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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Efficiency of Phase-Transfer Catalysis in Cyclopentene Epoxidation with Hydrogen Peroxide

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**Abstract**—The effect of the structure and amount of the phase-transfer catalyst (quaternary ammonium salts) and the solvent effect on cyclopentene oxidation with an aqueous hydrogen peroxide solution in the liquid–liquid two-phase system was studied. The phase-transfer catalyst and solvent ensuring high reaction rate and high selectivity with respect to target products were chosen.

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Today there is increasing interest in use of aqueous solutions of hydrogen peroxide instead of organic hydroperoxides and per acids as agents for oxidation of unsaturated compounds [1, 2], because 30% hydrogen peroxide solution is readily available, cheap, stable in transportation, and environmentally safe; furthermore, hydrogen peroxide has high relative content of available oxygen. These advantages make hydorgen peroxide promising as agent for various processes.

Analysis of procedures for preparing 1,2-epoxycyclopentane by oxidation of cyclopentene (CP) with isopropylbenzene hydroperoxide and aqueous solution of hydrogen peroxide (HP), made in [3], revealed technical and economical advantages of hydrogen peroxide.

Processes used for oxidation of unsaturated substrates with aqueous hydrogen peroxide solutions can be conventionally classed with respect to implementation, in accordance with the catalysts used. The first group includes oxidation processes performed on heterogeneous catalysts (titanium silicalite, zeolites), with alcohols, mainly methanol, used as solvent [3, 4]. The second group includes oxidation processes performed with soluble catalysts, compounds of Group V and VI metals (W, Mo, V) [5]. Among them, particular place is occupied by reactions performed in two-phase water–organic solvent systems.

The catalytic complex is formed directly in the reaction medium from sodium tungstate, phosphoric acid, hydrogen peroxide, and phase-transfer catalyst (PTC). Depending on the reaction temperature and pH of the aqueous phase, the process can be directed to synthesis of either 1,2-epoxycyclopentane (1,2-ECP) or 1,2-cyclopentanediol (1,2-CD) [6].

In this study we examined how the structure and amount of PTC and the nature of the solvent affect the efficiency of oxygen (peroxy group) transfer from the aqueous phase to the organic phase in which cyclopentene is oxidized.

## EXPERIMENTAL

Cyclopentene isolated from the C<sub>5</sub> fraction of pyrolysis was purified by fractional distillation to 98% purity. The solvents (chemically or analytically pure grade) were additionally purified by fractional distillation. Hydrogen peroxide (35% aqueous solution), sodium tungstate dihydrate, phosphoric acid (80%), and phase-transfer catalysts (Table 1) of chemically or analytically pure grade were used without any pretreatment.

A temperature-controlled glass reactor equipped with a reflux condenser, a thermometer, and a sampling neck was charged with the aqueous (sodium tungstate, phosphoric acid, hydrogen peroxide, water) and organic (phase-transfer catalyst, solvent, cyclopentene) phases, prepared in advance separately. The mixture was vigor-

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**Table 1.** Effect of the structure of the phase-transfer catalyst on the reaction of cyclopentene with an aqueous solution of hydrogen peroxide. Solvent 1,2-dichloroethane; initial concentration, M: CP in organic phase 5.0,  $H_2O_2$  in aqueous phase 4.0, sodium tungstate in aqueous phase 0.06; molar ratios:  $H_2O_2$ : CP = 1.3 : 1,  $Na_2WO_4 \cdot 2H_2O$  :  $H_3PO_4$  : PTC = 1 : 2 : 0.36; aqueous to organic phase volume ratio 1.6 : 1; 60°C; pH of aqueous phase 1.6

РТС	Number of C atoms in PTC cation	τ, min	Conversion, %		Yield based on CP loaded, %	
			СР	$H_2O_2$	1,2	ECP
Tetraethylammonium bromide (TEAB)	8	180	48.0	95.4	6.7	41.3
Tetraethylammonium iodide (TEAI)	8	200	35.1	96.7	7.6	27.5
Tetrabutylammonium bromide (TBAB)	16	180	94.5	93.5	8.8	85.7
[C <sub>14</sub> H <sub>29</sub> N(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ]Cl (Katamin AB)	23	140	99.7	92.3	4.8	94.9
[CH <sub>3</sub> (C <sub>9</sub> H <sub>19</sub> ) <sub>3</sub> N]Cl (Adogen 464)	28	140	99.8	95.3	7.6	92.2

ously stirred (600 rpm) with a single-blade power-driven stirrer. The reaction time was counted from the start of stirring. The reaction progress was monitored by hydrogen peroxide conversion, which was determined by iodometric titration. The products obtained were analyzed by chemical methods and gas-liquid chromatography.

Two consecutive reactions were shown to occur under the experimental conditions: CP epoxidation to 1,2-ECP [reaction (1)] and subsequent hydrolysis of the epoxide formed to 1,2-CD [reaction (2)]:



The CP epoxidation occurs in the organic phase, and the 1,2-ECP hydrolysis, in the aqueous phase. The formation of both 1,2-ECP and 1,2-CD is strongly influenced by the efficiency of the first limiting step, cyclopentene epoxidation.

Without PTC, the reaction of CP with an aqueous HP solution is slow and inefficient. This is illustrated by the

results of the CP epoxidation without PTC in dimethylformamide. In this case, the reaction mixture does not become fully homogeneous, probably because of the presence of salts, and is an emulsion. Despite the fact that the reaction was performed with vigorous stirring, the CP conversion in 3 h was as low as 6%, with the degree of nonselective HP decomposition reaching 50%.

Experiments were performed under the conditions ensuring the 1,2-CD formation. As seen from Table 1, with an increase in the total amount of carbon atoms in the PTC cation, the reaction rate, CP conversion, and 1,2-CD yield increase. TEAB and TEAI are ineffective PTCs, because they do not ensure sufficient transfer of the catalytic complex to the organic phase; the CP conversion is insignificant, whereas nonproductive HP decomposition is enhanced. At the same time, in the presence of such PTCs as Katamin AB and Adogen 464, the CP conversion is fast and selective.

Analytical studies of the transfer of ammonium salts from aqueous solutions into chloroform revealed correlation between the cation size and extraction constant [7]. For quaternary ammonium salts, the following equation was obtained:

$$\log K_0 = -2.00 + 0.54n, \tag{3}$$

where *n* is the number of C atoms in ammonium ions.



**Fig. 1.** Rate constant  $k_{\text{eff}}$  of cyclopentene conversion in its reaction with aqueous solution of hydrogen peroxide as a function of the PTC : Na<sub>2</sub>WO<sub>4</sub> molar ratio.

In accordance with this estimate, the PTCs used in this study can be ranked in the following performance order: TEAB : TEAI : TBAB : Katamin AB : Adogen 464 = 0.001 : 0.001 : 1 : 500 : 1000000. The CP conversion rate increases in the same order.

Unsymmetrical PTCs (Katamin AB and Adogen 464) are extracted more efficiently than the symmetrical PTCs. The extraction constant of Adogen 464, determined [8] from the experimentally found content of peroxy groups in the organic phase for the reaction under consideration, is  $(6.7 \pm 0.3) \times 10^4$ , which confirms high performance of this PTC.

The anion on PTC affects the CP epoxidation efficiency to a lesser extent. The use of iodides in this reaction is not appropriate. It is known [7] that the I- anion is considerably more lipophilic than the Cl- and Br- anions and can inhibit the main reaction owing to competition with the catalytic complex ion in its transfer to the organic phase. Furthermore, iodide ion is oxidized with hydrogen peroxide to molecular iodine.

The best results were obtained with Katamin AB and Adogen 464. Katamin AB used in production of disinfectants and synthetic detergents is readily available and cheap, which makes attractive its use in the process.

It was shown that, up to a certain limit, the PTC amount does not affect the rate of the reaction of CP with HP. This is due to the fact that the reaction rate is determined by the PTC concentration, which, in turn, is determined by the concentration of the component taken in deficiency. Figure 1 shows how the effective constant of the CP epoxidation with hydrogen peroxide in the 1,2-CD synthesis depends on the PTC : sodium tungstate molar ratio.

With an increase in the PTC : sodium tungstate molar ratio from 0.2 : 1 to 1.2 : 1, the reaction rate does not increase noticeably, because in this case the concentration of the active complex is determined by the sodium tungstate content. The CP conversion in the process remains on the level of 98–99%, and the HP conversion is 94–98%, with >98% selectivity with respect to 1,2-CD. As the PTC : sodium tungstate ratio is decreased to 0.05 : 1, the reaction rate drastically decreases, because the catalytic

**Table 2.** Solvent effect on the synthesis of 1,2-cyclopentanediol from cyclopentene and aqueous hydrogen peroxide solution. Phase-transfer catalyst Adogen 464; initial concentration, M: CP in organic phase 5.0,  $H_2O_2$  in aqueous phase 4.0, sodium tungstate in aqueous phase 0.06; molar ratio  $H_2O_2$ : CP = 1.3 : 1,  $Na_2WO_4$ ·2 $H_2O$  :  $H_3PO_4$  : PTC = 1 : 2 : 0.36; aqueous to organic phase volume ratio 1.6 : 1; 60°C; pH of the aqueous phase 1.6

Solvent	Relative dielectric	τ, min	Conversion, %		Yield based on CP loaded, %	
	permittivity e		СР	H <sub>2</sub> O <sub>2</sub>	1,2-ECP	1,2-CD
N,N-Dimethylformamide	36.71	180	98.0	96.8	21.4	76.6
<i>n</i> -Butanol	17.49	150	98.2	95.6	10.4	87.8
Dichloroethane	10.27	140	99.8	95.3	7.6	92.2
Trichloroethylene	3.42	140	99.6	94.4	7.2	92.4
Tetrachloroethylene	2.30	120	98.0	92.4	5.4	92.6
Xylene	2.27	120	99.3	92.9	5.9	93.4



Fig. 2. Rate constant  $k_{\text{eff}}$  cyclopentene conversion in its reaction with aqueous solution of hydrogen peroxide as a function of the relative dielectric permittivity  $\varepsilon$  of the solvent used.

complex concentration starts to be determined by the PTC concentration and decreases. Therefore, we suggested to use the PTC amounts with which the PTC : sodium tungstate ratio is no less than 0.3 : 1 to ensure high reaction rate and no more than 0.5 : 1 to avoid nonproductive PTC consumption.

The phase-transfer efficiency in the step of the 1,2-ECP formation is also affected by the solvent. It should be hydrophobic and inert under the reaction conditions; it should readily dissolve the catalytic complex and exhibit high extraction power [7]. Under the reaction conditions, all the solvents used (Table 2) are resistant to the effect of hydrogen peroxide.

For different solvents, the constants of PTC extraction from aqueous solutions differ by factors of tens and thousands. For example, the constant of TBAB extraction from aqueous solutions varies as follows: *n*-butanol (6.9) > 1,2-dichloroethane (6.1) > trichloroethylene (0.2) [7]. However, in this study we have not noticed so dramatic differences in the time of CP conversion and selectivity of final product formation (Table 2). We believe that the use of such an active PTC as Adogen 464 or Katamin AB levels off possible differences in the extraction ability of the solvents.

The solvents miscible with water (dimethylformamide, *n*-butanol) decrease the PTC activity owing to its solvation [7]. At the same time, the reaction rates in these solvents somewhat differ. The CP oxidation rate correlates with the dielectric permittivity of the solvent (Fig. 2).

The results presented in Table 2 and in Fig. 2 are consistent with the known data on the solvent effect on the rate of olefin epoxidation with per acids [9]. However, the low correlation coefficient of the CP oxidation rate with  $\varepsilon$  ( $R^2 = 0.75$ ) shows that, in our case, this parameter is not decisive. Strong effect on the rate of the reaction of CP with HP in the two-phase system is exerted by the capability of the solvent to extract the catalytic complex, the degree of phase transfer of the ions, and the degree of their solvation.

As seen from Fig. 2, polar solvents such as n-butanol and dimethylformamide are unsuitable for this reaction. They are miscible with water to different extents, with partial homogenization of the system. As a result, the olefin concentration in the organic phase and the reaction rate decrease. These solvents are basic, which also decreases the rate of epoxidation, which is an electrophilic reaction.

Nonpolar solvents such as alkyl halides and xylene do not differ significantly in the activity. All these solvents do not hinder the reaction sterically, readily dissolve the catalytic complex, and allow the reaction of CP with an aqueous HP solution to be performed in a short time with high selectivity.

Thus, in choosing a solvent for the reaction of CP with HP, the main criteria should be feasibility parameters such as the solvent availability and cost, and also the procedure for isolating reaction products.

The PTC after the reaction was found to remain in the organic phase, which opens possibilities for its reuse. In this case, the best solvents for the reaction of CP with aqueous HP solution are tetrachloroethylene and xylene. Their boiling points are higher than that of 1,2-ECP. Therefore, in isolation of the reaction product from their organic phase, 1,2-ECP can be separated from PTC by fractional distillation and the catalyst can be recycled as solution in the solvent chosen. 1,2-CD does not affect the organic phase separation, because it practically fully passes to the aqueous phase.

## CONCLUSIONS

(1) The rate of cyclopentene epoxidation with an aqueous solution of hydrogen peroxide increases with an increase in the length of the hydrocarbon chain of the phase-transfer catalyst. The nature of the anion affects the process to a considerably lesser extent. Katamin AB can be used as effective phase-transfer catalyst in cyclopentene epoxidation.

(2) For the reaction of cyclopentene with hydrogen peroxide to be performed at a high rate with high selectivity, it is necessary to use inert hydrophobic solvents with low dielectric permittivity.

(3) The use of tetrachloroethylene and xylene allows isolation of 1,2-epoxycyclopentane from the organic phase by fractional distillation and simultaneous recycling of the catalytic complex for its reuse in the form of a solution in the solvent chosen.

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