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### PHASE TRANSFER CATALYSIS OF OXOPEROXOHETEROPOLYANIONS AT EPOXIDATION OF UNSATURATED COMPOUNDS

*SUMMARY.* The advantages and disadvantages of the mechanisms of phase transfer catalysis are considered, including the flow of the epoxidation reaction both in the organic phase (IPC extraction mechanism) and at the interface (IPC mechanism involving PIF). Since the preferential localization of response to PIF or within the organic phase depends on the choice of the interphase carrier (on the hydrophilic-lipophilic balance of the ion pairs produced by the cation phase transfer ( $Q^+$ ) and anion reactant  $[PW_4O_{24}]^{3-}$ ), the effectiveness of salts of tetraalkylammonium and alkyipyridinium as interphase carriers in the epoxidation of chlorallylene is studied.

The study demonstrates that the interphase carrier efficiency depends on the structure of the cation, its lipophilicity, and surface reactivity, as well as on the anion nature. It is stated that the reactive anion  $[PW_4O_{24}]^{3-}$  displaces Br more effectively, than Cl from the original ion pair interphase carrier. The low reactivity of  $R_4N^+Br^-$  salts with the cation of symmetrical structure is detected, however, it has a positive dynamics in the output of epichlorohydrin with the increase in lipophilicity of the interphase carrier cation. The increase in reactivity of the interphase carrier in the range of homologues of  $R'R_3N^+Br^-$  alkyltrimethylammonium with increasing lipophilicity and surface reactivity (from the aqueous phase) is determined.

It is stated that the most effective surfactant interphase carrier is hexadecylpyridinium bromide, its high reactivity is caused by the formation of a "closer" contact with the  $[PW_4O_{24}]^{3-}$  ion, which promotes the stabilization of  $Q_3[PW_4O_{24}]$  complex and more effective interphase transfer.

The determined high reactivity of surfactant interphase carriers allows concluding that the most effective mechanism for the epoxidation in the two-phase systems is the mechanism of phase-transfer catalysis with the interface. The scheme of this mechanism is proposed.

**KEY WORDS.** Epoxidation, interphase catalysis, interphase carrier.

One of the most promising ways to improve the efficiency of basic organic and petrochemical syntheses is the use of heterophase reaction systems and interphase catalysis (IPC), able to provide a considerable increase in selectivity of chemical transformations and their technological effectiveness. Therefore, to seek effective interphase systems, characterized by simplicity and availability for a series of reactions, is a pertinent and important task of modern organic chemistry.

The unsaturated compound epoxidation by hydrogen peroxide under the interphase catalysis conditions relates to the recent trends intensively gathering force in organic chemistry. As compared to classical methods for epoxide synthesis, the epoxidation under the IPC conditions allows carrying out reactions under the milder conditions, with minimum consumption of reagents, at a higher rate, and a good selectivity. The study of fine organic synthesis reactions under the IPC conditions is of great interest both in terms of developing optimum methods for the specific substance synthesis and detailing the interphase catalysis mechanisms in various cases of its implementation. Being aware of a fine process mechanism provides an opportunity to influence its direction, to get the maximum recovery of a desired product, to select and develop the most efficient catalyst systems.

**The experiment.** The unsaturated substrate epoxidation was carried out in the two-phase aqueous organic system with the occurrence of phosphotungstic heteropoly compounds, which were formed in the aqueous phase of the system by mixing the aqueous solutions of  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ , and  $\text{H}_3\text{PO}_4$ . A sample weight of the interphase carrier ( $Q + X$ ) was placed into a thermostatically controlled reactor equipped with a magnetic stir bar ( $\omega = 1200$  rpm) and a backflow condenser at 323 K, the organic phase (OP) (the organic solvent was 1,2-dichloroethane and a substrate) was added. Then, the prepared aqueous phase (AP), previously brought to a specific pH value by 30%  $\text{H}_2\text{SO}_4$  or NaOH solution, was poured in. When required, after the reaction, the phases were separated by centrifugation. The mixture volume was 4 ml of the aqueous phase and 2 ml of the organic phase containing 6.13 mol/L chlorallylene or 4.94 mol/L cyclohexene in 1,2-dichloroethane.

**The preparation of the aqueous phase.** The required quantities of  $\text{Na}_2\text{WO}_4$  (0.8 M),  $\text{H}_3\text{PO}_4$  (85%),  $\text{H}_2\text{O}_2$  (30%, 11.8 M) aqueous solutions were placed into a weighing cup of a smaller volume. The volume of the aqueous phase was adjusted to 4 ml with water. The solution was stirred with a magnetic stir bar.

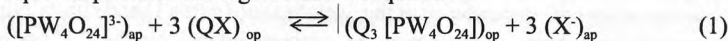
Tetramethylammonium chloride (TMAC), tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB) tetrabutylammonium bromide (TBAB); octyl-trimethyl-ammonium bromide (OTMAB) dodecyltrimethylammonium bromide (DDTMAB) hexadecyltrimethylammonium chloride (HDTMAC), hexadecyltrimethylammonium bromide (HDTMAB); hexadecylpyridinium chloride (HDPC), hexadecylpyridinium bromide (HDPB) were used as interphase carriers.

The products of the cyclohexene and chlorallylene epoxidation were analyzed by the GLC method using the *CHROM-5* gas chromatograph. The chromatographic analysis was carried out using a packed column, with the length of 2.5 m and the diameter of 3 mm; it was filled with CHROMATON N-AW-DMCS carrier of 0.200 – 0.250 mm, saturated with 5% Carbovax 20 M. The detector was ionization-flaming. The carrier gas was argon, the carrier gas velocity was 20 ml / min.  $T_{\text{ex}} = 523$  K,  $T_{\text{det}} = 523$  K, the temperature increase mode in the thermostat was programmable. The relative average quadratic deviation of chromatographic peak heights and areas at dosing with a microsyringe was 1%. In the process of cyclohexene epoxidation,

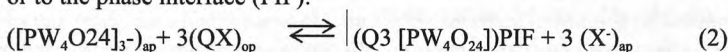
dodecane and, at the chlorallylene epoxidation, tridecane were used as internal standards.

According to the GLC data, in the process of chlorallylene epoxidation, the basic reaction product is epichlorohydrin, sufficiently stable to hydrolysis. In the process of cyclohexene epoxidation the basic reaction product is epoxy cyclohexane capable of being hydrolyzed in the acidic conditions forming cyclohexanediol - 1.2.

**Results and discussion.** To provide the unsaturated compound epoxidation with oxoperoxoheteropoly-compounds in the two-phase systems, an efficient interphase transfer of oxoperoxoheteropolyanions by the interphase transfer cations (QX) from the aqueous phase to the organic one is required:

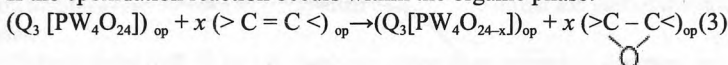


or to the phase interface (PIF):

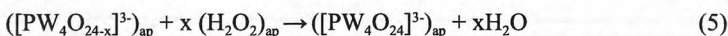
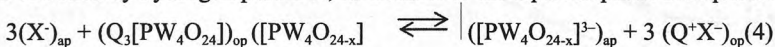


Theoretically, the epoxidation reaction of a substrate can occur both within an organic phase (extraction mechanism of IPC) and at the phase interface (IPC mechanism involving PIF). At that, each of these mechanisms has its own advantages and disadvantages.

If the epoxidation reaction occurs within the organic phase:



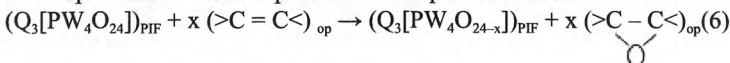
(x is the number of active  $\mu$ -peroxogroups in the composition of oxoperoxocomplex reacted), these conditions are favorable for the interaction between an organic substrate and oxoperoxocomplex. But the IPC effectiveness by the extraction mechanism will be low. Since the structure of  $\text{Q}_3 [\text{PW}_4\text{O}_{24}]$  oxoperoxocomplex in the interaction with the substrate is not completely destroyed [1], to ensure that  $\text{Q}_3 [\text{PW}_4\text{O}_{24-x}]$  complex is re-oxidized by hydrogen peroxide, its transfer to the aqueous phase is required:



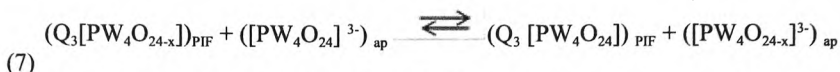
As a rule, the extraction mechanism of IPC is effective if a reacting  $[\text{PW}_4\text{O}_{24}]^{3-}(\text{Y}^-)$  anion is more lipophilic than  $[\text{PW}_4\text{O}_{24-x}]^{3-}(\text{X}^-)$  anion formed, i.e.  $K_{\text{Y/X}}^{\text{sel}} \geq 1$  [2-3].

In the systems studied, the lipophilicity of the formed  $[\text{PW}_4\text{O}_{24-x}]^{3-}$  anion cannot differ much from the lipophilicity of reacting  $[\text{PW}_4\text{O}_{24}]^{3-}$  anion, which impedes its transfer to the aqueous phase (Eq. 4) and re-oxidation stage (Eq. 5).

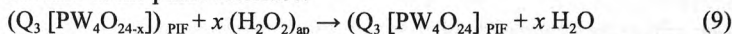
If the epoxidation reaction proceeds at the phase interface:



these conditions are less favorable for the interaction between an oxoperoxocomplex and an organic substrate than within the organic phase. However, in these conditions, on the stage of  $\text{Q}_3 [\text{PW}_4\text{O}_{24-x}]$  may occur not only in the aqueous phase:



but also at the phase interface:



The localization of the substrate epoxidation and oxoperoxocomplex reoxidation stages at the PIF may be more favorable than their behavior in different phases. In this case, the reaction rate should significantly depend on the maturity of the phase interface.

Fig. 1 demonstrates the dependence of the cyclohexene (curve 1) and chlorallylene (curve 2) epoxidation output on the reaction mass mixing intensity in the "l/l" systems with hexadecylpyridinium bromide present.

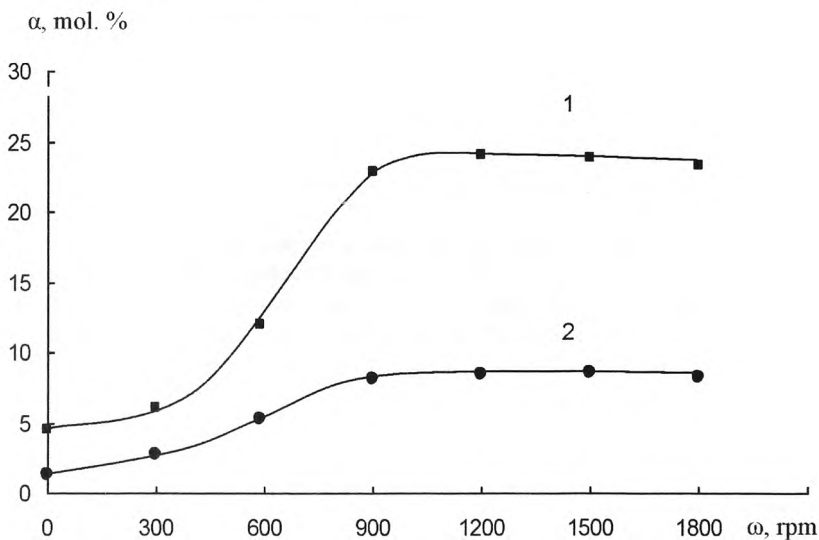


Fig. 1. The behavior of the epoxidation output versus the mixing intensity in the process of epoxidation: cyclohexene (curve 1):  $(C_{Na_2WO_4})_{ap} = 0.05$  M,  $(C_{H_3PO_4})_{ap} = 0.0125$  M,  $(C_{C_6H_{10}})_{op} = 4.94$  M,  $(C_{HDPB})_{op} = 0.036$  M, pH = 2.25; chlorallylene (curve 2):  $(C_{Na_2WO_4})_{ap} = 0.075$  M,  $(C_{H_3PO_4})_{ap} = 0.019$  M,  $(C_{C_3H_5Cl})_{op} = 6.13$  M,  $(C_{HDPB})_{op} = 0.056$  M, pH = 1;  $V_{ap} = 4$  ml,  $V_{op} = 2$  ml,  $(C_{H_2O_2})_{ap} = 4.0$  M,  $T = 50^\circ$  C,  $\tau = 1$  hour.

As Fig. 1 demonstrates, when  $\omega \geq 900$  rpm, the epoxide outputs in the process of chlorallylene and cyclohexene epoxidation do not depend any more on the intensity of system mixing. The general behavior of the curves corresponds to the known experimental dependence for the formation of the phase interface while mixing two liquids:  $\Delta F \sim \omega^p$ , where  $p = 0.5-0.6$  [4]. In this case, reaching the plateau, where the reaction rate depends on the intensity of mixing, can be related to setting the maximum

interface due to the balance between the rates of dispersion in the organic phase and coalescence of emulsion droplets.

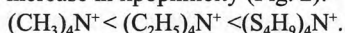
All the experiments described in this paper were carried out at  $\omega = 1,200$  rpm that allowed reproducing the kinetic data.

The interphase transfer efficiency and, thus, the predominant localization of the reaction at the PIF, or in the organic phase, depends on the choice of an interphase carrier, namely, on the hydrophilic-lipophilic balance (HLB) of ion pairs formed by the cation of ( $Q^+$ ) interphase carrier and the anion of ( $Y^-$ ) reagent. For the reactions proceeding by the extraction mechanism, the correspondence between the catalytic reactivity of interphase catalysts and their solubility in the organic phase [2] is stated in the data published, and for the reactions involving PIF, the catalytic reactivity of interphase carriers is expected to correlate with their surface reactivity [5].

In this work, the effectiveness of tetraalkylammonium and alkyipyridinium salts as interphase carriers in the process of the allyl chloride epoxidation was studied (Fig. 2).

As Fig. 2 demonstrates, the interphase carrier effectiveness depends on the cation structure, its lipophilicity and surface reactivity, as well as on the anion nature. According to Eq. 1 and 2, the anion nature can influence the effectiveness of ion exchange. From the experimental data (Fig. 2), it follows that the reactive  $[PW_4O_{24}]^{3-}$  anion displaces Br more effectively than Cl<sup>-</sup> from the initial ion pair of the interphase carrier.

The reactivity of  $R_4N^+Br^-$  salts with the cation of symmetrical structure is not high, but it slightly increases with the increase in the length of the alkyl radicals, i.e. with the increase in lipophilicity (Fig. 2):



The availability of the nitrogen atom charge is most likely to influence significantly the lipophilic  $Q^+$  cation ion pairs with peroxoheteropolyanions [5-6].

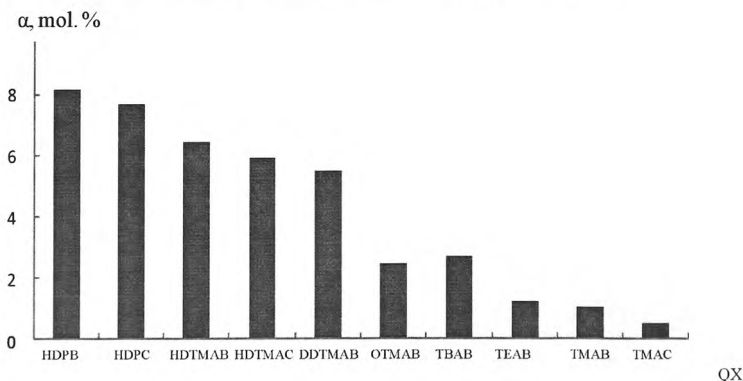
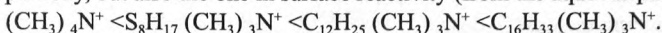


Fig. 2. The influence of the interphase carrier nature on the output of epichlorohydrin.  $V_{ap} = 4$  ml,  $V_{op} = 2$  ml,  $(C_{Na_2WO_4})_{ap} = 0.075$  M,  $(C_{H_3PO_4})_{ap} = 0.019$  M,  $(C_{H_2O_2})_{ap} = 4.0$  M,  $(C_{C_3H_5Cl})_{op} = 6.13$  M,  $(C_{QX})_{op} = 0.056$  M,  $T = 50$  °C,  $\omega = 1,200$  rpm,  $pH = 1$ ,  $\tau = 1$  hour

Among the alkyltrimethylammonium homologs, the reactivity also increases along with the increase in length of the long chain radical, i.e. not only the increase in lipophilicity, but also the one in surface reactivity (from the aqueous phase) (Fig. 2):



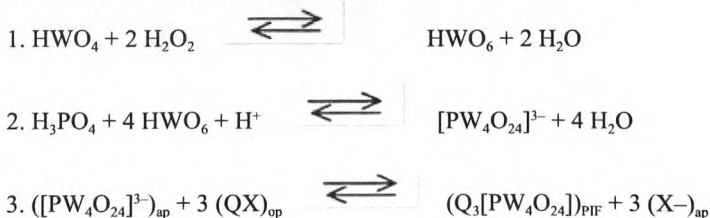
It should be noted that at the close total number of carbon atoms and, respectively, at comparable lipophilicity of dodecyltrimethylammonium bromide and tetrabutylammonium bromide, the reactivity of long chain DDTMAB cation, having the surface reactivity due to more discernible diphilicity, is far more intensive than the one of the TBAB symmetrical structure. It indicates that the IPC mechanism involving PIF is more effective than the extraction mechanism of IPC.

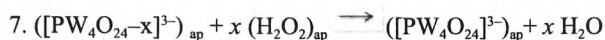
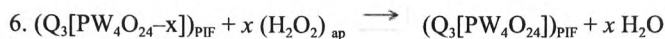
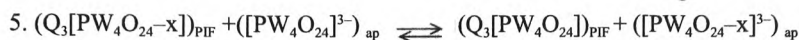
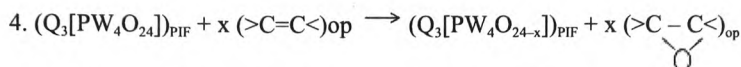
As Fig. 2 demonstrates, the most effective surfactant interphase carrier is hexadecylpyridinium bromide. The high reactivity of HDPB, the cation of which has only three substituents at the nitrogen atom and, accordingly, a higher availability of the nitrogen atom charge in comparison with the  $\text{R}(\text{CH}_3)_3\text{N}^+$  cations, may also be due to the formation of a "close" ionic contact with peroxyheteropolyanion, which favors the stability of the  $\text{Q}_3[\text{PW}_4\text{O}_{24}]$  complex and more efficient interphase transfer.

Moreover, in [7] it is supposed that the volume of the lipophilic cation may influence the efficiency of the interaction between the complex substrate and the nucleophilic one. Since electrophilic peroxyoxygen is a part of peroxyanion, lipophilic cations with a smaller volume, forming a "close" contact with the ion peroxyanion, better compensate their negative charge, increase the electrophilicity of peroxyoxygen, and facilitate the interaction of the complex with the nucleophilic substrate.

The experimental results, obtained in the process of chlorallylene epoxidation, are almost consistent with the data [8-10], where at the epoxidation of hexene-1 and cyclohexene in similar systems, it is found that HDPB has the highest reactivity. When the  $\text{R}'\text{R}_3\text{N}^+\text{Br}$  salts with a long chain hydrocarbon radical are used, the reactivity is sufficiently high and it increases with the increase in length of the radical, and the reactivity of the  $\text{R}_4\text{N}^+\text{Br}$  salts with the cation of symmetrical structure is not high, but it also increases with the increase in length of hydrocarbon radicals.

**Conclusion.** Thus, it can be concluded that in the process of both allyl chloride and cyclohexene epoxidations, depending on the nature of an interphase carrier, the localization of the epoxidation stage is possible both in the organic phase and in the PIF one. However, when it occurs, the reactivity of surfactant interphase carriers is significantly higher. Therefore, the most effective mechanism for epoxidation reactions in the two-phase systems is the mechanism involving PIF and IPC, which can be represented by the following scheme:





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