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Tri-liquid system in the synthesis of dialkyl peroxides using tetraalkylammonium salts as phase-transfer catalysts

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ABSTRACT

A highly effective method to synthesise dialkyl peroxides from alkyl hydroperoxides and alkyl bromides in a liquid–liquid–liquid system using tetraalkylammonium salts as phase-transfer catalysts is reported. This process was conducted in the presence of highly concentrated aqueous KOH solutions and cyclohexane as an organic solvent. In a liquid–liquid–liquid system, the phase-transfer catalyst forms an insoluble third-liquid phase between the organic and aqueous phases that enables the catalyst to be recycled multiple times. Dialkyl peroxides were obtained in high yields and with 100% selectivity.

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1. Introduction

The development of catalytic processes that afford an easy separation of the reaction mixture, easy removal of the catalyst, and facile reuse of the catalyst is one of the main aims of chemical research and the chemical industry today. These characteristics are reflected in phase-transfer catalysis (PTC). Particularly, PTC methods conducted in a liquid-liquid-liquid system (L-L-L PTC) have aroused considerable interest in recent years [1-12]. Compared to conventional liquid-liquid PTC (L-L PTC), the phase-transfer catalyst for L-L-L PTC can easily be recovered and recycled because in this system, the catalyst forms a third-liquid phase between the organic and aqueous layers. Moreover, reactions conducted under L-L-L PTC conditions proceed with higher reaction rates and yields. This system is also competitive with liquid-liquid-solid systems (L–L–S PTC) because it affords easy catalyst separation without necessitating immobilisation of the catalyst on a solid carrier. Therefore, additional costs associated with the use of expensive immobilised PTC catalysts can be avoided.

Dialkyl peroxides have mainly been used as initiators of free radical reactions and as cross-linking agents [13]. In previous papers, we have shown that phase-transfer catalysis is an effective method for the synthesis of dialkyl peroxides and peroxyesters, using both soluble phase-transfer catalysts, such as quaternary onium salts and crown ethers in two-phase L-L and L-S PTC systems [14,15], as well as insoluble PTC catalysts, such as polymer-supported quaternary onium salts and polyethylene glycols in a L-L-S PTC system [16,17]. Further, we have applied triphase L-L-L PTC to the synthesis of dialkyl peroxides using polyethylene glycols and their derivatives as PTC catalysts [18]. High yields of dialkyl peroxides were achieved, and because the catalyst formed an insoluble liquid phase, it could be reused several times. Thus, the present study has focused on the application of quaternary ammonium salts as phase-transfer catalysts in the synthesis of dialkyl peroxides with alkyl hydroperoxides and alkyl halides proceeding in a triphase liquid-liquid-liquid system. Tetraalkylammonium salts are typical phase-transfer catalysts, and they are most often used in organic synthesis, as they are relatively inexpensive and commercial available [19]. However, if they are used in two-phase systems, then they are dissolved in the reaction mixture and are thus difficult to separate. The separation of the PTC catalyst requires added process stages and generates additional costs and waste. This problem can be avoided by providing the process with a liquid-liquid-liquid system where the catalyst, which is a tetraalkylammonium salt, forms a separated liquid phase.

The model reaction of cumyl hydroperoxide with 1bromobutane (organic phase) in the presence of an aqueous solution of inorganic base (aqueous phase) and select quaternary ammonium salts (Q^+X^-) as phase-transfer catalysts (a third-liquid phase) was chosen for this study (Eq. (1)). Based on the obtained results a reaction mechanism was proposed.

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Ph—OOH + C₄H₉Br + KOH
$$\xrightarrow{\text{TBAB}; 50\% \text{ KOH}}$$
 Ph—OOC₄H₉ + KBr + H₂O

2. Experimental

2.1. Chemicals and catalysts

All chemicals and solvents used in this study were commercially available and used without further purification, unless stated otherwise. Tetrabutylammonium chloride (TBAC) and tetrabutylammonium bromide (TBAB) were obtained from Fluka Chemie AG. Benzyltributylammonium chloride (BTBAC), tetrapropylammonium bromide (TPrAB), tetraethylammonium bromide (TEAB) and tributylmethylammonium chloride (TBMAC) were purchased from Merck. Tetrabutylammonium hydrosulphate (TBAHSO₄), tetrapentylammonium bromide (TPeAB) and methyltrioctylammonium chloride (Aliguat 336) were obtained from AlfaAesar. Alkyl halides (purchased from Merck) and cyclohexane were distilled prior to use in kinetic measurements. The 1-methyl-1-phenylethyl hydroperoxide (cumyl hydroperoxide, CHP, 88% pure) was purchased from Aldrich and purified according to a procedure described in the literature [20].

2.2. Experimental procedure

The typical experiment was carried out in a two-neck roundbottom flask (25 cm³) that was placed in an oil bath with a temperature precision of ±1 °C. A 50 weight% (wt.%) aqueous solution of potassium hydroxide (6.0 mmol, 0.673 g), phase-transfer catalyst as a solid (0.3 mmol), cyclohexane (3 cm³) and CHP (3 mmol, 0.456 g) were agitated with a magnetic stirrer (magnetic stirring bar: 20 mm, Ø 6 mm; 500 rpm) at 50°C. Then, 1-bromobutane (3 mmol, 0.411 g) diluted in 2 cm³ of cyclohexane was added. The reaction was agitated for 4 h. At chosen times, the stirrer was stopped for 60s to allow adequate separation of the phases. Then, samples of the organic layer were withdrawn, diluted with methanol (5 cm³), and analysed by high performance liquid chromatography (HPLC).

Analysis: HPLC was performed on an Alliance, Waters 2690 liquid chromatography equipped with a Waters PDA detector, a Waters XBridge C18 $(2.1 \text{ mm} \times 30 \text{ mm}, 2.5 \mu \text{m})$ and Merck LiChrospher[®] Si 100 (250 mm \times 2 mm, 5 μ m) cartridge columns. Acetonitrile:water 70:30 (v/v) and hexane:2-propanol 99:1 (v/v)were used as the mobile phases (flow rate $0.25 \text{ cm}^3/\text{min}$). GC was performed using PerkinElmer chromatography equipped with a PerkinElmer Elite-624 column (30 m, 0.53 mm ID) and decane as the external standard.

Product isolation: Upon completion, the reaction mixture was filtered to remove solid KBr or KCl. The reaction mixture was then allowed to sit until layers clearly were separated from each other. Next, the organic phase was washed with water, 5% aqueous NaOH and again with water, after which it was dried over anhydrous MgSO₄. The organic solvent was recovered by distillation under reduced pressure.

Amount of the phase-transfer catalyst in a third-liquid phase: The amount of tetrabutylammonium bromide in a third-liquid phase was determined by a method described previously [21].

3. Results and discussion

3.1. The formation of a third catalyst phase

In the triphase L-L-L PTC system, the organic and aqueous phases were separated by a middle liquid phase containing the phase-transfer catalyst. This third-liquid phase appeared when the catalyst had negligible solubility in both of the other phases. Thus, reaction conditions that can influence the formation of this third catalyst phase were determined.

Based on experimental results, it was demonstrated that the concentration of aqueous solution of KOH affects the formation of triphase system (Table 1). The middle phase appeared when the aqueous solutions of KOH had a concentration between 20 and 50 wt.%. When using 60 wt.% KOH, the catalyst remained solid, whereas in the 10 wt.% KOH solution, it was dissolved. It was also observed that the third-liquid phase was formed at molar ratios of CHP to KOH from 1:1 to 1:3. When the molar ratio was 1:4, the catalyst partially precipitated in the form of a solid phase.

The formation of the third-liquid phase is also dependent on the type of phase-transfer catalyst used. The majority of previous work on L-L-L PTC used TBAB as a phase-transfer catalyst. Other symmetrical onium salts $(C_n H_{2n+1})_4 Z^+$, where n = 2-6, Z = N, P [22-27] or unsymmetrical benzyltributylammonium or phosphonium salt [7,8,10], were only applied in a few studies. In order to check the influence of the type the catalyst on the formation the L-L-L PTC in model process, the quaternary ammonium salts with cations having symmetrical (R_4N^+) and unsymmetrical (R_3N^+R') structures were used. The results summarised in Table 2 indicate that in the case of symmetrical ammonium salts a triphase system was observed only for salts with tetrapropyl and tetrabutyl cations. If TEAB and TPeAB were used, only two liquid phases were observed. For unsymmetrical quaternary salts different results

| Table 1 |
|---|
| The effect of the amount, concentration and type of base on the formation of a triphase system. |

| Concentration of base (wt.%) | Molar ratio of CHP:base | Molar ratio of catalyst:CHP | Number of phases after reaction |
|------------------------------|-------------------------|-----------------------------|---------------------------------|
| 60 KOH | 1:2 | 1:10 | _b |
| 50 KOH | 1:2 | 1:10 | 3 |
| 40 KOH | 1:2 | 1:10 | 3 |
| 30 KOH | 1:2 | 1:10 | 3 |
| 20 KOH | 1:2 | 1:10 | 3 |
| 10 KOH | 1:2 | 1:10 | 2 |
| 50 KOH | 1:3 | 1:10 | 3 |
| 50 KOH | 1:4 | 1:10 | 3 ^c |
| 40 NaOH | 1:2 | 1:10 | 3 |

a CHP, 0.456 g, 3.0 mmol; 1-bromobutane, 0.411 g, 3 mmol; TBAB as PTC catalyst, 0.0967 g, 0.3 mmol; KOH or NaOH, 6 mmol for molar ratio of CHP:base 1:2, 9 mmol for molar ratio of CHP:base 1:3 and 12 mmol for molar ratio of CHP:base 1:4; cyclohexane, 5 cm³; temperature, 50 °C; speed of agitation, 1000 rpm; reaction time, 4 h. ^b Precipitation.

^c Partial precipitation.

(1)

Table 2

The effect of the type and amount of phase-transfer catalyst on the formation of a triphase system.^a

| Molar ratio of catalyst:CHP | Catalyst | Number of phases after reaction |
|-----------------------------|---------------------|---------------------------------|
| 1:10 | TBAC | 3 |
| 1:10 | TBAB | 3 |
| 1:10 | TBAHSO ₄ | 3 |
| 1:10 | TBMAC | 3 |
| 1:10 | BTBAC | 3 ^b |
| 1:10 | TPrAB | 3 |
| 1:10 | TEAB | 2 |
| 1:10 | TPeAB | 2 |
| 1:10 | Aliquat 336 | 2 |
| 1:20 | TBAB | 3 |
| 1:50 | TBAB | 3 |

 $^a\,$ CHP, 0.456 g, 3.0 mmol; 1-bromobutane, 0.411 g, 3 mmol; KOH, 50 wt.%, 0,673 g, cyclohexane, 5 cm^3; temperature 50 °C; speed of agitation, 1000 rpm; reaction time, 4 h.

^b Precipitation.

were obtained. A third-liquid phase was formed when TBMAC was used but two-phase system was observed for Aliquat 336, whereas BTBAC under the reaction conditions precipitated in the form of a solid phase. These observations suggest that the structure of the ammonium cation has a significant effect on the formation of L–L–L PTC and the quaternary ammonium cation should have a proper hydrophility–lipophility balance [23]. Because of its greater hydrophilicity, TEAB is soluble in the aqueous phase, whereas TPeAB and Aliquat 336 are more lipophilic and thus dissolve in cyclohexane. In the cases of all salts with a tetrabutylammonium cation, a triphase liquid system was formed, and the anion carried no influence.

The polarity of the organic solvent is also an important factor that affects the formation of a third-liquid catalyst phase. To obtain a triphase system, it was necessary to use non-polar or weakly polar organic solvents such as cyclohexane or toluene. Relatively more polar solvents such as chlorobenzene caused the formation of only two phases, and the catalysts dissolved in chlorobenzene (Table 3).

It was also checked the stability of the triphase system at temperatures between 40 and 70 $^{\circ}$ C and found that it was stable in this range (Table 3).

All further experiments were carried out under conditions where a third-liquid phase formed, unless stated otherwise (Scheme 1).

3.2. The effect of agitation speed

The dependence of the reaction course on the rate of agitation was investigated. All of these experiments were carried out in two-neck round-bottom flasks with identical magnetic stirring bars (20 mm, \emptyset 6 mm) and under the following identical reaction conditions: 50 °C temperature, 50 wt.% KOH, cyclohexane (3 cm³), TBAB as the phase-transfer catalyst, and using the same amounts of reagents. The speed of agitation (from 100 to 1000 rpm (rota-

Table 3

The effect of type of organic solvent and temperature on the formation of a triphase system.^a

| Organic solvent | Temperature (°C) | Number of phases after reaction |
|-----------------|------------------|---------------------------------|
| Cyclohexane | 50 | 3 |
| Toluene | 50 | 3 |
| Chlorobenzene | 50 | 2 |
| Cyclohexane | 40 | 3 |
| Cyclohexane | 60 | 3 |
| Cyclohexane | 70 | 3 |

^a CHP, 0.456 g, 3.0 mmol; 1-bromobutane, 0.411 g, 3 mmol; TBAB as PTC catalyst, 0.0967 g, 0.3 mmol; KOH, 50 wt.%, 0,673 g, 6.0 mmol; organic solvent, 5 cm³; speed of agitation, 1000 rpm; reaction time, 4 h.



Scheme 1. Photograph of the triphase system.

tions per minute)) was the only reaction parameter changed. The results are shown in Fig. 1. It was observed that once above 100 rpm, the course of the model reaction was independent of stirring rate. Interestingly, even in the absence of agitation, a fair yield of product was obtained. These results indicate that mass transfer is not a rate-determining step and that the transport of anions from one phase to the other occurs quickly.

3.3. The effect of type and amount of phase-transfer catalyst

Fig. 2 shows the influence of the type of phase-transfer catalysts on alkylation of CHP. In these experiments quaternary ammonium salts that formed a third-liquid phase were used. The reactions were performed in the presence of 50 wt.% KOH and cyclohexane at 50 °C. Similar experiment was conducted without a phase-transfer catalyst. The best yields of peroxide were obtained using tetrabutylammonium salts $- (C_4H_9)_4N^+X^-$, irrespective of anion X. A lower yield of product was obtained with unsymmetrical salt TBMAC. A comparison of the reaction course with and without phase-transfer catalyst clearly indicates that the addition of quaternary ammonium salts as phase-transfer catalysts has a pronounced effect on the reaction course relative to the course of reaction in the absence of catalyst. TBAB was chosen for all further reactions.

The effect of the amount of phase-transfer catalyst in the range of 1-10 mol% in reference to the amount of CHP on the reaction course of alkylation of CHP with 1-bromobutane was investigated. The reactions were carried out under identical conditions. It was found that as the amount of catalyst increased from the rate of the model reaction also increased.



Fig. 1. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of TBAB at different agitation rates: (♦) 1000; (■) 700; (▲) 500; (●) 300; (○) 100; (□) 0. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50 wt.% KOH, 0.673 g, 6.0 mmol; TBAB, 0.0967 g, 0.3 mmol; cyclohexane, 3 cm³; temperature, 50 °C.



Fig. 2. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of different phase-transfer catalysts (0.3 mmol): (◆) TBAB; (■) TBAC; (▲) TPrAB; (●) TBAHSO₄; (○) TBMAC; (□) without catalyst. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50 wt % KOH, 0.673 g, 6.0 mmol; cyclohexane, 3 cm³; temperature, 50 °C; speed of agitation, 500 rpm.

3.4. The effect of concentration, type and amount of inorganic base

The influence of the concentration of KOH in aqueous solution in the range of 20–50 wt.% is depicted in Fig. 4. The reaction rate and yield of the peroxide increased with increasing concentration of KOH. The reason for this increase could be that at higher concentrations of KOH, the hydration level of all anions present in the system tends to decrease, and hence their reactivity increases [28,29]. In the reaction that used a 40 wt.% solution of KOH, the reaction proceeded with better product yields than when 40 wt.% NaOH was used.

In order to examine the influence of amount of KOH on the course of alkylation of CHP, experiments at various molar ratios of CHP to KOH: 1:1, 1:2, 1:3 and 1:4 were carried out. The results



Fig. 3. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of different amount of TBAB (mol%): (◆) 10%; (▲) 5%; (▲) 1%. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50% KOH, 0.673 g, 6.0 mmol; cyclohexane, 3 cm³; temperature, 50 °C; speed of agitation, 500 rpm.



Fig. 4. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of TBAB at different concentration of and type of inorganic base, wt.% (6.0 mmol): (♦) 50% KOH; (■) 40% KOH; (▲) 30% KOH; (●) 40% NaOH. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; TBAB, 0.0967 g, 0.3 mmol; cyclohexane, 3 cm³; temperature, 50 °C; speed of agitation, 500 rpm.

shown in Fig. 5 indicate that the lowest yields of product were obtained when stoichiometric quantities of KOH and CHP were used. The use of excess KOH at amounts greater than 1:2 did not appear to enhance the reaction rate and product yield. This lack of enhancement could be explained as follows: at a molar ratio of CHP to KOH of 1:1, the concentration of the aqueous phase decreases during the reaction to such a level that the ammonium salt could dissolve in the aqueous phase, and thus, the amount of ammonium salt in a third-liquid phase could be smaller than at molar ratios of 1:2 to 1:4. However, when a ratio above 1:2 was used, the concentration of the aqueous phase was high enough to maintain a constant amount of catalyst in a third-liquid phase.



Fig. 5. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of TBAB at different molar ratios KOH (50 wt.%):CHP: (\blacklozenge) 4:1; (\blacksquare) 3:1; (\blacktriangle) 2:1; (\blacklozenge) 1:1. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; TBAB 0.0967, 0.3 mmol; cyclohexane, 3 cm³; temperature, 50 °C; speed of agitation, 500 rpm.



Fig. 6. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of TBAB at different solvents (3 cm^3) : (\blacklozenge) cyclohexane; (\blacksquare) toluene. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50 wt.% KOH, 0.673 g, 6.0 mmol; TBAB 0.0967 g, 0.3 mmol; temperature, 50 °C; speed of agitation, 500 rpm.

3.5. The effect of an organic solvent

The effects of an organic solvent on the model reaction were investigated using cyclohexane and toluene under conditions where the triphase system was formed (Fig. 6). Using cyclohexane as the solvent resulted in a higher yield of product than this when toluene was used. Furthermore, cyclohexane can be easily removed from the reaction mixture, then purified and reused.

3.6. The effect of temperature

To examine the effect of the temperature on the course of reaction between CHP and 1-bromobutane, experiments were carried out at 40, 50, 60 and 70 $^{\circ}$ C (Fig. 7). It was observed that the reaction rate increased with increasing temperature. Peroxy compounds are thermally unstable, thus reaction temperatures did not exceed



Fig. 7. Variation of the yield of peroxide with the time on stream during the reaction of CHP with 1-bromobutane in the presence of TBAB at different temperatures: (\blacklozenge) 70 °C; (\blacksquare) 60 °C; (\blacklozenge) 50 °C; (\bigcirc) 40 °C. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50 wt.% KOH, 0.673 g, 6.0 mmol; TBAB 0.0967 g, 0.3 mmol; cyclohexane, 3 cm³; speed of agitation, 500 rpm.

Table 4

Yields of dialkyl peroxides obtained by reaction of CHP with the corresponding alkyl bromide.^a



^a Alkyl bromide, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50% KOH, 0.673 g, 6.0 mmol; TBAB, 0.0967 g, 0.3 mmol; cyclohexane, 3 cm³; temperature, 50 °C; speed of agitation, 500 rpm; reaction time, 5 h.

^b Based on the determination of isolated products.

70 °C. HPLC analysis indicated that peroxy reagents were stable under reaction conditions (50 wt.% KOH, 40–70 °C). The selectivity of CHP was 100%.

3.7. Synthesis of dialkyl peroxides

CHP was used in reactions with a variety of alkyl bromides to prepare dialkyl peroxides under a triphase system. High yields of the corresponding peroxides were obtained (Table 4). In the case of butyl 1-methyl-phenylethyl peroxide, the catalyst was also recovered and reused in the next process. It is known that quaternary onium salts can undergo decomposition in the presence of bases or at high temperatures. Tributylamine, which is the product of Hofmann degradation under the reaction conditions used, was not observed in the reaction products.

3.8. The comparison of two-phase and triphase liquid systems and the reaction mechanism

In the case of TBAB, where an aqueous solution of KOH and cyclohexane (as an organic solvent) is used, the triphase liquid system was formed in broad range of KOH concentration, molar ratio of CHP:KOH and amount of TBAB (Tables 1 and 2) and the course of the reaction strongly depended on these factors (Figs. 3–5). Thus, in order to compare the model reaction courses carried out in twophase and triphase liquid systems different phase-transfer catalysts were used. TBAB was chosen for the L–L–L PTC system, whereas Aliquat 336 and TPeAB were used in the L–L PTC. The other reaction conditions remained the same. The results indicate that yields of dialkyl peroxide were lower in the L–L PTC system than in the L–L–L PTC system (Fig. 8). Higher activity of the triphase system is proba-



Fig. 8. The comparison of the model reaction course carried out in: (+) L-L-L PTC with TBAB; () L-L PTC with Aliquat 336. Reaction conditions: 1-bromobutane, 0.411 g, 3.0 mmol; CHP, 0.456 g, 3.0 mmol; 50 wt.% KOH, 0.673 g, 6.0 mmol; phasetransfer catalyst, 0.3 mmol; cyclohexane, 3 cm3; temperature, 50°C; speed of agitation, 500 rpm.

bly due to the high concentration of reagents and the phase-transfer catalyst in the third-liquid phase [1,4,6,10-12]. There is about 89% of TBAB remaining in a third-liquid phase when 50% KOH at molar ratio of KOH to CHP of 2:1 and cyclohexane as the organic solvent were used.

The reaction of alkylation between alkyl hydroperoxide and alkyl halide under liquid-liquid-liquid conditions using tetraalkylammonium salts may involve the following steps (see Scheme 1 in [18]):

(1) The formation of a potassium salt of cumyl hydroperoxide $(PhC(CH_3)_2OO^-K^+)$ occurs at the interface between an inorganic phase and a third phase (Eq. (2)).

$$PhC(CH_3)_2OOH + K^+OH^- \rightarrow PhC(CH_3)_2OO^-K^+ + H_2O$$
(2)

It was assumed that the deprotonation of alkyl hydroperoxide proceeds without participation of phase-transfer catalyst because as shown in Fig. 2, reaction of synthesis dialkyl peroxides occurred even in the absence of a phase-transfer catalyst. The formed salt $(PhC(CH_3)_2OO^-K^+)$, is mainly situated near the interface an inorganic phase and a third phase. K⁺ cannot be extracted to the organic phase, and this salt cannot dissolve in aqueous phase due to the salting effect [30,31].

(2) An ion exchange between $(PhC(CH_3)_2OO^-K^+)$ and tetraalkylammonium salt (Q⁺Br⁻) leads to the formation of a lipophilic ion pair $Q^+PhC(CH_3)_2OO^-$ in a third-liquid phase:

$$Q^+Br^- + PhC(CH_3)_2OO^-K^+ \rightarrow Q^+PhC(CH_3)_2OO^- + K^+Br^-$$
 (3)

The peroxy anion in this ion pair is in a highly reactive form due to low interactions with bulky quaternary ammonium cation and reduced water levels for hydration in the presence of highly concentrated aqueous KOH solutions.

(3) In the next step, one can assume that the transfer of 1bromobutane from the organic phase to boundary between the organic phase and a third-liquid phase or into a third-liquid phase occurs; there, 1-bromobutane subsequently undergoes the desired reaction:

$$Q^+PhC(CH_3)_2OO^- + C_4H_9Br \rightarrow PhC(CH_3)_2OOC_4H_9 + Q^+Br^-$$

(4) The product (dialkyl peroxide) is transferred to the organic phase.

4. Conclusion

In summary, a simple and useful method of synthesis of dialkyl peroxides from alkyl hydroperoxides and alkyl bromides using quaternary onium salts as phase-transfer catalysts under triphase liquid-liquid-liquid conditions was developed. In a previous paper we have revealed that polyethylene glycols and their derivatives could be also used as PTC catalysts in this system [18]. The studies demonstrate that the formation of triphase system depends on the concentration and amount of base in aqueous phase, the polarity of organic solvents and type of PTC catalyst. In the case of polyethylene glycols tri-liquid system have appeared for more concentrated solutions of inorganic base and at a higher molar ratio of KOH to CHP than in the case of the quaternary salts. The results of these studies clearly indicate that higher reaction rates can be achieved in the L-L-L system than in the conventional L-L PTC. This is due to the formation of third-liquid catalyst rich phase where the main reaction occurs. The course of the reaction stronger depended on the molar ratio of CHP to KOH and the structure of phase-transfer catalyst when polyethylene glycols were used.

Both these methods use reagents, such as cyclohexane and guaternary ammonium salts or polyethylene glycols that are relatively inexpensive and readily available in high purity on a commercial scale. Moreover, separation and recovery of the phase-transfer catalyst from the reaction mixture can easily be performed because the catalyst forms an insoluble liquid phase. Thus, these methods are of practical value for the synthesis of mixed dialkyl peroxides.

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