

Phase-transfer catalytic reaction of 2,4,6-tribromophenol and dibromomethane: effect of potassium hydroxide

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Abstract

The reaction of 2,4,6-tribromophenol with dibromomethane in an alkaline solution of KOH/dibromomethane two-phase medium, catalyzed by tetrabutylammonium bromide (TBAB or QBr), was carried out. Both mono-substituted as well as bi-substituted products were found to have formed during or after the reaction, when dibromomethane was used both as organic solvent as well as organic-phase reactant. The active catalyst tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ) was identified during the reaction, from which the organic-phase reaction was inferred to be the rate controlling step. The mass transfer of both the catalysts viz. QBr and ArOQ between the two phases was found to be fast. A peculiar phenomenon was observed while investigating the effect of KOH on the reaction rate, viz. the reaction rate does not monotonously increase or decrease with increase in the amount of KOH. This phenomenon is attributed to the activity of ArOQ, the distribution of active catalyst (ArOQ) between the two phases and the hydration of active catalyst in the organic phase, both of which are affected by the amount of KOH. An effective method is proposed to determine the two intrinsic rate constants of the organic-phase reaction, based on the reaction carried out at high KOH concentration. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Synthesis of acetal; Phase-transfer catalysis; Effect of KOH; Kinetic model; Organic solvent

1. Introduction

Phase-transfer catalysis (PTC) is one of the promising methods in organic synthesis of specialty chemicals. In the last 20 years, a steadily increasing number of papers and patents dealing with phase transfer topics and related to their applications have been published in the literature. PTC is not merely important for substitutional reactions but it is being extensively ap-

plied in polymer chemistry, heterocyclic chemistry, organometallic synthesis and pharmaceutical manufacture [1–4] nowadays. In general, quaternary ammonium salts are widely used as the phase transfer catalyst to synthesize specialty chemicals from two immiscible reactants [5–8]. The reaction mechanism is often complicated and several factors affect the conversion of reactants.

Williamson synthesis and alkoxymercuration have been well developed in organic chemistry to synthesize ethers. In the past years, expensive dialkyl sulfate was used as an alkylating agent

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for the reaction of dialkyl sulfate with alkoxide salt in aqueous solution to obtain the desired ether product. In contrast, the reactions, in which low cost alkyl halides are suitable to be employed as alkylating agents in the organic synthesis of ethers by the alkylation, are slow. Fortunately, the synthesis of ethers is enhanced by adding a small amount of quaternary ammonium salt in the two-phase reaction [9,10]. Wang and Chang [9,10], have synthesized acetal compounds through the reaction of alcohol and dibromomethane, catalyzed by tetrabutylammonium bromide (QBr or TBAB) in an alkaline solution of KOH/organic solvent two-phase medium. However, only formation of the bi-substituted product was observed and only the second intrinsic rate constant of the organic-phase reaction was determined by using compounds other than dibromomethane as organic solvent in that study. Formation of mono-substituted product was not observed and the first intrinsic rate constant of the organic-phase reaction was also not determined.

In the PTC/OH reaction, the amount of alkaline compound is an important factor affecting the conversion (or the yield). However, detailed investigations of the effect of the amount of alkaline compound on the conversion are still lacking. In the present study, synthesis of acetal compound through the reaction of 2,4,6-tribromophenol with dibromomethane, catalyzed by QBr in an alkaline solution of KOH/dibromomethane two-phase medium, was hence carried to determine the effect of KOH. A peculiar dependence of the reaction on the amount of KOH have been observed, which is explained on the basis of the activity of tetrabutylammonium 2,4,6-tribromophenoxide (ArOQ), the distribution of active catalyst ArOQ between the two phases and the hydration of ArOQ in the organic phase. Formation of mono-substituted as well as bi-substituted products were observed during or after the reaction, when dibromomethane was used as both organic-phase reactant as well as organic solvent. An effective method is also proposed to determine the two

intrinsic rate constants of the organic-phase reactions.

2. Experimental section

2.1. Materials

Dibromomethane (CH_2Br_2), 2,4,6-tribromophenol ($\text{C}_6\text{H}_2\text{Br}_3(\text{OH})$, ArOH), potassium hydroxide, TBAB ($(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$) and other reagents were all G.R. grade chemicals for synthesis.

2.2. Procedures

2.2.1. Two-phase reaction

A 125 ml-four necked Pyrex flask, able to serve the purposes of agitating the solution, inserting the thermometer taking samples, and feeding the reactants was used as the reactor. A reflux condenser was attached to the port of the reactor to recover the reactants and water. The reactor was submerged into a constant temperature water bath, the temperature of which could be controlled to $\pm 0.1^\circ\text{C}$. To start the experimental run, known quantities of 2,4,6-tribromophenol, potassium hydroxide and QBr or TBAB, and bi(2,6-dibromophenoxide) (internal standard) were dissolved in deionized water for 1 h and introduced into the reactor. Then, dibromomethane, acting as both organic-phase reactant as well as organic solvent, was introduced to start the reaction. The mixture was stirred mechanically by a two-blade paddle (5.5 cm) at 1000 rpm. During the reaction, an aliquot sample of 0.1 ml was withdrawn from the solution at a specific time. The sample was immediately introduced into methanol at 4°C for dilution and retarding the reaction, and then analyzed by HPLC.

The products (mono-substituted and bi-substituted) as well as the reactant were identified by NMR and IR. The molecular weights of the

two products were measured by using GC-Mass and the contents of both reactants and products were determined by HPLC. The results obtained from NMR and IR were very consistent with the published data. An HPLC model LC9A (Shimadzu), equipped with an absorbance detector (254 nm, SPD-6A), was used. The column used was Shim pack CLC-ODS RP-18 (5 μ m), and the eluent was CH₃CN/CH₃OH/H₂O = 6/6/1 for mono-substituted and bi-substituted product, and CH₃CN/CH₃OH/H₂O = 2/2/1 (with 1% acetic acid) for ArOQ, with a flow rate 2.0 ml/min.

2.2.2. Organic-phase reaction

The aim of the present study was to determine the two intrinsic rate constants of organic-phase reactions. Measured quantities of CH₂Br₂ (30 ml), bi(2,6-dibromophenoxide) (internal standard) were hence introduced into the Pyrex flask (100 ml), which was immersed in a constant temperature water bath. ArOQ was then added to the reactor to start the reaction. During the reaction, an aliquot sample of 0.1 ml was withdrawn from the solution at a specific time. The sample was immediately introduced into dichloromethane at 4°C for diluting and retarding the reaction, and then analyzed by HPLC.

2.2.3. Synthesis of active catalyst (ArOQ), mono-substituted product ArOCH₂Br and bi-substituted product ArOCH₂OAr

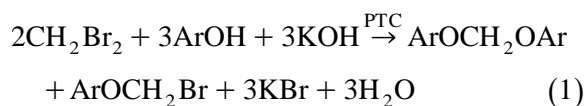
2.2.3.1. Synthesis of active catalyst (ArOQ). To synthesize the active catalyst, measured quantities of KOH (1.8 g) and 2,4,6-tribromophenol (10 g) were dissolved in water (100 ml) at 60°C. Then, QBr or TBAB (10 g) was introduced to the reactor. The mixture solution was agitated for 1 h, producing a white precipitate. The solid content was then filtered and washed with alkaline solution of KOH for five times to remove TBAB catalyst. The extracted solid was then dried in a vacuum oven at 50°C, and the white powder thus obtained was identified as ArOQ.

2.2.3.2. Synthesis of mono-substituted product ((α -bromomethyl 2,4,6-tribromophenyl)ether, ArOCH₂Br). Measured quantities of 2,4,6-tribromophenol (4 g), KOH (2 g) and TBAB catalyst (1 g) were dissolved in water (50 ml) at 60°C. Then, CH₂Br₂ (70 ml) was added to start the reaction for several hours. The solid content produced was removed by filtration. The filtrate was then washed with KOH solution several times and then introduced into a refrigerator to precipitate the bi-substituted product. The residue solution was further concentrated in a rotary evaporator. The solid contents, which contained mono-substituted and bi-substituted products, were dissolved into CH₃OH and separated by column chromatography. The column length was 40 cm and was 3.8 o.d. filled with 40–60 mesh glass beads.

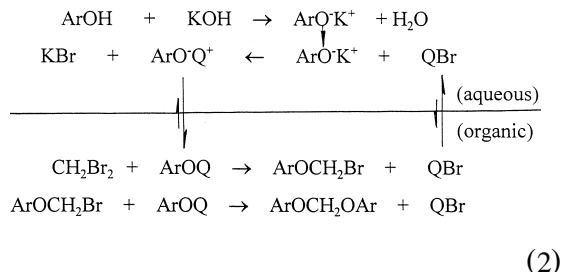
2.2.3.3. Synthesis of bi-substituted product (bi(2,4,6-tribromo phenoxide)methane, ArOCH₂OAr). Measured quantities of 2,4,6-tribromophenol (8 g), and KOH (3 g) were dissolved in water (100 ml). Then, measured quantities of TBAB catalyst (2.5 g), CH₂Br₂ (20 ml) were added to start the reaction at 60°C to obtain white crystals of the bi-substituted product. The mother liquid was removed by filtration. These white crystals were washed with KOH solution for five times. The white powder, which was identified as bi(2,4,6-tribromophenoxide)-methane, was then obtained by drying the sample in a vacuum oven at 50°C.

3. Reaction mechanism and kinetic model

The overall reaction of 2,4,6-tribromophenol (ArOH) with dibromomethane, catalyzed by QBr or TBAB in an alkaline solution of KOH/dibromomethane two-phase medium, can be expressed as



In this study, the presence of ArOQ (or active catalyst) was detected in the reaction mixture. Thus, based on this experimental observation, the reaction mechanism is proposed as



in which, ArO^- and Q^+ represent 2,4,6-tribromophenoxide anion, and tetrabutylammonium cation, respectively. The above reaction indicates that the active catalyst (ArOQ) is produced from the reaction of potassium 2,4,6-tribromophenoxide (ArOK) and QBr in the aqueous phase. It is then transferred to the organic phase and reacts with CH_2Br_2 to produce the desired products (ArOCH_2Br and ArOCH_2OAr). There are two sequential reactions of ArOQ in the organic phase with CH_2Br_2 . First, CH_2Br_2 reacts with ArOQ to produce the mono-substituted product (ArOCH_2Br). This mono-substituted product (ArOCH_2Br) further reacts with ArOQ to produce the bi-substituted product (ArOCH_2OAr). The TBAB catalyst (QBr), which is generated in the organic phase, is transferred to the aqueous phase for further regeneration. In this work, 2,4,6-tribromophenol (aqueous-phase reactant) was used as the limiting reactant because dibromomethane acts as organic-phase reactant as well as organic solvent. The corresponding reactions are classified as organic-phase reaction and two-phase reaction, respectively.

3.1. Organic-phase reaction (intrinsic reaction rate constants)

Based on the experimental data, the reaction in the organic phase is inferred to be the rate-determining step in this two-phase phase-transfer catalytic reaction. As mentioned above, the ac-

tive catalyst (ArOQ) could be easily synthesized from the reaction of 2,4,6-tribromophenol with TBAB in an alkaline solution of KOH. Therefore, the organic-phase reaction can be carried out directly from ArOQ and the organic-phase reactant (CH_2Br_2). Nevertheless, two consecutive substitution reaction steps are involved in the formation of the first and final products. The rate constant of the first reaction in the organic phase has not been determined previously. Hence, the rate constants are obtained in this study from the material balance, which is based on the following reaction mechanism.

In this reaction, it is reasonable to assume a constant concentration of dibromomethane, i.e., $[\text{CH}_2\text{Br}_2]_o = [\text{CH}_2\text{Br}_2]_{o,i} = \text{constant}$, because dibromomethane acts both as organic-phase reactant as well as organic solvent. The rate equations for the reactions of ArOCH_2Br and ArOCH_2OAr with ArOQ in the organic phase are

$$\frac{d[\text{ArOCH}_2\text{Br}]}{dt} = k_1[\text{ArOQ}][\text{CH}_2\text{Br}_2]_i - k_2[\text{ArOQ}][\text{ArOCH}_2\text{Br}] \quad (3)$$

$$\frac{d[\text{ArOCH}_2\text{OAr}]}{dt} = k_2[\text{ArOQ}][\text{ArOCH}_2\text{Br}] \quad (4)$$

$$\frac{d[\text{ArOQ}]}{dt} = -k_1[\text{ArOQ}][\text{CH}_2\text{Br}_2]_i - k_2[\text{ArOQ}][\text{ArOCH}_2\text{Br}] \quad (5)$$

The initial conditions of ArOCH_2Br , ArOCH_2OAr and ArOQ are

$$\begin{aligned}
 [\text{ArOCH}_2\text{Br}] &= [\text{ArOCH}_2\text{OAr}] = 0, \\
 [\text{ArOQ}] &= [\text{ArOQ}]_i; \quad t = 0.
 \end{aligned} \quad (6)$$

In order to find the rate constants k_1 and k_2 , we define k_r as

$$k_r = \frac{k_2}{k_1} \quad (7)$$

Thus, combining Eqs. (3) and (4), we obtain

$$\frac{d[\text{ArOCH}_2\text{Br}]}{d[\text{ArOCH}_2\text{OAr}]} = \frac{1}{k_r} \frac{[\text{CH}_2\text{Br}_2]_i}{[\text{ArOCH}_2\text{Br}]} - 1 \quad (8)$$

Solving for $[\text{ArOCH}_2\text{Br}]$ from Eq. (8) gives

$$\begin{aligned} & [\text{ArOCH}_2\text{Br}] \\ &= \frac{[\text{CH}_2\text{Br}_2]_i}{k_r} \\ &\times \left\{ 1 - \exp \left[- \frac{k_r}{[\text{CH}_2\text{Br}_2]_i} \right. \right. \\ &\times ([\text{ArOCH}_2\text{Br}] \\ &\left. \left. + [\text{ArOCH}_2\text{OAr}]) \right] \right\} \quad (9) \end{aligned}$$

The dependence of $[\text{ArOCH}_2\text{Br}]$ and $[\text{ArOCH}_2\text{OAr}]$ on reaction time were obtained from the experiments. Therefore, the plot between $[\text{ArOCH}_2\text{Br}]$ and $([\text{ArOCH}_2\text{Br}] + [\text{ArOCH}_2\text{OAr}])$ with an implicit time using Eq. (9), was used to find a constant value of k_r by curve fitting. For this purpose, a linear relation between k_1 and k_2 , as shown in Eq. (7) is also obtained. Thus, substituting Eq. (7) into Eqs. (3)–(5), we obtain

$$\begin{aligned} \frac{d[\text{ArOCH}_2\text{Br}]}{dT_1} &= [\text{ArOQ}][\text{CH}_2\text{Br}_2]_i \\ &\quad - k_r[\text{ArOQ}][\text{ArOCH}_2\text{Br}] \quad (10) \end{aligned}$$

$$\frac{d[\text{ArOCH}_2\text{OAr}]}{dT_1} = k_r[\text{ArOQ}][\text{ArOCH}_2\text{Br}] \quad (11)$$

$$\begin{aligned} \frac{d[\text{ArOQ}]}{dT_1} &= [\text{ArOQ}][\text{CH}_2\text{Br}_2]_i \\ &\quad + k_r[\text{ArOQ}][\text{ArOCH}_2\text{Br}] \quad (12) \end{aligned}$$

where $T_1 = k_1 t$.

Eqs. (10)–(12) can be solved numerically to find the relations between $[\text{ArOCH}_2\text{Br}]$, $[\text{ArOCH}_2\text{OAr}]$, $[\text{ArOQ}]$ and T_1 [13]. Therefore,

the theoretical value of $[\text{ArOCH}_2\text{Br}]$ (or $[\text{ArOCH}_2\text{OAr}]$) at T_1 could be obtained. Meanwhile, the actual values of $[\text{ArOCH}_2\text{Br}]$ (or $[\text{ArOCH}_2\text{OAr}]$) vs. reaction time were obtained from the experiments. Therefore, the values of t and T_1 can be determined by equating the experimental and theoretical values of $[\text{ArOCH}_2\text{Br}]$ (or $[\text{ArOCH}_2\text{OAr}]$) are searched, i.e., k_1 can be thus determined. For this, the intrinsic rate constants of the organic-phase reaction (k_1 and k_2) are obtained from the above kinetic model, using the experimental data. In this work, the value of k_r was determined by using a computer software [14]. The estimated results are presented in Figs. 1 and 2, and the values of the intrinsic rate constants of the organic-phase reaction (k_1 and k_2) are presented in Table 1.

3.2. Two-phase reaction (intrinsic reaction rate constants)

In the two-phase reaction, the organic-phase reaction is the rate-determining step. In addition, it was observed that the concentration of active catalyst (ArOQ) remained at a constant value during the reaction. Therefore, the mass transfer of ArOQ from aqueous phase to organic phase is believed to be fast. The material ba-

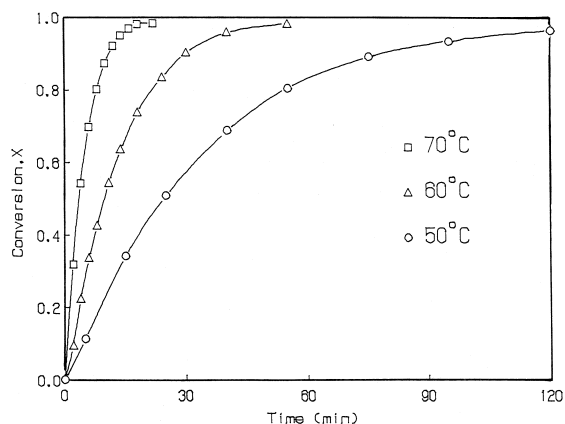


Fig. 1. Effect of temperature on the conversion of CH_2Br_2 in the organic-phase reaction; 0.16 g of ArOQ, 30 ml of CH_2Br_2 , 700 rpm.

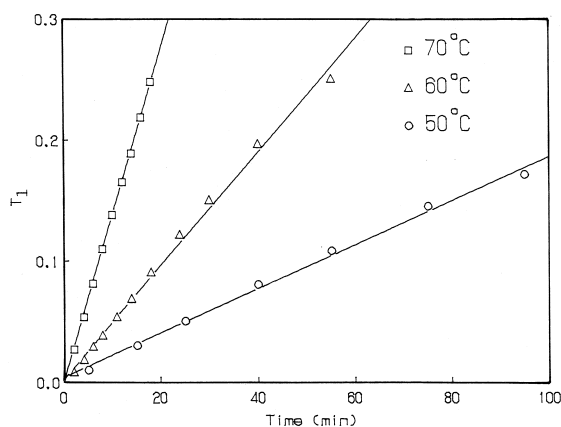


Fig. 2. A plot of T_1 -value vs. time at various temperatures for the organic-phase reaction; 0.16 g of ArOQ, 30 ml of CH_2Br_2 , 700 rpm.

lances for the reactions of CH_2Br_2 and ArOCH_2Br with ArOQ in the organic phase are

$$\frac{d[\text{ArOCH}_2\text{Br}]}{dt} = k_1[\text{ArOQ}][\text{CH}_2\text{Br}_2]_i - k_2[\text{ArOQ}][\text{ArOCH}_2\text{Br}], \quad (13)$$

$$\frac{d[\text{ArOCH}_2\text{OAr}]}{dt} = k_2[\text{ArOQ}][\text{ArOCH}_2\text{Br}]. \quad (14)$$

The initial condition of ArOCH_2Br and ArOCH_2OAr are

$$[\text{ArOCH}_2\text{Br}] = [\text{ArOCH}_2\text{OAr}] = 0; \quad t = 0 \quad (15)$$

Since the concentrations of both ArOQ and CH_2Br_2 in the organic phase in the two-phase reaction are constant, Eq. (13) can be integrated to obtain

$$[\text{ArOCH}_2\text{Br}] = \frac{k_{1,\text{app}}[\text{CH}_2\text{Br}_2]_i}{k_{2,\text{app}}} \times \left\{ 1 - \exp(-k_{2,\text{app}}t) \right\} \quad (16)$$

Table 1
Intrinsic rate constants of organic-phase reaction (k_1 and k_2)

	Temperatures		
	50°C	60°C	70°C
k_1 (l/mole/min)	1.93×10^{-3}	4.35×10^{-3}	13.75×10^{-3}
k_2 (l/mole/min)	0.43	0.75	2.23

Substituting Eq. (16) into Eq. (14), we obtain

$$\frac{d[\text{ArOCH}_2\text{OAr}]}{dt} = k_{1,\text{app}}[\text{CH}_2\text{Br}_2]_i \times \left\{ 1 - \exp(-k_{2,\text{app}}t) \right\} \quad (17)$$

Integrating Eq. (17) and from Eq. (15), we obtain

$$[\text{ArOCH}_2\text{OAr}] = [\text{CH}_2\text{Br}_2]_i \left\{ k_{1,\text{app}}t - \frac{k_{1,\text{app}}}{k_{2,\text{app}}} \times \left[1 - \exp(-k_{2,\text{app}}t) \right] \right\} \quad (18)$$

where $k_{1,\text{app}}$ and $k_{2,\text{app}}$ are the apparent rate constants of the two organic-phase reactions, i.e.,

$$k_{1,\text{app}} = k_1[\text{ArOQ}]_{\text{org},i} \quad (19)$$

$$k_{2,\text{app}} = k_2[\text{ArOQ}]_{\text{org},i}. \quad (20)$$

Eqs. (16) and (18) give the concentration profiles of the first product (ArOCH_2Br) and the final product (ArOCH_2OAr), respectively, which can be experimentally monitored during the reaction. Therefore, the apparent rate constants of the organic-phase reactions ($k_{1,\text{app}}$ and $k_{2,\text{app}}$) (or the intrinsic rate constants (k_1 and k_2)) can be obtained from the experimental data

Table 2
Effect of the amount of KOH on the $k_{i,\text{app}}$ -value; $i = 1, 2$

Amount of KOH (g)	$[\text{ArOQ}]_{\text{org},i} \times 10^3$ M	$(k_{1,\text{app}} \times 10^3) / ([\text{ArOQ}]_{\text{org},i})$	$(k_{2,\text{app}}) / ([\text{ArOQ}]_{\text{org},i})$
5	7.97	0.19	0.03
10	7.84	0.62	0.17
15	7.77	2.62	0.55
20	7.81	3.91	0.68
25	7.95	4.22	0.74
35	7.76	4.32	0.74
45	7.81	4.27	0.74

Reaction conditions: 1 g of 2,4,6-tribromophenol; 0.078 g of TBAB catalyst, 10 ml of H_2O , 30 ml of CH_2Br_2 , 700 rpm, 60°C.

on the dependence of $[\text{ArOCH}_2\text{Br}]$ and $[\text{ArOCH}_2\text{OAr}]$ on reaction time, through parameter identification [14]. The estimated results are presented in Table 2.

4. Results and discussion

4.1. Identification of the reaction mechanism

In the present work, no formation of byproduct was observed. Therefore, the conversion of 2,4,6-tribromophenol (X) relating to the two products are

$$X = [\text{mole of ArOCH}_2\text{OAr} + \text{mole of ArOCH}_2\text{OAr}] / [\text{ArOH}]_i$$

The conversion of 2,4,6-tribromophenol at various temperatures is shown in Fig. 1. In the two-phase reaction, the presence of ArOQ, which was synthesized from the reaction of 2,4,6-tribromophenol (ArOH) and QBr in an alkaline solution of KOH, was detected in the organic phase. It is thus obvious that ArOQ was transferred to the organic phase from the aqueous phase. In addition, ArOQ can also be synthesized from the reaction of ArOK and QBr. The mono-substituted product ArOCH_2Br and bi-substituted product ArOCH_2OAr were also synthesized from the reaction of ArOQ and CH_2Br_2 in the absence of water. Thus, the reaction mechanisms shown in Eq. (2) is proposed.

The ion-pair extraction mechanism operating in such reactions is proposed by Starks [5]. The active catalyst (ArOQ), which is produced from the reaction of ArOK and TBAB in the aqueous phase, transfers to the organic phase reacts with the organic-phase reactant. In this work, large amounts of ArOQ (about 99% of the catalyst) were detected in the organic phase. This confirms that ArOQ exists in the organic phase and reacts with CH_2Br_2 in that phase. The nucleophilic agent (ArO^-) is actually carried by the quaternary ammonium cation (Q^+ , or R_4N^+) to the organic phase for this reaction.

As shown in Fig. 2, a plot between T_1 -values and t -values at various temperatures yields a straight line of slope k_1 , corresponding to the organic-phase reaction. The values of k_1 and k_2 , as obtained from the organic-phase reaction at various temperatures, are given in Table 1. The Arrhenius plots of $\ln(k_1)$ vs. $1/T$ and $\ln(k_2)$ vs. $1/T$ were plotted. The activation energies corresponding to k_1 and k_2 were thus found to be 20.33 and 16.98 kcal/mole, respectively. It is obvious that the k_2 -value is much larger than the k_1 -value. Nevertheless, the concentration of organic-phase reactant (CH_2Br_2) is much larger than that of the first product (ArOCH_2Br). Thus, the first product (ArOCH_2Br) is still detected during the reaction.

In order to compare the reaction rate in aqueous phase and the mass transfer rate of ArOQ from the aqueous phase to organic phase with the overall reaction rate, two extra experiments for the formation of ArOQ by different sequential addition of reactants in the two-phase reaction were carried out in the work. The first experiment involved mixing of CH_2Br_2 (30 ml), water (10 ml), KOH (0.4 g), and 2,4,6-tribromophenol (10 g) in a reactor at 60°C. Then, the TBAB catalyst (0.078 g) was added to start the reaction (i.e., ArOQ not formed). Thus, in this reaction, TBAB catalyst was added after CH_2Br_2 . Thus, ArOQ is formed in situ during the reaction. In the second experiment, water (10 ml), KOH (0.4 g), 2,4,6-tribromophenol (1 g) and TBAB (0.078 g) were mixed in the reactor at 60°C, and then CH_2Br_2 is added to start the reaction (i.e., ArOQ formed before starting the reaction). Both the contents of ArOQ and the conversion of 2,4,6-tribromophenol, and the yield of mono-substituted and bi-substituted products were obtained from these two experiments carried out at low KOH concentration and are presented in Figs. 3–5.

As shown in Fig. 3, the formation of ArOQ either prior to the addition of CH_2Br_2 or after the addition of CH_2Br_2 does not influence the final result, i.e., the reaction is not affected by

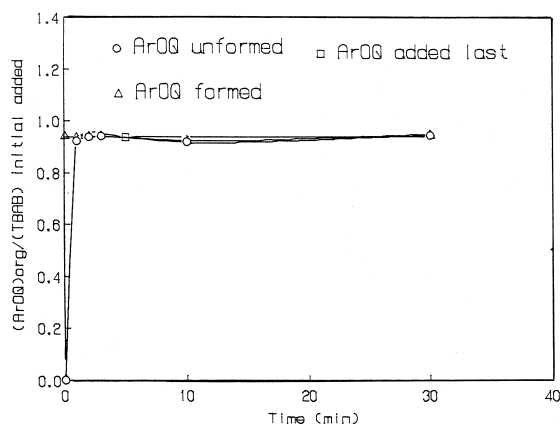


Fig. 3. Effect of the sequence of addition of reactants on the distribution of ArOQ in the organic phase at low concentration of KOH; 1 g of 2,4,6-tribromophenol, 0.4 g of KOH, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm. ArOQ unformed: TBAB added after the addition of CH₂Br₂; ArOQ formed: TBAB added before the addition of CH₂Br₂.

the sequence of addition of CH₂Br₂ and ArOQ. Also, as shown in Fig. 3, no ArOQ was detected in either of the two phases at the beginning of the reaction for the case of ArOQ unformed. The concentration of ArOQ in the organic phase increased from zero to a certain value and then stabilized at that value within 1 min. About 95% of the catalyst in the ArOQ form (i.e., $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$) at relatively low

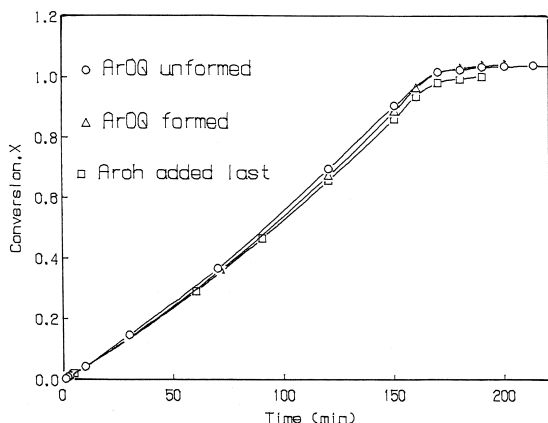


Fig. 4. Effect of the sequence of addition of reactants on the conversion of CH₂Br₂ at low concentration of KOH; 1 g of 2,4,6-tribromophenol, 0.4 g of KOH, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm. ArOQ unformed: TBAB added after the addition of CH₂Br₂; ArOQ formed: TBAB added before the addition of CH₂Br₂.

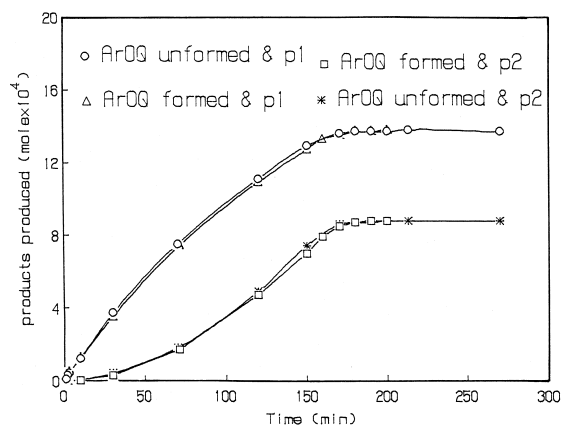


Fig. 5. Effect of the sequence of addition of reactants on the yields of products at low concentration of KOH; 1 g of 2,4,6-tribromophenol, 0.4 g of KOH, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm [P₁: ArOCH₂Br, P₂: ArOCH₂OAr].

KOH concentration stays in the organic phase. Actually, the reaction is expected to be complete in about 2–3 h. This result indicates that the transfer rate of ArOQ from aqueous phase to the organic phase is fast compared to the rate of the organic-phase reaction. The resistance to this mass transfer is negligible compared to the reaction rate in the organic phase. The induction period, in which the mass transfer is important during the early stages of the reaction, has been found to be short in the present study, i.e., the effect of mass transfer can be neglected for agitation speeds greater than 600 rpm.

In addition, Fig. 3 also shows that the reaction is not affected by the sequence of addition of the reactants. Furthermore, as shown in Figs. 4 and 5, the conversion of 2,4,6-tribromophenol and the yields of mono-substituted and bi-substituted products are also not influenced by the sequence of addition of CH₂Br₂ and ArOQ. Thus, the reaction in the aqueous phase appears to be fast and the resistance to this reaction in the aqueous phase appears negligible compared to the reaction rate in the organic phase. Similar results were obtained for the reaction carried out at high KOH concentration.

In addition, experiments were also carried out to investigate the transfer rate of QBr from

organic phase (30 ml of CH_2Br_2) to the aqueous phase (10 ml of H_2O). At the beginning of these mass transfer experiments, TBAB catalyst was dissolved in the organic solvent (0.008 M) and an appropriate amount of water was added. No QBr was detected in the aqueous phase at the beginning of these experiments. However, QBr was detected after 1 min and its concentration (0.0025 M) in the aqueous phase stabilized after 1 min. This result also suggests that the transfer of QBr (or TBAB catalyst) is fast, compared to the reaction in the organic phase, which usually takes 2–3 h to complete. Therefore, it is expected that the yields of the first and final products are independent of the sequence of addition of ArOQ catalyst or CH_2Br_2 .

4.2. Effect of the concentration of KOH on the reaction

In the PTC/OH catalyzed reaction, the reaction rate is known to be greatly affected by the concentration of the alkaline compound. It may influence the distribution of ArOQ between the two phases, as well as the hydration of ArOQ in the organic phase, and hence the reaction rate. Thus, the effect of KOH on the overall reaction rate carried out in 10 ml of water, was investigated in this study. It was found that the reaction rate does not monotonously increase or decrease with the amount of KOH in the aqueous phase. Hence, it was interesting to study the effect of the concentration of KOH on the reaction rate in more detail.

4.2.1. Less than 2.5 g of KOH

As can be seen from Fig. 6, the reaction rate increases when the amount of KOH is increased from 0.1 g to 0.3–0.4 g, and then decreases when the amount of KOH is further increased to 2.5 g. The change in the concentration of ArOQ in the organic phase as a function of time at various KOH concentrations is shown in Fig. 7. It can be seen that more than 90% of $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$ stays in the organic phase when 0.1 g to 0.3–0.4 g of KOH is

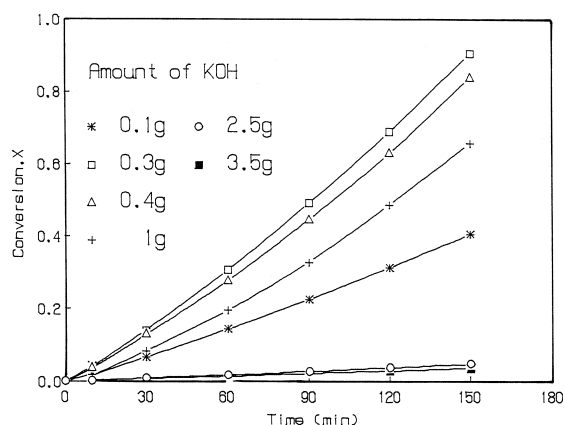


Fig. 6. Effect of the amount of KOH on the conversion of CH_2Br_2 at low concentration of KOH; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H_2O , 30 ml of CH_2Br_2 , 60°C, 700 rpm.

used. However, only about 25% of $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$ remains in the organic phase when the amount of KOH used is 2–2.5 g. This effect of the amount of KOH on $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$ is presented in Fig. 8. For the amount of KOH between 0.4–2.5 g, $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$ decreases with the increase in the amount of KOH. Thus, from Figs. 8–10, it can be seen that the apparent rate constants, $k_{1,\text{app}}$ and $k_{2,\text{app}}$ obviously depend on the distribution of ArOQ in the organic phase.

4.2.2. 2.5 g to 5 g of KOH

Figs. 6 and 11 shows that the reaction rate is insensitive to the variations in the amount of KOH from 2.5 g to 5 g. Also, as shown in Fig. 7, only 25% of $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$ stays in the organic phase when 2.5 g of KOH is used. Nevertheless, more than 90% of $(\text{ArOQ})_{\text{org}}/(\text{TBAB})_{\text{initial added}}$ remains in the organic phase when 5 g of KOH is used. This result thus suggests that the content of ArOQ in the organic phase increases with increasing KOH. However, the reaction rate does not correspondingly increase with the increase in ArOQ. This peculiar phenomenon can be explained by arguing that the activity of ArOQ decreases with increase in the amount of KOH [11,12].

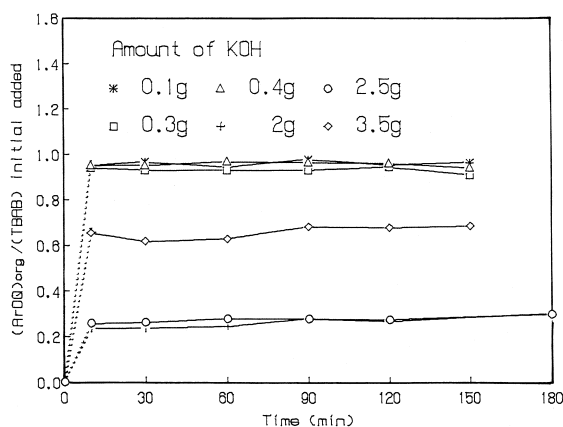


Fig. 7. Effect of the amount of KOH on the concentration of ArOQ in the organic phase at low concentration of KOH; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm.

4.2.3. More than 5 g of KOH

As shown in Fig. 11, the reaction rate reduces when 5 g of KOH is used. Only 5% conversion of 2,4,6-tribromophenol is obtained after 3 h of reaction. However, the reaction rate increases abruptly when the amount of KOH is increased from 5 g to 25 g. However, with more than 25 g of KOH, the rate does not increase further. Thus, the two factors, which affect the reaction rate consequent to variations in the concentration of alkaline agent in the aqueous phase, are: (a) distribution of ArOQ between the

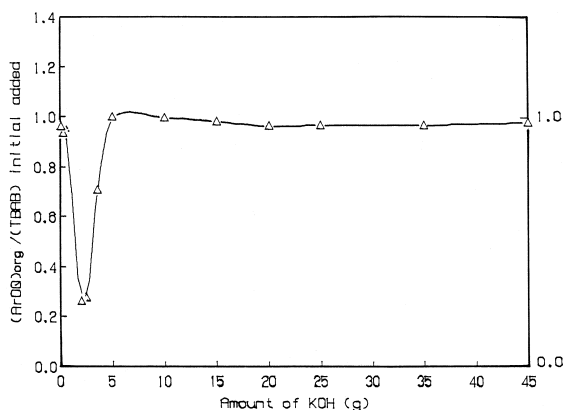


Fig. 8. Effect of the amount of KOH on the concentration of ArOQ in the organic phase; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm.

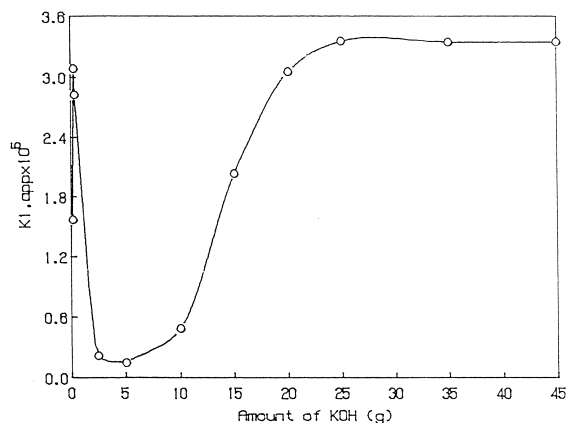


Fig. 9. Effect of the amount of KOH on the $k_{1,app}$ -value; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm.

two phases, and (b) hydration of ArOQ in the organic phase, i.e., the activity of ArOQ within the organic phase.

Variations in the value of the ratio $(ArOQ)_{org}/(TBAB)_{initial\ added}$ at various amounts of KOH in the two-phase reaction at large KOH concentrations, are shown in Fig. 12. It can be seen that the concentration of ArOQ remains at a constant value throughout the reaction and is independent of the amounts of KOH at high concentration. This experimental data supports our preliminary assumption of constant concentration of ArOQ in the organic phase. The cor-

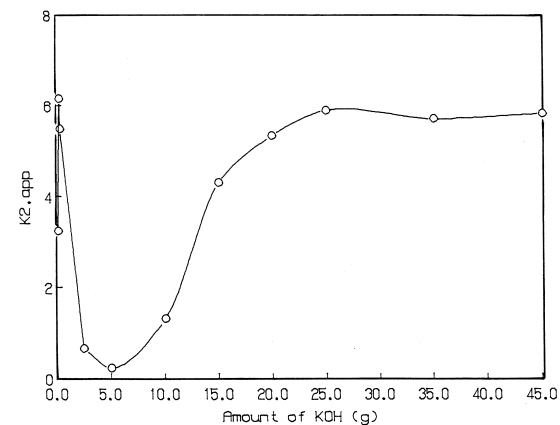


Fig. 10. Effect of the amount of KOH on the $k_{2,app}$ -value; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H₂O, 30 ml of CH₂Br₂, 60°C, 700 rpm.

responding intrinsic rate constants (k_1 and k_2) are given in Table 2. At high alkaline concentration, the obtained k_1 and k_2 values are the same as those obtained from the organic-phase reactions.

As can be noted from Table 2, the intrinsic rate constants k_1 and k_2 depend on the amount of KOH. The magnitudes of both k_1 and k_2 increase with increase in the amount of KOH. The reason is that hydration of ArOQ in the organic phase influences the reaction rate. During the PTC reaction, water is simultaneously present with ArOQ into the organic phase. The activity of ArOQ thus decreases due to the shielding effect of water [11] at low KOH concentration (2.5 g to 5 g of KOH). On the other hand, dehydration of ArOQ becomes significant when the amount of KOH is further increased (larger than 5 g of KOH). We may therefore infer that the extent of hydration is increased when 5 g of KOH is used and it greatly increases when the amount of KOH is further increased. Thus, the reaction rate greatly increased with increase in the amount of KOH from 5 g to 25 g. At 25 g of KOH, the phenomenon of hydration disappears. Thus, the magnitudes of intrinsic rate constants (k_i -values; $i = 1, 2$) obtained in this study contain the influence of hydration. These are not the real

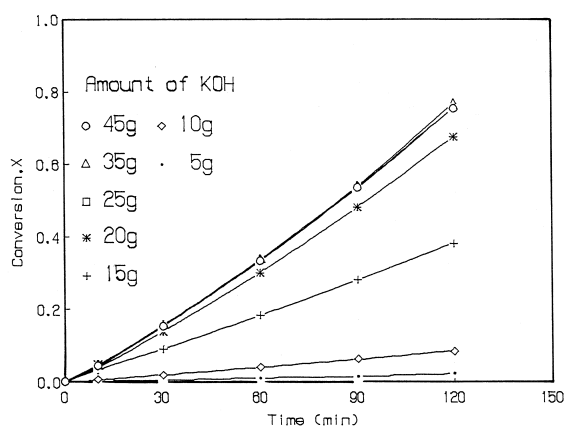


Fig. 11. Effect of the amount of KOH on the conversion of CH_2Br_2 at high concentration of KOH; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H_2O , 30 ml of CH_2Br_2 , 60°C, 700 rpm.

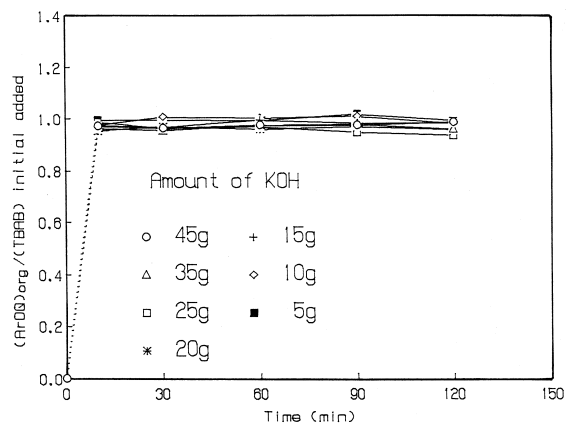


Fig. 12. Effect of the amount of KOH on the concentration of ArOQ in the organic phase at high KOH concentration; 1 g of 2,4,6-tribromophenol, 0.078 g of TBAB catalyst, 10 ml of H_2O , 30 ml of CH_2Br_2 , 60°C, 700 rpm.

intrinsic rate constants of the reaction wherein there is less than 25 g of KOH. Thus, the k_i -values obtained for KOH concentrations larger than 25 g should be the intrinsic rate constants because the influence of hydration is eliminated. The average values of the intrinsic rate constants obtained in this study are $k_1 = 4.27 \times 10^{-3}$ 1/mole/min, and $k_2 = 0.74$ 1/mole/min, respectively.

5. Conclusion

In the present work, dibromomethane is used as organic-phase reactant as well as organic solvent in the synthesis of bi(2,4,6-tribromophenoxide)methane from the reaction of 2,4,6-tribromophenol and dibromomethane in an alkaline solution of KOH/dibromomethane two-phase medium, catalyzed by TBAB. The organic-phase reaction has been found to be the rate-determining step. The mass transfer of active catalyst ArOQ or TBAB between the two phases and the rate of aqueous-phase reactant are fast. Two products, viz. α -bromomethyl 2,4,6-tribromophenyl ether and bi(2,4,6-tribromophenoxide)methane were obtained. The conversion of 2,4,6-tribromophenol first increases, then decreases and then again increases up to a limiting value with continuous increase

in the amount of KOH. This peculiar phenomenon is explained by arguing that the activity of ArOQ, distribution of ArOQ between the two phases and hydration of ArOQ in the organic phase, are affected by the amount of KOH. The magnitudes of intrinsic rate constants (k_1 and k_2) of the organic-phase reactions are experimentally determined at high alkaline concentrations, to be 4.27×10^{-3} l/mole/min and 0.74 l/mole/min, respectively. The corresponding activation energies for these two organic-phase reactions are 20.33 and 16.98 kcal/mole, respectively.

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