compared with that of benzyl alcohol.

The selectivity and the yield of benzaldehyde of a typical run are plotted against the conversion of benzyl alcohol in Figure 6. The results show that the yield of benzaldehyde increases and a maximum yield of 91% is obtained at 91% conversion of benzyl alcohol. When the conversion is higher than 91%, both the yield and selectivity of benzaldehyde decreased because of the formation of benzoic acid.

Effect of the Concentration of Hypochlorite Ion in the Aqueous Phase. Experimental results demonstrate that increasing the concentration of hypochlorite ion in the aqueous phase from 0.045 to 0.140 M and keeping the concentration of benzyl alcohol at 0.134 M resulted in an increase in the initial reaction rate of benzyl alcohol from 1.5×10^{-3} to $4.4 \times 10^{-3} \text{ M min}^{-1}$.

According to the results in Table I, at pH 9.0, 0 °C, and 0.025 M initial concentration of phase-transfer catalyst (Bu_4NCl), the equilibrium relationship between the concentration of the tetrabutylammonium hypochlorite ion pair in dichloromethane and the concentration of hypochlorite ion in the aqueous phase can be expressed as (eq 12)

$$1/[\text{Bu}_4\text{N}^+\text{OCl}^-]_{\text{org}} = 23.0 + 44.5/[\text{OCl}^-]_{\text{aq}} \quad (29)$$

By substituting the value of the concentration of hypochlorite ion in the aqueous phase, the concentration of the tetrabutylammonium hypochlorite ion pair in dichloromethane can be evaluated.

The plot of the logarithmic initial oxidation rate of benzyl alcohol against the logarithmic concentration of tetrabutylammonium hypochlorite ion pair in organic

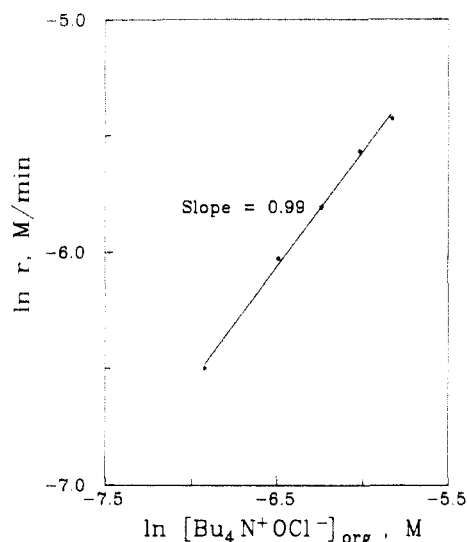


Figure 7. Effect of the concentration of tetrabutylammonium hypochlorite ion pair in the organic phase on the initial reaction rate. Temperature = 0 °C; $[Cl^-]_{aq}^0 = 0.70$ M; $V_{org}/V_{aq} = 1.0$; organic solvent, CH_2Cl_2 ; $[Q]_0 = 0.025$ M; $[C_6H_5CH_2OH]_{org} = 0.134$ M; pH = 9.0; stirring rate = 600 rpm.

phase yields a straight line as shown in Figure 7. The intercept and the slope of the straight line are 0.362 and 0.990, respectively. Accordingly,

$$\ln r = \ln (-d[C_6H_5CH_2OH]/dt) = \ln k_5' + m \ln [Bu_4N^+OCl^-]_{org} = 0.362 + 0.990 \ln [Bu_4N^+OCl^-]_{org} \quad (30)$$

where $k_5' = k_5[C_6H_5CH_2OH]_{org}$. By substituting the concentration of benzyl alcohol into the term of intercept, the reaction rate constant in the organic phase is found to be

$$k_5 = \exp(0.362)/0.134 = 10.7 \text{ M}^{-1} \text{ min}^{-1} \quad (31)$$

The reaction order of the tetrabutylammonium hypochlorite ion pair in the organic phase is 0.990, which correlates well with the assumption of 1.00 in the theoretical analysis, eq 16.

Effect of the Concentration of Benzyl Alcohol. The initial reaction rate of benzyl alcohol increases from 1.5×10^{-3} to 4.4×10^{-3} M min⁻¹ when the concentration of benzyl alcohol increases from 0.045 to 0.134 M, as shown in Figure 8. Plotting the logarithmic initial reaction rate of benzyl alcohol against the logarithmic concentration of benzyl alcohol yields a straight line. The intercept and the slope of the straight line are found to be -3.48 and 0.980, respectively. The relationship between the initial reaction rate of benzyl alcohol and the concentration of benzyl alcohol can be expressed as

$$\ln r = -3.48 + 0.980 \ln [C_6H_5CH_2OH]_{org} \quad (32)$$

Comparing eqs 28 and 32, n is equal to 0.980 and k_{obs} is equal to $\exp(-3.48) \text{ min}^{-1}$ and is also equal to the term $k_5[Q^+OCl^-]_{org}$.

Substituting 0.140 M hypochlorite ion concentration in the aqueous phase into eq 29, the concentration of the tetrabutylammonium hypochlorite ion pair in dichloromethane is evaluated to be 2.93×10^{-3} M, which in turn can be substituted into the term of k_{obs} of eq 32. The reaction rate constant, k_5 , is

$$k_5 = \exp(-3.48)/2.93 \times 10^{-3} = 10.6 \text{ M min}^{-1} \quad (33)$$

The reaction rate constant evaluated from eq 33 agrees well with the result in eq 31. The reaction order of benzyl alcohol evaluated from eq 32 is 0.980, which is approxi-

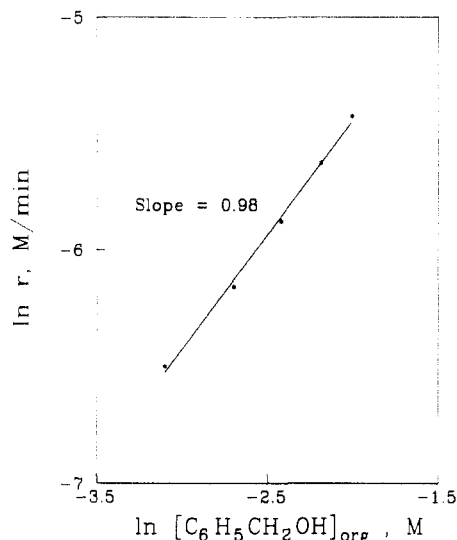


Figure 8. Effect of the concentration of benzyl alcohol in the organic phase on the initial reaction rate. Temperature = 0 °C; $[Cl^-]_{aq}^0 = 0.70$ M; $V_{org}/V_{aq} = 1.0$; organic solvent, CH_2Cl_2 ; $[Q]_0 = 0.025$ M; $[OCl^-]_{aq}^0 = 0.140$ M; pH = 9.0; stirring rate = 600 rpm.

Table II. Effect of the Temperature on the Reaction Rate Constant^a

temp, °C	$10^3[Bu_4N^+OCl^-]_{org}$, M	k_{obs} , min ⁻¹	k_5 , M ⁻¹ min ⁻¹
0	2.93	0.033	11.2
5	3.22	0.044	13.6
10	3.53	0.074	21.0
15	4.13	0.108	26.2
20	4.76	0.200	42.0

^a $[Cl^-]_{aq}^0 = 0.70$ M; $V_{org}/V_{aq} = 1.0$; organic solvent, CH_2Cl_2 ; $[Q]_0 = 0.025$ M; $[C_6H_5CH_2OH]_{org}^0 = 0.134$ M; $[OCl^-]_{aq}^0 = 0.140$ M; pH = 9.0; stirring rate = 600 rpm.

mately equal to 1, and also correlates well with the assumption of eq 16 in the theoretical analysis.

Effect of the Temperature. As shown in the previous section, the equilibrium concentration of tetrabutylammonium hypochlorite ion pair in the organic phase depends on the reaction temperature. As shown in column 2 of Table II, $[Bu_4N^+OCl^-]_{org}$ at a constant temperature is calculated by eq 12 using the data of the slopes and intercepts of eq 12 presented in Table I. Otherwise, according to eq 28, k_{obs} can be obtained when the initial reaction rate and $[C_6H_5CH_2OH]_{org}$ at a constant temperature are obtained. The results are shown in column 3 of Table II. The value of k_{obs} is further divided by $[Bu_4N^+OCl^-]_{org}$, which is illustrated in column 2 of Table II, the reaction rate constant of benzyl alcohol oxidation, k_5 , is obtained as shown in column 4 of Table II.

A straight line is obtained from plotting the logarithmic rate constant of benzyl alcohol oxidation against the reciprocal of temperature as shown in Figure 9. The slope of this line is -5240, which corresponds to an activation energy of 10.4 kcal/mol.

Effect of the Concentration of the Phase-Transfer Catalyst. The effect of the concentration of the phase-transfer catalyst on the conversion of benzyl alcohol is shown in Figure 10. Increasing the concentration of phase-transfer catalyst from 0 to 0.05 M increases the conversion of benzyl alcohol from 0.028 to 0.821 after 60 min. These results indicate that the concentration of phase-transfer catalyst significantly affects the conversion of benzyl alcohol. The observed reaction rate constant, k_{obs} , increases with an increase of concentration of the phase-transfer catalyst, as shown in Table III. The results indicate that increasing the concentration of tetrabutyl-

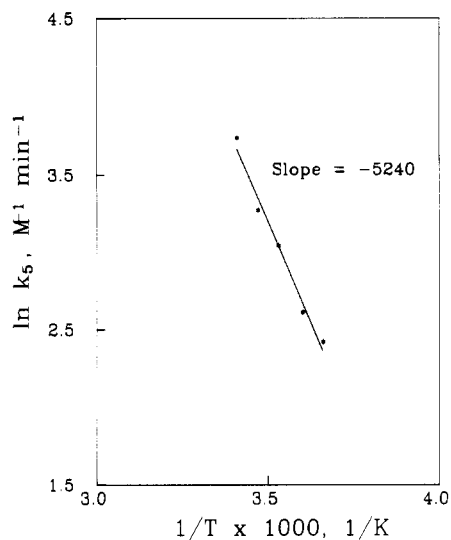


Figure 9. Effect of temperature on the reaction rate constant. $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{Q}]_0 = 0.025 \text{ M}$; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

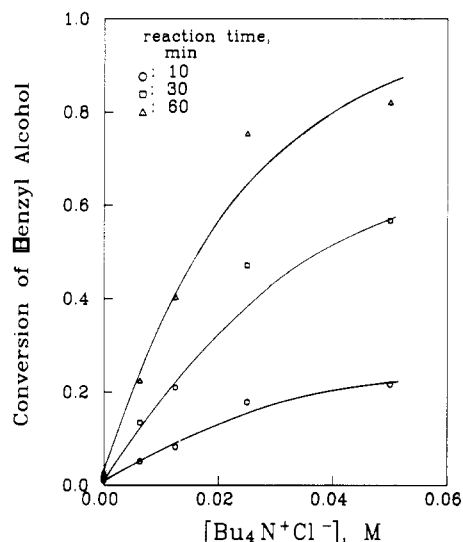


Figure 10. Effect of the concentration of the phase-transfer catalyst on the conversion of benzyl alcohol. Temperature = 0°C ; $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

Table III. Effect of the Concentration of the Phase-Transfer Catalyst on the Observed Reaction Rate Constant

$[\text{Q}]_0, \text{M}$	$10^3 k_{\text{obs}}, \text{min}^{-1}$	$[\text{Q}]_0, \text{M}$	$10^3 k_{\text{obs}}, \text{min}^{-1}$
0	0.750	0.0250	32.8
0.0063	9.63	0.0500	45.3
0.0125	15.4		

^a Temperature = 0°C ; $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

ammonium chloride from 0 to 0.05 M increases the observed reaction rate constant, k_{obs} , from 0.75×10^{-3} to $45.30 \times 10^{-3} \text{ min}^{-1}$.

Effect of the Volume Ratio. As shown in Figure 11, the theoretical analysis and experimental results for the conversion of benzyl alcohol are plotted against the reaction time. According to the theoretical analysis, for $\Theta_b = 1.04$, $\Theta_c = 5.22$, and 0.134 M, an initial concentration of benzyl alcohol, and V_r ranging from 0.1 to 3.0, the conversion of benzyl alcohol can be calculated by solving eq

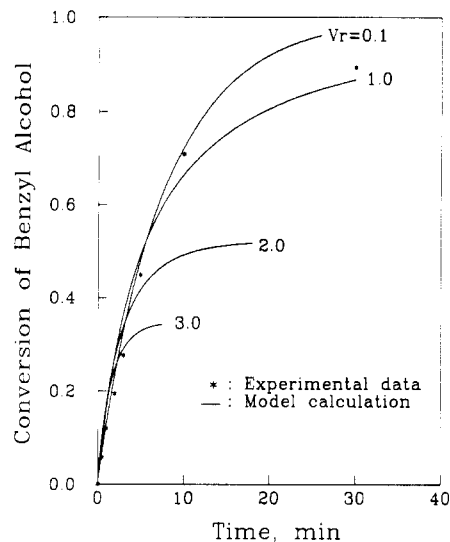


Figure 11. Conversion of benzyl alcohol against time with the volume ratio as the parameter. Temperature = 20°C ; $[\text{Cl}^-]_{\text{aq}}^0 = 0.70 \text{ M}$; organic solvent, CH_2Cl_2 ; $[\text{Q}]_0 = 0.025 \text{ M}$; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

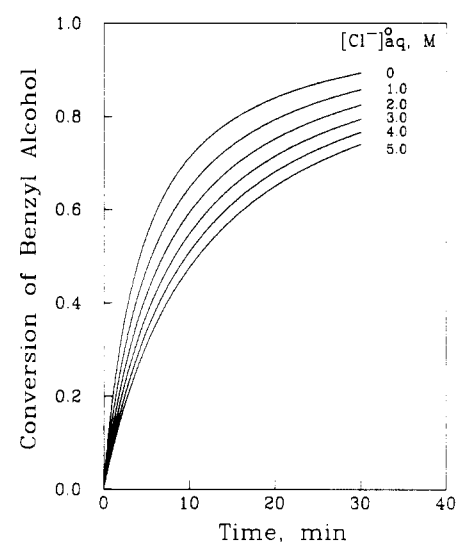


Figure 12. Conversion of benzyl alcohol against time with the initial concentration of chloride in the aqueous phase as the parameter. Temperature = 20°C ; $V_{\text{org}}/V_{\text{aq}} = 1.0$; organic solvent, CH_2Cl_2 ; $[\text{Q}]_0 = 0.025 \text{ M}$; $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0 = 0.134 \text{ M}$; $[\text{OCl}^-]_{\text{aq}}^0 = 0.140 \text{ M}$; pH = 9.0; stirring rate = 600 rpm.

21. The results reveal that the experimental results of the conversion of benzyl alcohol fit well with the results by the theoretical analysis at $V_r = 1.0$. According to the theoretical analysis, decreasing the volume ratio from 3.0 to 0.1 increases significantly the conversion of benzyl alcohol, from 0.343 to 0.920, after 20 min from the beginning of a run. The lower conversions of benzyl alcohol for the larger organic/aqueous volume ratios, $V_r = 2.0$ and 3.0, are because of the moles of hypochlorite ion in the aqueous phase being less than in benzyl alcohol in the organic phase. Therefore, the hypochlorite ion reactant in the aqueous phase is exhausted before the benzyl alcohol is completely reacted in the organic phase. The conversion of benzyl alcohol is low for the larger organic/aqueous volume ratios.

Effect of the Initial Concentration of Chloride Ion in the Aqueous Phase. The chloride ion in the aqueous phase competing with hypochlorite ion to form quaternary ammonium ion pairs decreases the efficiency of the extraction of the tetrabutylammonium hypochlorite ion pair from the aqueous phase into the dichloromethane phase,

as described in the theoretical analysis. Increasing the concentration of chloride ion in the aqueous phase decreases the reaction rate at a constant concentration of hypochlorite ion in the aqueous phase. Figure 12 shows a plot of the conversion of benzyl alcohol versus reaction time with the initial concentration of chloride ion in the aqueous phase as a parameter. The curves are obtained by solving eq 21 for a given set of conditions. As shown in Figure 12, increasing the concentration of chloride ion in the aqueous phase from 0 to 5.0 M decreases the conversion of benzyl alcohol from 0.893 to 0.740 after 30 min from the beginning of a run.

Conclusions

The experimental results for the extraction hypochlorite ion pair from the aqueous phase into a dichloromethane phase correlate well with the results of the theoretical analysis. The extraction constant of hypochlorite ion from the aqueous into the dichloromethane phase at 20 °C is obtained. The equilibrium constants, K_1 – K_4 , are evaluated to be equal to 0.05 M⁻¹, 17.4, 0.004 M⁻¹, and 87.7, respectively. Both the experimental results and the theoretical analysis show that the reaction order is one with respect to both benzyl alcohol and the tetrabutylammonium hypochlorite ion pair in the organic phase. The activation energy of the oxidation of benzyl alcohol in the organic phase is 10.4 kcal/mol. The experimental results show that the selectivity of benzaldehyde is almost 100%. Only a trace of benzoic acid is detected, and only when the conversion of benzyl alcohol is higher than 91%. At the same operating conditions, the conversion of benzyl alcohol of the theoretical analysis correlates well with the experimental results.

Acknowledgment

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Nomenclature

K_1, K_3 = equilibrium constants, M⁻¹
 K_2, K_4 = distribution ratio of ion pairs between organic and aqueous phases
 $K_{\text{OCl}^-/\text{Cl}^-}$ = ion-exchange selectivity coefficient
 k_5 = reaction rate constant, M⁻¹ min⁻¹
 k_{obs} = observed reaction rate, min⁻¹
 m = reaction order of quaternary ammonium hypochlorite ion pair in the organic phase
 n = reaction order of benzyl alcohol in the organic phase
 N_0 = initial total moles of phase-transfer catalyst, mol
 Q^+ = quaternary ammonium cation
 r = reaction rate of benzyl alcohol, M min⁻¹
 S = slope of $1/[\text{Q}^+\text{OCl}^-]_{\text{org}}$ versus $1/[\text{OCl}^-]_{\text{aq}}$
 t = time, min⁻¹
 V = volume of solution
 x = conversion of benzyl alcohol, $1 - [\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} / [\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0$

Subscripts

aq = aqueous phase
 org = organic phase
 QCl = quaternary ammonium chloride ion pair
 QOCl = quaternary ammonium hypochlorite ion pair
 r = organic and aqueous volume ratio
 0 = initial state

Superscript

0 = initial state

Greek Symbols

Θ_b = defined as $[\text{OCl}^-]_{\text{aq}}^0 / [\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0$
 Θ_c = defined as $[\text{Cl}^-]_{\text{aq}}^0 / [\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}}^0$

Registry No. C₆H₅CH₂OH, 100-51-6; C₆H₅CHO, 100-52-7; calcium hypochlorite, 7778-54-3; tetrabutylammonium chloride, 1112-67-0.

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Kinetics of Reactions of Benzyl Chloride/*p*-Chlorobenzyl Chloride with Sodium Sulfide: Phase-Transfer Catalysis and the Role of the Omega Phase

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The reactions of benzyl chloride and *p*-chlorobenzyl chloride with sodium sulfide were carried out both in the solid-liquid and liquid-liquid modes with phase-transfer catalysis. Tetrabutylammonium bromide was found to be the most efficient catalyst for the system among six catalysts tried. In the solid-liquid mode, the reaction was found to be mass transfer controlled with an activation energy of 2.3 kcal/mol, whereas the liquid-liquid reaction was found to be kinetically controlled with an activation energy of 11.3 kcal/mol. The reactivities of benzyl chloride and *p*-chlorobenzyl chloride were compared under different controlling regimes. The effect of the Ω phase on the rate of solid-liquid reaction was also studied. A maximum rate enhancement by factors of 12 and 57 was obtained for benzyl chloride and *p*-chlorobenzyl chloride, respectively, with a calculated amount of water compared to no extra water. The importance of mass-transfer resistance was assessed at the maximum rate.

The reactions of organic halides like benzyl chloride and *p*-chlorobenzyl chloride with sulfide ions result in the formation of diaryl sulfides. These diaryl sulfides find many applications as additives for extreme pressure lubricants, as antiwear additives for motor oils, as stabilizers for photographic emulsions, in refining and recovery of precious metals, and in different anticorrosive formulations. The conventional method of manufacture of these compounds involves refluxing the corresponding organic halide with aqueous solutions of sodium sulfide. The reaction, however, proceeds very slowly because of the low mutual solubilities of the nucleophile in the organic medium and the substrate in the aqueous medium. The second synthetic route is the reduction of sulfoxides which involves the use of expensive and special reducing agents like P₄S₁₀ in CH₂Cl₂, chloromethylsilane-NaI in CH₃CN, and Mo(CO)₆ in CH₃COOH.

The organic sulfides can also be produced with phase-transfer catalysis, but none of the published works deal with the detailed kinetics and mechanism of such reactions which are also academically interesting. It was, therefore, thought desirable to study the phase-transfer-catalyzed reaction of benzyl chloride and *p*-chlorobenzyl chloride with sodium sulfide in liquid-liquid and solid-liquid systems and to assess the role of mass transfer in the system. It was also thought desirable to assess the role of

the Ω phase in the solid-liquid system.

Literature Review

Shriner et al. (1930) synthesized dibenzyl sulfide with 83% yield by heating an aqueous methanolic solution of sodium sulfide with benzyl chloride on a steam bath under continuous stirring for 3 days. Bacon and Kochling (1964) improved the method of Shriner et al. (1930) by carrying out the reaction under refluxing conditions, which reduced the reaction time from 3 days to 15 h. Voronkov et al. (1969) synthesized dibenzyl sulfide by adding benzyl chloride dropwise with vigorous stirring to an aqueous sodium sulfide solution at 60-65 °C. Then the whole reaction mixture was stirred for 4 h at 90 °C. Pinkish crystals of dibenzyl sulfide were obtained in 97% yield. Similarly, they produced di-*p*-chlorobenzyl sulfide both in the presence and absence of benzene as a solvent. Landini and Rolla (1974) prepared a number of symmetrical sulfides using tributylhexadecylphosphonium bromide (TBHDPPB) as the phase-transfer catalyst. Thus, benzyl chloride was consumed in less than 10 min upon heating at 70 °C under vigorous stirring with aqueous sodium sulfide in the presence of the catalyst. Kim and Noh (1975) synthesized bis-(*p*-nitrophenyl) sulfide in the presence of Aliquat 336 as the phase-transfer catalyst by heating *p*-nitrochlorobenzene with aqueous sodium sulfide