Synthesis of Formaldehyde Acetals by Phase Transfer Catalysis

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By employing phase transfer catalysis, formaldehyde acetals were synthesized from the reaction of alcohols and dibromomethane at moderate temperatures. Using a high alkaline concentration, the reaction could be improved to obtain a 100% yield by reacting dibromomethane and 1-alcohol employing tetrabutylammonium bromide (TBAB) as a phase transfer catalyst. Six kinds of alcohols with various structures, four sorts of solvents with various dielectric constants and seven types of catalysts were examined to test their reactivities to the reactions. Only one unique product with two alkoxides substituents was observed which indicated the presence of a rather fast reaction rate during the second reaction of the organic phase. The reaction was dramatically enhanced by adding a small amount of quaternary ammonium salt (QX) to obtain a 100% yield utilizing the alcohols with nonbonding electron pairs within a short period of reaction time. The conversion was also observed to be strongly dependent upon the structure of the quaternary ammonium salts. The reaction rate and the product yield were satisfactorily accounted for the chemical reaction equilibrium of alcohols and KOH in the aqueous phase, the hydration of the active catalyst (QOR) in the organic phase and the distribution of QOR between two phases.

Methods of synthesizing ethers, i.e. Williamson synthesis and alkoxymercuration have been developed in organic chemistry. In recent years, the most popular way of synthesizing these ethers has been in employing expensive dialkyl sulfate as an alkylating agent for the reaction of dialkyl sulfate and alkoxide salt in aqueous solution to obtain the product yield.[1—4]. Thus, the low cost alkyl halides are suitable in serving as the alkylating agent in the organic synthesis of ethers by the alkylation. However, the reaction rate in the organic phase which utilizes alkyl halides as the reactants is a quite slow process. The synthesis of ethers is fortunately well known to be capable of being enhanced by adding a small amount of quaternary ammonium salt in the two-phase reaction.[5—7]

The synthesis of dialkoxymethane was often previously obtained from the reaction of alcohols and formaldehyde.[8] Webb, Duke, and Smith[9] employed alcohol and aldehyde for synthesizing acetals and low molecular weight oligoformals, $RO(CH_2O)_xR$. In 1967, Sato et al.[8] carried out experiments for the reaction of alcohol and polyphosphoric acid in a DMSO solvent. A wide molecular weight distribution of the various formaldehyde dialkyl acetals was obtained. Effectively obtaining a uniquely desired product by utilizing such a method is therefore very difficult. Additionally, the separation and purification of the desired product was also difficult to be implemented.

The formaldehyde acetals were recently synthesized by Cornelis and Laszlo[10] by reacting alcohol and dichloromethane in a 50% sodium hydroxide solution applying Tixoget VP clay as a catalyst. However, completing the reaction for such a low reaction rate takes roughly three days. The technique of phase transfer catalysis (PTC) was employed in 1976 by Dehmlow and Schmidt[11] for synthesizing formaldehyde acetals from alcohols and dichloromethane in the aqueous phase. Only 50—60% of the yield was obtained after 15 h. The primary purpose of the present study lies in synthesizing formaldehyde acetals from the reaction of alcohols and dibromomethane in an alkaline solution of KOH/organic solvent by phase transfer catalysis.[12—14] The product yield was observed to be low in employing a 50% potassium hydroxide solution owing to the fact that dibromomethane is not an effective organic substrate. The primary motivation of the present research lies in promoting the reaction rate and also in increasing the product yield by employing a rather quite high alkaline concentration (or employing a solid form of alkali) in the syntheseis of acetals by reacting alcohols and dibromomethane in a phase transfer catalytic reaction. The effect of the amount of KOH on the concentration of the active catalyst (QOR) in the organic phase, which would consequently influence the reaction rate, is discussed. A unique product of high yield is produced by reacting alcohols and dibromomethane in a fast two-phase chemical reaction.

Experimental

Materials: Those reactants, i.e. 1-C_4H_9OH, 1-$C_7H_{15}OH$, 1-$C_8H_{17}OH$, *cyclo*-$C_6H_{11}OH$, $C_2H_5OC_2H_4OH$, $C_2H_5OC_2H_4OC_2H_4OH$, dibromomethane, and other reagents were all guaranteed grade (G.R.) chemicals.

Procedures: (A) Two-Phase Phase Transfer Catalytic Reaction. The reactor was a 150 ml three-neck Pyrex flask, serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the feed. The reactor was submerged into a constant temperature water bath in which the temperature could be controlled to within ±0.1 °C. Known quantities of KOH and the reactant were prepared and dissolved in water and solvent for 1 h at an appropriate temperature. The solution was then introduced into the reactor, which was thermostated at the desired temperature. Measured quantities of dibromomethane and internal standard (toluene), which were also

at the desired temperature, were then added to the reactor. To initiate the reaction, a quaternary ammonium salt (QX) was added to the reactor. Following completion of the reaction, the agitator was turned off, and the organic and aqueous phases of the solution were separated in a few seconds. After separation, 0.5 ml of the organic-phase sample was immediately diluted with an excess amount of water (4 ml) and solvent (4 ml) at 4 °C so as to quench the reaction or with anhydrous magnesium sulfate and solvent (chlorobenzene) (4 ml) so as to terminate the reaction, depending upon the solubility of the product in water. Taking a sample generally took less than 20 s.

The products were analyzed by GC, mass spectrum, IR, and NMR. Gas chromatography (GC) was carried out by utilizing a Shimadzu GC-9A instrument. A 7G 0.525mm×15 m glass column which contains 100% poly(dimethylsiloxane) was employed for separating the components and in experimentally analyzing them. The detector is an FID and the injection temperature is 220—250 °C. Mass spectra were obtained from a JEOL JMS-100 mass spectrometer at the ionization potentials of 12 eV. The infrared spectrophotometer (IR) is a product of Perkin–Elmer, Model 983. The spectra of ^{1}H NMR were obtained in the $CDCl_3$ solvent by a 400 MHz, Brucker Co.

(B) Detection of the Active Catalyst (QOR) in the Organic Phase. Two experimental sets were conducted in this study. First, the experiments were carried out such that the active catalyst ($[(C_4H_9)_4N]OR$, QOR) would become synthesized in the aqueous phase from the reaction of alcohols and KOH in the aqueous solution with the addition of TBAB catalyst. QOR would consequently be transferred to the organic phase without containing dibromomethane. The concentration of QOR in the organic phase was measured by the GC instrument. Second, QOR was directly detected and measured from the organic phase in the phase transfer catalytic reaction. The data obtained from these two experimental procedures were the same for utilizing the same reaction conditions.

The active catalyst (QOR) was analyzed by employing the thermolysis of quaternary ammonium salts, commonly known as "Hoffmann Elimination".[15] Gas chromatography was carried out for the sake of analyzing the tertiary amine applying a Shimadzu GC-9A instrument.

(C) The Number of Hydration Accompanied by the Active Catalyst (QOR) Transferring to the Organic Phase. Measured quantities of alcohol and toluene were added to the alkaline solution of KOH/organic solvent. The solution was agitated for 1 h at 50 °C. The water content in the organic phase was measured by Karl–Fischer titration. The mixture was next continuously agitated for 10 min after adding a measured quantity of the TBAB catalyst. Dibromomethane was then added to the mixture so as to initiate the reaction. An aliquot sample of the organic phase was withdrawn from the solution at chosen time for the sake of measuring the water content via Karl–Fischer titration. The number of hydration was thus obtained by subtracting the water content in the blank test (i. e. without an addition of TBAB catalyst) from the water content in the reaction run (i. e. with an addition of TBAB catalyst) and dividing the concentration of QOR. The water content in the organic phase was observed to be insensitive to the reaction time and also highly dependent upon the content of KOH in the solution significantly.

(D) Analysis and Purification of the Desired Product. Two procedures were carried out in this study for analyzing the products, depending upon the solubility in water. For products which were partially soluble in water, i. e. $(C_2H_5OC_2H_4O)_2CH_2$ and $(C_2H_5OC_2H_4OC_2H_4O)_2CH_2$, the sample (0.5 ml) was withdrawn from the reactor and put into a flask containing anhydrous magnesium sulfate and solvent (chlorobenzene) (4 ml) at −4 °C. By this, the reaction was terminated and the product was pushed into the organic phase (chlorobenzene). Those organic soluble products are $(1\text{-}C_4H_9O)_2CH_2$, $(1\text{-}C_7H_{15}O)_2CH_2$, $(1\text{-}C_8H_{17}O)_2CH_2$, and $(cyclo\text{-}C_6H_{11}O)_2CH_2$. The sample (0.5 ml), which was withdrawn from the reactor, was put into a flask containing 4 ml of water and 4 ml of chlorobenzene at 4 °C so as to terminate the reaction. The organic-aqueous two phases were next separated by centrifugation. The organic sample obtained from these two different procedures were analyzed by GC.

Acetals are theoretically more stable in an alkaline solution than in an acidic solution. The relative impurities in the reaction solution are alcohols, aldehydes, water, and quaternary ammonium salts. The organic soluble products were washed several times by an alkaline solution to remove quaternary ammonium salt. Water and alcohol were next removed from the product by sodium metal. Aldehyde could be removed by precipitation following polymerization. The solvent was finally stripped by applying a rotary vacuum evaporator. The purity of the product was indicated by GC analyzer to be greater than 98%.

Results and Discussion

The overall chemical reaction can be expressed as

$$2ROH + 2KOH + CH_2X_2 \xrightarrow{QX} CH_2(OR)_2 + 2H_2O + 2KX \quad (1)$$

where ROH and CH_2X_2 represent the alcohol and the dibromomethane respectively. Actually, alcohol was added to the aqueous alkaline solution and the organic solvent mixture in the presence of a small amount of the quternary ammonium salt (QX). Alcohol first reacted with KOH so as to form potassium alkoxide (ROK) in the aqueous phase. ROK next further reacted with QX in the aqueous phase to produce quaternary ammonium alkoxide (QOR) which is more soluble in the organic solvent. Dibromomethane next reacted with QOR in forming the desired product, dialkoxymethane $CH_2(OR)_2$, the unique product in the organic phase. The reaction steps can be proposed as

$$\begin{array}{l} 2ROH + 2KOH \rightleftarrows 2ROK + 2H_2O \\ \qquad\qquad\qquad\quad \downarrow \\ 2KX \;\; + 2QOR \leftarrow 2ROK + 2QX \\ \qquad\quad \downarrow \qquad\qquad\quad \nwarrow \qquad\qquad (aqueous) \\ \hline \qquad\qquad\qquad\qquad\qquad\qquad (organic) \\ CH_2X_2 + QOR \xrightarrow{k_1} CH_2(OR)X + QX \\ CH_2(OR)X + QOR \xrightarrow{k_2} CH_2(OR)_2 + QX \end{array} \quad (2)$$

The function of the well-known Williamson synthesis of ethers lies in employing the reaction of sodium

alkoxide and alkyl halide in an organic solution. Nevertheless, the synthesis of sodium alkoxide was carried out by reacting sodium metal and alcohol in an anhydrous condition. Two reaction steps are suggested here to occur in the organic phase. The present reaction system is observed from a comparison of the phase transfer technique with that of the conventional one to have the following advantages of:

(1) First synthesizing potassium alkoxide (ROK) is unnecessary. ROK is in situ synthesized during the two-phase reaction. The decomposition of ROK which occur due to humidity in the air can therefore the prevented;

(2) The product becomes easily separated from the reactant once a high conversion of the product is obtained. The product is obtained simply by evaporating the solvent;

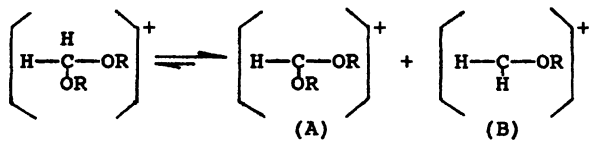
(3) A high yield of product can be obtained.

The product yield obtained by PTC is generally dependent upon the structure of the reactants, solvents, phase transfer catalysts, and the amount of KOH being utilized in the reaction. In those factors which affect the conversion of the reactants, the conversion of dibromomethane is defined as X,

$$X = 1 - [CH_2Br_2]/[CH_2Br_2]_0 \quad (3)$$

where the subscript "0" represents the initial concentration of dibromomethane presented in the reaction.

A. Identification of the Product. (i) Mass Spectrum. The products obtained from the reactants, **1**, **2**, and **3** are depicted in Table 1. They are saturated acetals of a long chain without branch. The fragment of these three products in a mass spectrum analysis is similar to that of ethers. However, the chief difference between acetals and ethers is that acetals would not generate a molecular peak. The reason is that the stability period of the molecular ion of the acetal compound is comparatively short ($<10^{-5}$ s).[16] Nevertheless, the following cation was formed with greater stability. Therefore, form (A), whose molecular weight is less than that of the original acetal by **1**, can be detected by the sensor of the mass spectrum, i. e.



(4)

Product **4** is a cyclic saturated acetal, which is relatively difficult to break two C–C bonds from which the characteristics of the fragment contains C_2 and C_4. Products **5** and **6** are polyethers which contain multi C–O–C groups with the molecular formula, $[C_2H_5O(C_2H_4O)_n]_2CH_2$. The stability of the molecular ion becomes decreased with the augmentation of the n-value. The peak can therefore not be detected since the presence of the product molecular ion is a quite short time period. However, the final product can be detected via the mass spectrum.

(ii) Infrared Spectrum and NMR Spectrum. The products obtained from the phase transfer catalytic reaction were detected via the infrared spectrum and NMR spectrum.[16] The absorbed frequencies of the corresponding bond by the infrared spectrum and the chemical shifts of the obtained dialkoxymethane are consistent with previously published documents.

Dibromethane, which is employed as the reactant, is generally not an effective organic substrate. Except for the absence of other organic substrates, dibromomethane then has the opportunity to react with other reactant owing to its low reactivity. Two sequential reaction steps are illustrated in Eq. 2 to be presented in the organic phase. On the basis of experimental observations, the first product, $CH_2(OR)X$, was not detected during and after the reaction. The second reaction rate is indicated by these results to be quite fast, as compared to the first reaction rate in the organic phase. The first reaction in the organic phase would therefore become the rate-controlling step. A high yield could be obtained in synthesizing formaldehyde acetals via phase transfer catalysis. For example, as shown in Table 1, a 83.22% conversion was obtained by employing 1-butanol as the reactant within 2 h.

The reaction, which follows Eq. 1, can lead towards a higher product yield by employing different kinds of reactants. The factors which affect the reaction rate are: (i) the acidity of the leaving group of the substrate, (ii) the acidity of the nucleophile, (iii) the polarity of solvent, and (iv) the steric effect. For (i), the reactivity of the substrate increased by increasing the acidity of the substrate, i. e. the reactivity of bromide ion is greater than that of chloride ion. In the experiments, the reaction rate as well as the yield was rather low whenever dichloromethane was employed as the substrate. Dibromomethane is therefore more reactive than that of dichloromethane. For (ii), the reactivity of the nucleophile becomes decreased with the increase of the acidity of the nucleophile. In general, a high basicity of the nucleophile was obtained by using an alkyl group with a nonbonding electron pair, i. e. 2-ethoxyethanol or 2-(2-ethoxyethoxy)ethanol. For (iii), solvents of appropriate polarity are recommended to decrease the solvation for the sake of enhancing the reaction rate. For (iv), the steric effect is a comparatively relevant factor which affects the reaction rate in synthesizing organic chemicals.

B. Factors Affecting the Conversion. (i) Effects of the Amount of Water. Table 2 illustrates the effects of quaternary ammonium salt and the amount of water upon the conversion of $C_2H_5OC_2H_4OH$ (Runs 1—4) and 1-C_4H_9OH (Runs 5—13) so as to produce $(C_2H_5OC_2H_4O)_2CH_2$ and $(1\text{-}C_4H_9O)_2CH_2$ products respectively. The conversion (also for the reaction rate) is indicated by Runs 1—3 to be highly dependent upon the addition of the phase

Table 1. Effects of the Solvents on the Conversion of Alcohols (9.17×10^{-2} mol); 10 ml of H_2O, 0.028 mol of CH_2Br_2, 30 g of KOH, 1 g of TBAB, 50 ml of Solvent, 1020 rpm, 50 °C.

Reactants		Conversion, X (%)			
		Chloro-benzene	Dibutyl ether	Xylene	Benzene
1	1-Butanol (2 h)	83.22	58.94	49.65	55.48
2	1-Heptanol (2 h)	81.44	50.16	41.94	44.90
3	1-Octanol (2 h)	82.17	52.00	46.49	49.35
4	*cyclo*-Hexanol (2 h)	81.37	53.60	48.94	47.89
5	2-Ethoxy-ethanol (0.5 h)	92.82	87.86	79.61	73.86
6	2-(2-Ethoxy-ethoxy)-ethanol (0.5 h)	98.58	98.87	96.21	92.21
	Dielectric constant	5.62	3.08	2.27	2.28

Table 2. Effects of the Quarternary Ammonium Salts and Water on the Conversion of $C_2H_5OC_2H_4OH$ and C_4H_9OH

Run no.	Reaction time/h	H_2O g	CH_2Br_2 g	CH_2Cl_2 g	Conversion[a] (X/%)	
$(C_2H_5OC_2H_4O)_2CH_2$ product						
1	0.5	10	4.8	—	92	(Adding PTC)
2	0.5	10	4.8	—	27	(No PTC)
3	2	10	4.8	—	52	(No PTC)
4	6	50	4.8	—	42	(Adding PTC)
$(C_4H_9O)_2CH_2$ product						
5	2	0	4.8	—	83	(Adding PTC)
6	2	10	4.8	—	83	(Adding PTC)
6a	3	10	4.8	—	90	(Adding PTC)
7	6	10	4.8	—	1.3	(No PTC)
8	9	10	4.8	—	2.1	(No PTC)
9	2	30	4.8	—	29	(Adding PTC)
10	2	50	4.8	—	11	(Adding PTC)
11	2	75	4.8	—	7.1	(Adding PTC)
12[b]	2	10	—	2.35	6.9	(Adding PTC)
13[b]	3.5	10	—	2.35	11.9	(Adding PTC)

a) 9.17×10^{-2} mol of alcohol, 50 ml of chlorobenzene (solvent), 30 g of KOH, 1 g of TBAB catalyst, 50 °C. b) Dichloromethane was used as the organic reactant.

transfer catalyst in the reaction of $C_2H_5OC_2H_4OH$ and CH_2Br_2. By adding a slight amount of quternary ammonium salt, the conversion becomes increased from 27 to 92% at 0.5 h of reaction time. A higher conversion (also for the reaction rate) is indicated by Runs 3 and 4 to be able to be obtained employing a small amount of water, even though the reaction system lacks a phase transfer catalyst.

For the reaction of 1-butanol and dibromomethane in a two-phase reaction, the results are also exhibited in Runs 5—11, Table 2. A 83% of conversion 1-butanol is indicated by Run 5 to have been obtained when no water was added to the reaction system. However, water is produced from the reaction of KOH and 1-butanol. Therefore, the conversions of 1-butanol for the cases of adding a small amount of water (Runs 6 and 6a) and without adding water (Run 5) are almost the same. By adding a small amount of quaternary ammonium salts, the conversion is increased from 1.3% (or 2.1%) to 83% (Runs 6,7, and 8). The conversion is indicated by Runs 9—11 to be relatively low when utilizing a large amount of water (>30 ml of water) even if the reaction is in the presence of transfer catalysis. Thus, a low amount of water and the addition of quternary ammonium salt to the reaction system is recommended for the sake of obtaining a high yield of the acetals.

Additionally, the acidity of the bromide ion is greater than that of the chloride ion. Therefore, as expected, the product yield obtained from the reaction of 1-butanol and dichloromethane is quite low. These results

are also demonstrated in Runs 12—13, Table 2.

(ii) Effects of the Alcohol Reactants. The effects of the nucleophilic agent upon the yield of the products are depicted in Table 1. The primary alcohols (1-C_4H_9OH, 1-$C_7H_{15}OH$, and 1-$C_8H_{17}OH$) notably have the same conversion. This occurs since these three reactants have the same pK_a values which are approximately equal to 16. The equilibrium of chemical reaction of 1-alcohols and potassium hydroxide in the aqueous phase will therefore obviously become an important factor which affects the product yield and the reaction rate. The product yield from the reaction of cyclohexanol and dibromomethane was 81% which was almost the same as that obtained from the reaction of 1-butanol and dibromomethane. Additionally, there is an ethoxyl group for the 2-ethoxyethanol and 2-(2-ethoxyethoxy)ethanol, which possesses two nonbonding electron pairs. The basicity increased once the reactants reached an ionic state. The reaction rate was consequently enhanced. More than 90% of product yield was obtained during the first 30 min of reaction.

(iii) Effects of the Solvents. Dibromomethane reacts with tetrabutylammonium alkoxide (QOR) in the organic phase in forming the first and final products. Dibromomethane, which possesses weak dipole moment, would form a weak dipole–dipole bond with the organic solvent. However, this kind of dipole–dipole bond does not significantly affect the reaction rate. Nevertheless, QOR would solvate with a polar organic solvent. This solvation would result in less energy in the nucleophilic agent than that in the transition state compound. The activation energy therefore becomes high due to the solvation of QOR with a high polar solvent which is unsuitable in the present reaction system. The low polarity solvent would neither solvate with QOR, nor pull the tetrabutylammonium ion (Q^+) apart from the alkoxide ion (OR^-). Thus, the reactivity of the low polar solvent is also low. The effects of the solvent (or dielectric constant) upon the conversion is shown in Table 1. Chlorobenzene and dibutyl ether with the appropriate polarity are observed in this table to be the best solvent to obtain a higher yield of product for various sorts of alcohols.

(iv) Effects of the Phase Transfer Catalysts. Seven types of quaternary ammonium salts have been employed in this study for testing their reactivities in the reaction of alcohol. The effects of the phase transfer catalyst upon the conversion are indicated in Table 3. A high conversion is observed with TBAH or TBAB as a phase transfer catalyst for various sorts of alcohols. An emulsion solution has notably formed once NCNTAB was employed as a phase transfer catalyst. Separating the product from the emulsion solution is generally difficult. NCNTAB is therefore unsuitable to serve as a phase transfer catalyst in the present reaction system.

(v) Effects of the Amount of KOH. The reactivity of dibromomethane is generally quite low. For obtaining the product from the reaction of alcohol and dibromomethane, the role of adding KOH becomes a relatively important factor which affects the conversion of the reactants. Table 4 depicted the experimental results for the effects of the amounts of KOH upon the conversion of 1-butanol in a phase transfer catalytic reaction. The conversion is observed in this table to be highly dependent upon the amount of KOH added to the reaction system. Low conversion was obtained utilizing a low amount of KOH. Only 4.1% of conversion of dibromomethane is exhibited in Table 4 to have been obtained for using 5 g of KOH which is equivalent to 50% of KOH in the aqueous solution. The concentration of KOH for employing 5 g of KOH in this study is substantially greater than that of the common dosage utilized during the two-phase phase transfer catalytic reaction.[17,18] The conversion has increased with the augmentation of KOH amount. A high concentration of KOH (or large amount of KOH) is therefore recommended in the reaction for the sake of obtaining a higher acetal yield.

Alkaline was usually added in excess amount relative to its stoichiometric quantity during the two-phase phase transfer catalytic reaction for synthesizing ethers. A 15% alkaline solution would generally be high enough to obtain a rather fast chemical reaction rate for most cases.[17,18] However, as shown in Table 4, the product yield for synthesizing acetals by phase transfer catalysis is quite low in the present study even though a 100% alkaline solution was utilized (21% yield). The synthesis of acetals via phase transfer catalysis should therefore be carried out at a large amount of KOH (>30 g) so as to obtain a high product yield.

The effect of the amount of added KOH (or added H_2O) is clearly indicated from the data in Tables 2 and 4 to have a marked effect upon the conversion. The greatest catalytic activity observed in the reaction of dibromomethane with alcohol evidently takes place at a slight amount of water. The water added to the system is hypothesized here to have been coated upon the surface of potassium hydroxide and it is this aqueous salt coating which dissolves the TBAB catalyst and alcohol from the aqueous phase. This new region of the reaction system, the omega phase,[19] which was found in using crown ether as the catalyst, appears to be intimately related in the catalytic reaction process.

The number of hydrations, which are accompanied by the ion-pair molecules transferring from the aqueous phase to the organic phase, becomes decreased with the augmentation of the KOH content in the aqueous phase. The reaction therefore became enhanced by increasing the content of KOH in the aqueous phase. With the less hydration of reactant molecule with water, the greater degree of naked ion appears which are more reactive.[19,20] The reaction rate has become retarded by applying a large amount of water. The dependency of the number of hydration on the amount of KOH in

Table 3. Effects of the Catalysts on the Conversion of Alcohols (9.17×10^{-2} mol); 10 ml of H_2O, 0.028 mol of CH_2Br_2, 30 g of KOH, 0.003 mol of Catalyst, 50 ml of Chlorobenzene, 1020 rpm, 50 °C

Reactants	Conversion, X (%)						
	TBAB	TEAC	TBAH	BTEAC	BTBAB	NCNTAB	BTMAC
1-Butanol (2 h)	83.22	18.23	89.71	8.59	—	—	—
1-Heptanol (2 h)	81.44	15.89	72.62	11.45	—	—	—
1-Octanol (2 h)	82.17	20.40	82.75	11.21	—	—	—
cyclo-Hexanol (2 h)	81.37	8.78	81.34	4.78	—	—	—
2-Ethoxy-ethanol (0.5 h)	92.82	31.71	95.84	27.87	—	—	—
2-(2-Ethoxy-ethoxy)-ethanol (0.5 h)	98.58	73.38	99.99	69.03	82.00	81.50	59.00

TBAH: tetrabutylammonium hydroxide, TBAB: tetrabutylammonium bromide, BTBAB: benzyltributylammonium bromide, NCNTAB: hexadecyltrimethylammonium bromide, BTMAC: benzyltrimethylammonium chloride, TEAC: tetraethylammonium chloride, BTEAC: benzyltriethylammonium chloride.

the aqueous phase for the 1-octanol and 2-(2-ethoxyethoxy)ethanol reaction systems is depicted in Fig. 1. No water molecules (or very few) are observed in this figure to have been accompanied with the active catalyst (QOR), transferring to the organic phase when more than 15 g KOH was employed in the reaction. For the amount of KOH less than 15 g, the number of hydration has decreased with the increase in the amount of KOH in the aqueous phase. This tendency is consistent with the relation between the product yield and the amount of KOH, which is depicted in Table 4.

Table 4. Effects of the Amount of KOH on the Conversion of 1-Butanol (9.17×10^{-2} mol); 10 ml of H_2O, 0.028 mol of CH_2Br_2, 1 g of TBAB, 50 ml of Chlorobenzene Solvent, 2 h, 1020 rpm, 50 °C

KOH (g)	0	5	10	15	20	25	30	45	60
Conversion (X/%)	0	4.1	21	47	66	76	83	84	84

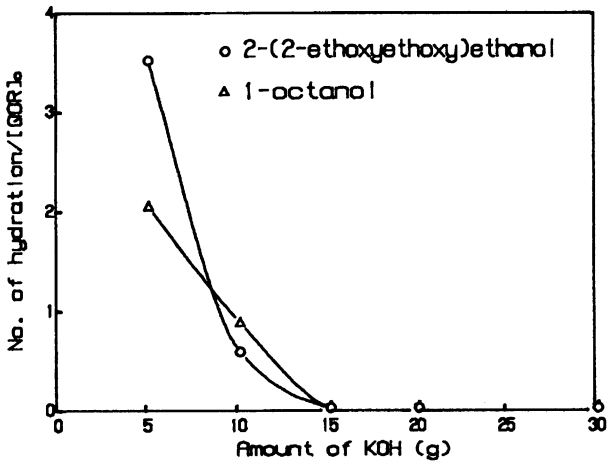


Fig. 1. The dependency of the number of hydration accompanied by the active catalyst (QOR) on the amount of KOH in the aqueous solution; 9.17×10^{-2} mol of alcohol, 10 ml of H_2O, 50 ml of chlorobenzene, 1 g of TBAB catalyst, 4.8 g of CH_2Br_2, 1020 rpm, 50 °C.

Additionally, the active catalyst (QOR) was detected in the organic phase during the two-phase phase transfer catalytic reaction. The dependency of the concentration of QOR in the organic phase on the amount of KOH being added to the reactor is provided in Table 5. 63.66% of QOR (or 56.09% of QOR) was observed in this table to stay in the organic phase when 5 g of KOH (approximately 50% of KOH) being added to the reactor for 1-octanol reaction system (or 2-(2-ethoxyethoxy)ethanol reaction system). Nevertheless, most of QOR (>90%) is observed in the organic phase when more than 10 g of KOH being added to the reactor. A high concentration of QOR in the organic phase would theoretically be favorable for a phase transfer catalytic reaction. Therefore, on the basis of the number of hydration and the distribution of the active catalyst at very high alkaline concentration (>15 g of KOH), it is reasonable to account that a high product yield (and

Table 5. Effects of the Amount of KOH on the Percentage of the Active Catalyst, ($[(C_4H_9)_4N]OR$, QOR) in the Organic Phase for the 1-Octanol and 2-(2-Ethoxyethoxy)ethanol Reaction Systems; 9.17×10^{-2} mol of Alcohol, 10 ml of H_2O, 4.8 g of CH_2Br_2, 1 g of TBAB Catalyst, 50 ml of Chlorobenzene Solvent, 2 h, 1020 rpm, 50 °C

KOH (g)	% of QOR in the organic phase				
	5	10	15	20	30
1-Octanol	63.66	91.01	91.77	91.23	94.31
2-(2-Ethoxy-ethoxoy)ethanol	56.09	92.68	92.58	93.10	92.53

the reaction rate) at high concentration of QOR in the organic phase was obtained for the present reaction system.

Conclusion

Formaldehyde acetals were synthesized in this present study by successfully reacting dibromomethane and alcohols via phase transfer catalysis. The primary advantage of employing phase transfer catalysis was observed to be that a unique product of acetals was obtained from the reaction solution at a relatively short reaction time in an high alkaline concentration solution. The effects of the reactants, solvents, amounts of potassium hydroxide, amount of water and catalysts on the product yield were studied. Alcohol with nonbonding electron pairs, i. e. 2-ethoxyethanol or 2-(2-ethoxyethoxy)ethanol, were observed to have a high reactivity to obtain a higher yield. It would be recommended that chlorobenzene or dibutyl ether with appropriate polarity is the most excellent solvent for synthesizing acetals. Among the several sorts of quaternary ammonium salts, TBAB and TBAH would provide a higher reactivity to obtain a high yield of the desired product. Only a high yield of product (or high reaction rate) could be obtained at a rather high alkaline concentration and by employing a slight amount of water in the phase transfer catalytic reaction.

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