Epoxidation of cycloolefins with hydrogen peroxide in the presence of heteropoly acids combined with phase transfer catalyst

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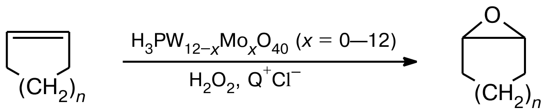
Oxidation of cycloolefins (cyclohexene, cyclooctene, and cyclododecene) with a 30% solution of hydrogen peroxide at 65 °C in the presence of heteropoly acids (HPA) $H_3PW_{12-x}Mo_xO_{40}$ (x = 0—12), which are precursors of active peroxo complexes, and phase transfer catalysts Q^+Cl^-, where Q^+ is the quaternary ammonium cation containing C_4—C_{18} alkyl groups or $[C_5H_5NC_{16}H_{33}]^+$, was studied. The catalytic activity decreases in the HPA series: $H_3PW_{12}O_{40} > H_3PW_9Mo_3O_{40} > H_3PW_6Mo_6O_{40} > H_3PW_3Mo_9O_{40} > H_3PMo_{12}O_{40}$. The state of the $H_3PW_{12}O_{40}$—H_2O_2 system was studied using UV, IR, and ^{31}P NMR spectroscopies with variation of the $[H_2O_2]$: [HPA] ratio from 2 to 200 during cyclohexene epoxidation. Despite different catalytic precursors, the reaction proceeds through the same peroxo complex.

Key words: oxidation of cyclic olefins, phase transfer catalysis, heteropoly acids.

Epoxidation of olefins is of significant interest for fine organic synthesis. Products formed in this process are of independent significance and/or are valuable chemicals for syntheses of biologically active substances.[1] Industrial olefin epoxidation is carried out in the presence of alkaline-earth metal chlorides promoted by chlorine-containing substances. This method has several disadvantages, one of which is the use of chlorine-containing reagents. An increasing attention is being given recently to phase transfer oxidation catalysis in the presence of molybdenum and tungsten compounds, which are efficient catalysts for oxidation with hydrogen peroxide solutions of various organic substrates, *viz.*, olefins, alcohols, and aromatic hydrocarbons.[2,3] Under the conditions of phase transfer catalysis, promising catalysts of oxidation are peroxo complexes $PW_xO_y^{z-}$ formed in the H_2O_2—H_3PO_4—Na_2WO_4 [4,5] and $H_3PW_{12}O_{40}$—H_2O_2 systems.[6,7] It has been shown[6,7] by IR and ^{31}P NMR spectroscopies that the $PW_4O_{24}^{3-}$ anion forms in both cases under certain conditions. This anion is sufficiently stable in water and organic solvents. Its structure has been established by X-ray diffraction analysis.[8] It has been shown[6,9] that the oxidation of various organic substrates with 35% H_2O_2 can be efficient when $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$ is used as a catalyst. It is asserted[10] that this catalyst retains its structure during the reaction. Other authors[6—10] believe that in all cases the epoxidation of olefins proceeds through the same $PW_4O_{24}^{3-}$ peroxo complex, although different catalytic precursors are used.

In this work, we studied the mechanism of epoxidation of cyclic olefins



with a 30% solution of hydrogen peroxide in the presence of $H_3PW_{12-x}Mo_xO_{40}$ (x = 0—12) as a precursor of the active peroxo complex and phase transfer catalysts Q^+Cl^-, where Q^+ is the quaternary ammonium cation ($[(C_4H_9)_4N]^+$ (**1**), $[(n\text{-}C_6H_{13})_4N]^+$ (**2**), and $[CH_3(n\text{-}C_8H_{17})_3N]^+$ (**3**)) or *N*-hexadecylpyridinium ($[C_5H_5N$—$C_{16}H_{33}]^+$ (**4**)).

Experimental

Reagents. Heteropoly acids $H_3PW_{12}O_{40}$ and $H_3PW_{11}VO_{40}$ (reagent grade) were purified by recrystallization from water; $H_3PW_{12}O_{40}$ (pure grade) was purified by extraction with ether; $H_3PW_{12-x}Mo_xO_{40}$ (x = 0—12) were synthesized according to a described procedure.[11,12] Purity of HPA was monitored by ^{31}P NMR. The number of water molecules in the HPA crystal hydrates was determined by the gravimetric method using a calcination temperature of 500 °C. Before use cyclohexene (reagent grade) was purified by distillation. Cyclooctene (98%), cyclododecene (Acros), and cyclooctadiene (Aldrich) were used.

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The following solvents were used without additional purification: dichloromethane, dichloroethane, benzene, chloroform (reagent grade), and hexane (pure grade). *N*-Hexadecylpyridinium chloride (98%, Lancaster or Acros), $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ (Lancaster), and $[(C_4H_9)_4N]Cl$ (reagent grade) were used as phase transfer catalysts.

Samples for experiments and IR spectroscopic studies were prepared similarly to described procedures[**6,13**] with some changes: $H_3PW_{12}O_{40} \cdot 15.4\ H_2O$ (4.0101 g, 1.27 mmol) in water (5 mL) was stored for 0.5 h in a magnetically stirred solution of 33.4% H_2O_2 (250 mmol). To the solution was added $[C_5H_5NC_{16}H_{33}]Cl$ (1.3631 g, 3.81 mmol) or $[(C_4H_9)_4N]Cl$ (1.22 g, 3.81 mmol). The formed precipitate of $Q_3\{PO_4[WO(O_2)_2]_4\}$ (for $[C_5H_5NC_{16}H_{33}]_3\{PO_4[WO(O_2)_2]_4\}$, 3.187 g) was filtered off. To isolate $K_2[W_2O_3(O_2)_4(H_2O)_2] \cdot 2H_2O$, KCl (4.722 g, 53.72 mmol/1.27 mmoles of HPA) was added to the filtrate (V = 34 mL), and the mixture was left for 15—20 h at 5 °C. The precipitated white crystals were separated from the mother liquor and washed with minor amounts of water and EtOH. IR absorption spectra were recorded in the 400—4000 cm^{-1} region on a Bomem MB-102 FTIR spectrometer as a suspension in Nujol.

Kinetic measurements. Reactions were carried out in a shaken reactor of the "catalytic duck" type[**14**] equipped with a reflux condenser and a jacket for maintaining a constant temperature. The temperature of the reaction was maintained at 20—65 °C using a water thermostat with an accuracy of ±0.1 °C. The frequency of reactor shaking was chosen in such a way ($\geq$ 600 rpm) that the reaction rate was independent of the shaking frequency.

Procedures for preparation of the reaction mixture. *Method A.* At 20 °C, HPA (0.026 mmol), 31.8% H_2O_2 (0.056—5.6 mmol), the corresponding solvent (10 mL), Q^+Cl^- (0.078 mmol), and olefin (18 mmol) were simultaneously loaded into a reactor and rapidly heated (for 1—2 min) to 65 °C using a thermostat. After this, the reaction was carried out with intense stirring.

Method B. HPA (0.026 mmol) was pretreated with a solution of 30% H_2O_2 (0.056—5.6 mmol) for 0.5 h at 40 °C. The resulting solution was loaded into a reactor, the corresponding solvent (10 mL) and Q^+Cl^- (0.078 mmol) were added, and the solution was stored for 0.5 h at 20 °C. After olefin (18 mmol) was introduced, the reactor was heated to 65 °C, and the reaction was performed with intense stirring.

Samples of an organic phase were taken at specified intervals and analyzed by GLC on a Tsvet-500 chromatograph (flame-ionization detector, metallic column 3 m×2 mm, 0.4% OV-225 on graphitized thermal carbon black, nitrogen as carrier gas, 30 mL min^{-1}; temperatures 150, 100, and 120 °C of the evaporator, column, and detector, respectively).

Reaction products were identified by GLC-MS using an LKB-2091 instrument (Sweden) (glass capillary column 40 m, Carbowax 20M/Lukopren G 1000 = 1/3; electron impact, 70 eV).

Physicochemical measurements. Samples for ^{31}P NMR spectroscopy were prepared using a described procedure.[6] 30% H_2O_2 (0.34—34 mmol) was added to $H_3PW_{12}O_{40}$ (0.5 g, 0.17 mmol) in water (1 mL), and the mixture was stirred for 0.5 h. To the resulting solution of the complex $CHCl_3$ (3 mL) and $[CH_3(n\text{-}C_8H_{17})_3N]^+Cl^-$ (0.3 g, 0.53 mmol) were added. The organic layer was separated and analyzed by ^{31}P NMR and UV spectroscopies. ^{31}P NMR spectra were measured on a Bruker MSL-400 instrument (161.978 MHz, scan 10 kHz, pulse duration 30 μs, pulse delay 15 s; chemical shifts of ^{31}P were measured relatively to the external standard (85% H_3PO_4)).

Procedure of determination of the HPA state under conditions of two-phase oxidation. The HPA state in the presence of H_2O_2 and cycloolefin was studied by spectrophotometry at 20 °C. The absorbance of solutions was determined relatively to equimolar solutions containing no HPA using a Specord M-40 UV—VIS spectrophotometer in 1-mm cells, whose temperature was maintained at a constant level.

Results and Discussion

Epoxidation of cyclic olefins with hydrogen peroxide occurs at 65 °C in a two-phase water—solvent system in the presence of molybdenum or tungsten compounds, mainly by the $PW(Mo)_xO_y{}^{z-}$ peroxo complexes formed in an aqueous HPA—H_2O_2 medium in combination with a phase transfer catalyst (Tables 1 and 2). Under these conditions, 1,2-epoxycycloalkanes form in 70—90% yields. However, we failed to oxidize vinylcyclohexane to the epoxide using this procedure.

The obtained data show that the reaction rate (estimated from the slope ratio of the initial regions of the epoxidation product concentration—time curves, see Fig. 1) in the presence of HPA depends substantially on the order of introduction of the reactants. The HPA introduced immediately after mixing of all reactants (solvent, H_2O_2, cyclohexene, and *N*-hexadecylpyridinium chloride) exhibits a lower catalytic activity than the HPA preliminarily stored in a solution of H_2O_2. This result and ^{31}P NMR data indicate that the variation of the

Table 1. Oxidation of cycloolefins in the HPA—H_2O_2—QCl system at 65 °C with formation of the corresponding 1,2-epoxycycloalkanes (18 mmoles of olefin, [olefin] : [H_2O_2] = 1 : 2 (mol mol^{-1}), 10 mL of $C_2H_4Cl_2$, 0.026 mmoles of HPA, [HPA] : [QCl] = 1 : 3 (mol mol^{-1}))

Cycloolefin	HPA	QCl	t/h	C^a	S^b
				%	
Cyclohexene	$H_3PW_{12}O_{40}$	**4**	7	85	92
Cyclohexene	$H_3PW_{12}O_{40}$	**3**	7	40	92
			24	80	90
Cyclohexene	$H_3PW_{12}O_{40}$	**1**	7	6	88
Cyclohexene	$H_3PW_{11}MoO_{40}$	**4**	6	49	83
Cyclohexene	$H_3PW_9Mo_3O_{40}$	**4**	6	58	85
Cyclohexene	$H_3PW_3Mo_9O_{40}$	**4**	8	10	85
Cyclohexene	$H_3PW_{11}VO_{40}$	**4**	6	50	75
Cyclohexene	$H_3PWMo_{11}O_{40}$	**4**	5	18	75
Cyclohexene	$H_3PMo_{12}O_{40}$	**4**	5	16	77
Cyclooctene	$H_3PW_{12}O_{40}$	**4**	0.15	95	94
Cyclododecene	$H_3PW_{12}O_{40}$	**4**	1.0	80	85
Vinylcyclohexane	$H_3PW_{12}O_{40}$	**4**	1.0	—	

[a] Conversion.

[b] Selectivity.

Table 2. Influence of the solvent nature on the oxidation of cyclooctene ($H_3PW_{12}O_{40}$—H_2O_2—$[C_5H_5NC_{16}H_{33}]Cl$, 18 mmoles of cyclooctene, [cyclooctene] : $[H_2O_2]$ = 1 : 2 (mol mol^{-1}), 10 mL of solvent, 0.026 mmoles of $H_3PW_{12}O_{40}$, $[H_3PW_{12}O_{40}]$: $[[C_5H_5NC_{16}H_{33}]Cl]$ = 1 : 3 (mol mol^{-1}), 65 °C)

Solvent	t/min	C^a	S^b
		%	
$CHCl_3$	10	88	94
$C_2H_4Cl_2$	90	98	88
C_6H_6	100	97	84
MeCN	120	64	81

^{a} Conversion.
^{b} Selectivity.

$[H_2O_2]$: $[H_3PW_{12}O_{40}]$ ratio from 2 to 200 leads to the formation of various peroxo complexes with the general formula $[P_mW_nO_o(O_2)_p]^{x-}$, which differ strongly in the catalytic activity in epoxidation. The maximal activity is observed at the molar ratio $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 200. Comparing these data with the ^{31}P NMR spectroscopic data for HPA solutions with H_2O_2 (Fig. 2), one can see that at $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 2 the spectrum contains one intense signal at δ –15.7 typical of Keggin´s heteropoly anion.[15] At $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 30 the intensity of the signal with δ –15.7 decreases, and new signals with δ –8.9, –7.3, 0.4, 1.5, 2.4, and 6.7 appear in the spectrum indicating, perhaps, the decomposition of the heteropoly anion. At $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 200 the spectrum exhibits only one pronounced signal with δ 2.5, which can be assigned[6,13] to the $PW_4O_{24}^{3-}$ anion. According to the published data,[13] in an H_2O_2 excess HPA can decompose to two anions: $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. We attempted to elucidate the character of compounds, which formed from $H_3PW_{12}O_{40}$ at $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 200, using IR spectra. The IR spectrum of the compound (Fig. 3, curve *1*) prepared by the precipitation of the peroxo complex with *N*-hexadecylpyridinium chloride contains absorption bands of the PO_4^{3-} ion (1087, 1060, and 1038 (shoulder) cm^{-1}), W=O double bond (987 and 960 cm^{-1}), O—O bond (855 and 844 cm^{-1}), antisymmetric and symmetric vibrations of W—O—O (591 and 525 cm^{-1}), and absorption bands at 721, 649, 571, and 548 cm^{-1}. All the above frequencies are characteristic of the $Q_3\{PO_4[WO(O_2)_2]_4\}$ peroxo complexes.[13,25] The absorption bands at 683, 795, and 774 cm^{-1} are assigned to the absorption of the cation Q^+ = $[C_5H_5NC_{16}H_{33}]^+$. The latter are also observed in the spectrum of $[C_5H_5NC_{16}H_{33}]Cl$.

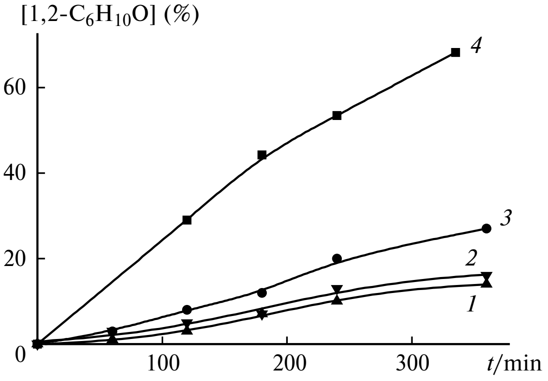

Fig. 1. Concentration of 1,2-epoxycyclohexane in the presence of the $H_3PW_{12}O_{40}$—H_2O_2—$[C_5H_5NC_{16}H_{33}]Cl$ catalytic system at 65 °C with simultaneous introduction of all reactants (*1*) and with preliminary "activation" of HPA in a solution of H_2O_2 (*2*—*4*): $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 200 (*1*, *4*), 2 (*2*), and 30 (*3*).

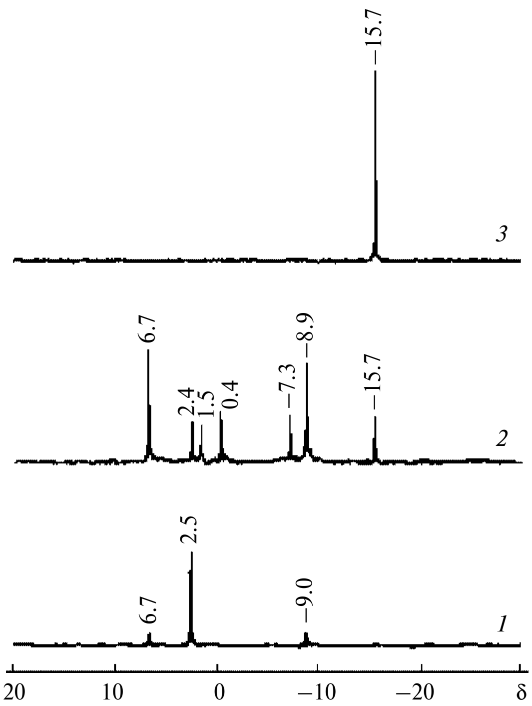

Fig 2. ^{31}P NMR spectra of solutions of $H_3PW_{12}O_{40}$ stored in a solution of H_2O_2 followed by the extraction of the peroxo complexes in $CHCl_3$ with the phase transfer catalyst $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ at $[H_2O_2]$: $[H_3PW_{12}O_{40}]$ = 2 (*1*), 30 (*2*), and 200 (*3*).

The IR spectra of the compound formed after KCl was added to the solution (see Fig. 3, curve *2*) contains the following absorption bands: 965, 952 (shoulder), 835, 767, 616, 566, and 552 cm^{-1}. According to the data in Ref. 13, they refer to the $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ peroxo complex.

The data obtained suggest that $H_3PW_{12}O_{40}$ reacts with H_2O_2, decomposing to two anions (Fig. 4).

Both anions contain η^2,η^1-peroxo bonds and act as efficient oxygen carriers in the two-phase system. It has been shown[16] that tertiary amines, alcohols, and alkenes are readily oxidized in the presence of

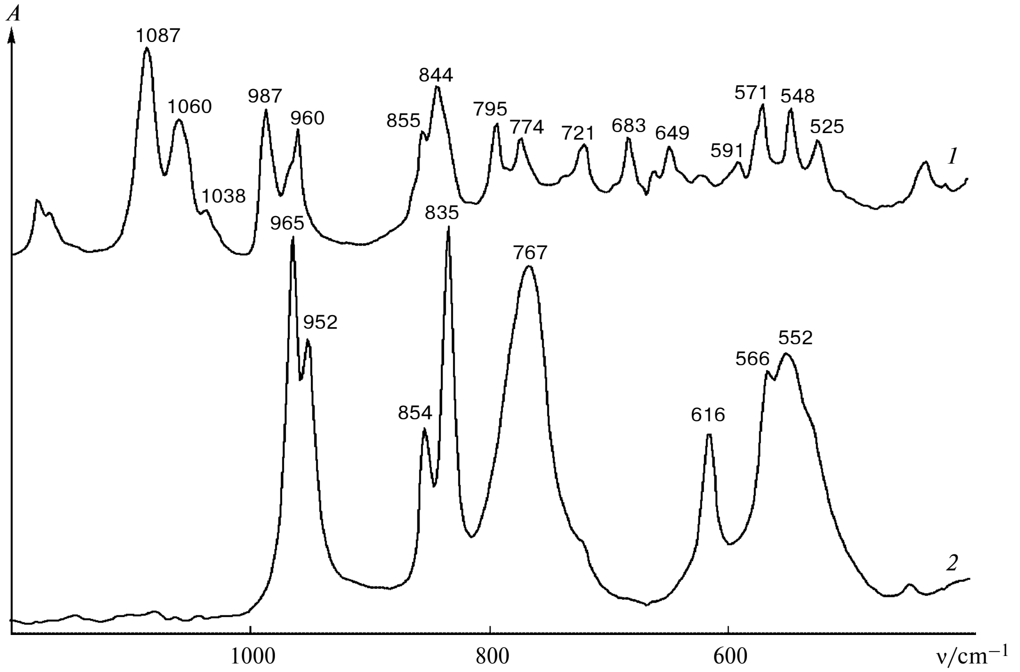

Fig. 3. IR spectra of complexes synthesized from $H_3PW_{12}O_{40}$: *1*, $[C_5H_5NC_{16}H_{33}]_3\{PO_4[WO(O_2)_2]_4\}$ and *2*, $K_2[W_2O_3(O_2)_4(H_2O)_2] \cdot 2H_2O$.

the $[(C_6H_{13})_4N]_2[W_2O_3(O_2)_4(H_2O)_2]$ catalyst. However, this complex is strongly inferior to the $[(C_6H_{13})_4N]_3\{PO_4[WO(O_2)_2]_4\}$ compound in activity. Comparing the data[16] with our results, we can assert with a high probability that $[C_5H_5NC_{16}H_{33}]_3\{PO_4[WO(O_2)_2]_4\}$ rather than $[C_5H_5NC_{16}H_{33}]_2[W_2O_3(O_2)_4(H_2O)_2]$ is an active species in epoxidation of cyclic olefins under the experimental conditions.

Experiments on cyclohexene epoxidation in a two-phase system containing different HPA and an equivalent amount of the phase transfer catalyst, *N*-hexadecylpyridinium chloride, showed that the activity of HPA changed in the series $H_3PW_{12}O_{40} > H_3PW_9Mo_3O_{40} > H_3PW_{11}VO_{40} > H_3PW_3Mo_9O_{40} > H_3PWMo_{11}O_{40} \gg H_3PMo_{12}O_{40}$.

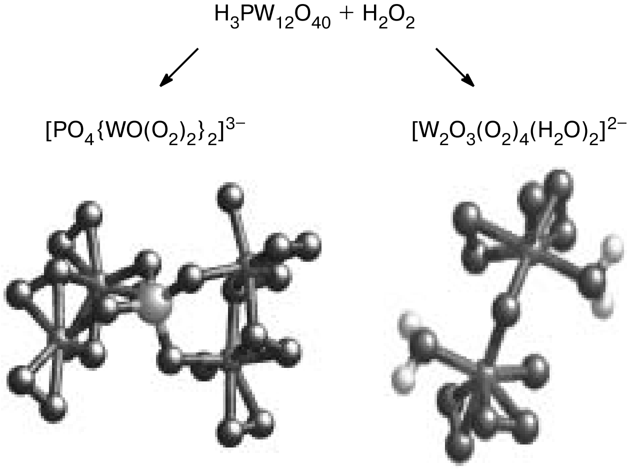

Fig. 4. Scheme of formation of peroxo complexes during the decomposition of HPA by a solution of H_2O_2 at $[H_2O_2] : [H_3PW_{12}O_{40}] = 200$.

A synergistic effect was observed[20,21] for the oxidation of olefins in the presence of the molybdotungsten HPA to form dialdehydes. The authors[20,21] ascribed this effect to several factors: first, an increase in acidity of the solution on going from $H_3PMo_{12}O_{40}$ to $H_3PW_{12}O_{40}$; second, the mixed molybdotungsten HPA introduced directly into the reaction medium were assumed to form peroxo complexes more easily. Our experimental data indicate the absence of this effect. A reason for the inconsistency is probably related to differences in the experimental procedures. An increase in the catalytic activity of the peroxo complexes on going from $H_3PMo_{12}O_{40}$ to $H_3PW_{12}O_{40}$ can be explained by the difference in electronegativity of the elements.[22]

It follows from our data (see Table 1) that the lipophilicity of the phase transfer catalyst is an important characteristic of this process. Our experiments showed that the activity of the catalytic systems depends on the length and structure of the chain of the quaternary ammonium cation and decreases in the series $[C_5H_5N(CH_2)_{15}CH_3]^+ > [(n\text{-}C_6H_{13})_4N]^+ > [CH_3(n\text{-}C_8H_{17})_3N]^+ > [(C_4H_9)_4N]^+$. This series agrees with the sequence of logarithms of extraction constants, which were experimentally determined for bromides of quaternary ammonium bases in the water—1,2-dichloroethane system.[18]

The nature of the solvent also has a substantial effect on the distribution of the catalyst between the organic and aqueous phases. The catalytic activity of the $H_3PW_{12}O_{40}$—H_2O_2—$[C_5H_5NC_{16}H_{33}]Cl$ system in cyclooctene oxidation decreases in the following order of solvents: $CHCl_3 > 1,2\text{-}C_2H_4Cl_2 > C_6H_6 > CH_3CN$ (see Table 2).

Therefore, low-boiling chlorine-containing hydrocarbons (chloroform, 1,2-dichloroethane) are the most appropriate solvents for this reaction. Their application enhances the yield and selectivity of the process (see Table 2), which agrees with the published data.[17]

The state of $H_3PW_{12}O_{40}$ in the system under study was examined by UV spectroscopy. For this purpose, the $[H_2O_2] : [H_3PW_{12}O_{40}]$ ratio was varied during cyclohexene epoxidation in a solution of $CHCl_3$ in the presence of the quaternary ammonium salt $[CH_3(n\text{-}C_8H_{17})_3N]Cl$. The spectrum of the solution at $[H_2O_2] : [H_3PW_{12}O_{40}] = 200$ (Fig. 5, *a*) contains one maximum at 248 nm. The addition of cyclohexene to the system results in the disappearance of the band at 248 nm, and a band at 261 nm appears. The intensity of this band changes substantially after the repeated addition of H_2O_2. After this, the band at 248 nm characteristic of the initial complex appears again, and its intensity increases in time.

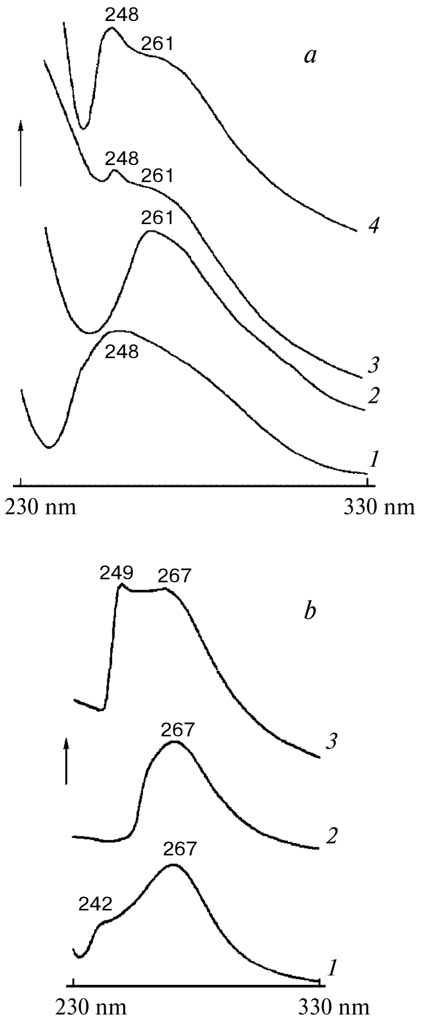

Fig. 5. UV spectra of compounds formed upon the formation of the active peroxo complex (solvent $CHCl_3$) in the $H_3PW_{12}O_{40}$—H_2O_2—$[CH_3(n\text{-}C_8H_{17})_3N]Cl$, $[H_2O_2] : [H_3PW_{12}O_{40}] = 200$ (*a*) and $H_3PW_{12}O_{40}$—H_2O_2—$[CH_3(n\text{-}C_8H_{17})_3N]Cl$, $[H_2O_2] : [H_3PW_{12}O_{40}] = 2$ (*b*) systems: *1*, initial sample; *2*, after addition of 100 μL of cyclohexene; *3*, sample *2* after addition of 100 μL of H_2O_2; and *4*, sample *3* after 15 min.

These results agree well with the ^{31}P NMR data. The ^{31}P NMR spectrum of the initial $H_3PW_{12}O_{40}$—H_2O_2—$[CH_3(n\text{-}C_8H_{17})_3N]Cl$ solution (Fig. 6) contains one signal with δ 2.5 ($PW_4O_{24}^{3-}$ anion). When adding cyclohexene to the solution, the intensity of the band decreases sharply, and lines with δ –8.8 and 6.6 appear in the spectrum. After the addition of H_2O_2 to the system, the intensity of the signal characteristic of $PW_4O_{24}^{3-}$ (δ 2.5) increases again.

Based on the obtained data, we can assume that, when cyclohexene is introduced into the solution, the complex formed at $[H_2O_2] : [H_3PW_{12}O_{40}] = 200$ transforms into an inactive form depleted in the "active" oxygen atoms, which are involved in cyclohexene oxidation. The com-

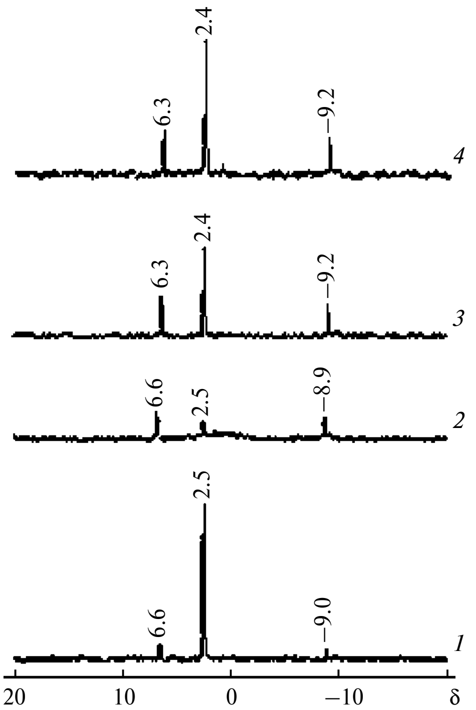

Fig. 6. ^{31}P NMR spectra of compounds formed upon the formation of the active peroxo complex (solvent $CHCl_3$) in the $H_3PW_{12}O_{40}$—H_2O_2—$[CH_3(n\text{-}C_8H_{17})_3N]Cl$ system, $[H_2O_2] : [H_3PW_{12}O_{40}] = 200$: *1*, initial sample; *2*, after addition of 100 μL of cyclohexene; *3*, sample *2* after addition of 100 μL of H_2O_2; and *4*, sample *3* after addition of 100 μL of H_2O_2.

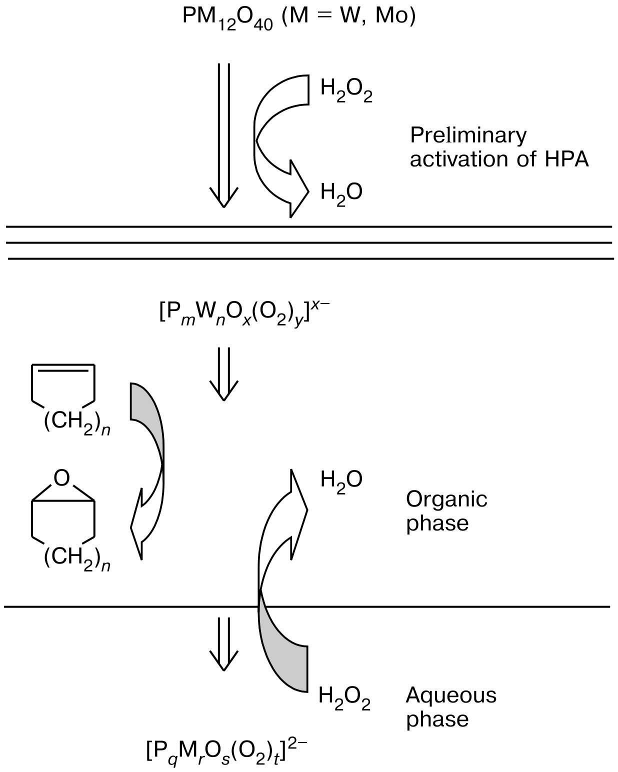

Fig. 7. Scheme of the mechanism of olefin epoxidation.

plex returns to the initial, active state after the addition of a new portion of H_2O_2.

The UV spectrum of a solution of $H_3PW_{12}O_{40}$—H_2O_2—$[CH_3(n\text{-}C_8H_{17})_3N]Cl$ at $[H_2O_2] : [H_3PW_{12}O_{40}] = 2$ has the maximum at 267 nm characteristic of Keggin´s anion (see Fig. 5, *b*). According to the data,[23,24] in the electronic spectra of Keggin´s anions of $XM_{12}O_{40}{}^{x-8}$ (T_d symmetry) the first charge transfer band $\varphi_0 \to \varphi_1{}^*$ appears at ~267 nm. Another absorption band observed in the spectrum of the working solution at 242 nm is attributed, most likely, to the presence of a minor admixture in the initial quaternary ammonium salt $[CH_3(n\text{-}C_8H_{17})_3N]Cl$. This is indicated by the fact that the initial spectrum of the $[C_5H_5NC_{16}H_{33}]_3(PW_{12}O_{40}) \cdot 2H_2O$* complex diluted by $CHCl_3$ does not contain an absorption maximum in a region of 242 nm. The spectrum obtained after the introduction of cyclohexene and then H_2O_2 at room temperature indicates partial decomposition of the $[PW_{12}O_{40}]^{3-}$ anion by H_2O_2: the spectrum contains the same bands as those in the spectrum of the $H_3PW_{12}O_{40}$—H_2O_2—$[CH_3(n\text{-}C_8H_{17})_3N]Cl$ system at $[H_2O_2] : [H_3PW_{12}O_{40}] = 200$ (see Fig. 5, *b*).

Thus, in all the cases, epoxidation proceeds through the same peroxo complex despite different catalytic precursors.

The data obtained suggest that the mechanism of oxidation of cycloolefins with hydrogen peroxide in a two-phase system in the presence of HPA can be described by the scheme in Fig. 7. In an aqueous phase, the heteropoly acid interacts with H_2O_2 to form an active peroxo complex, which is captured by the $[CH_3(n\text{-}C_8H_{17})_3N]^+$ ion and transferred to an organic phase. The reaction preferentially occurs in an organic phase through the transport of oxygen from the peroxo complex to the substrate. The subsequent regeneration of the peroxo complex with hydrogen peroxide occurs at the interface.

The data presented in this work and earlier by other authors[6,7,19] suggest that the catalytic properties of the $PW(Mo)_xO_y{}^{z-}$ peroxo complex are substantially affected by the heteropoly anion composition, the order of introduction of reactants into the reaction system, and the nature of the solvent and phase transfer catalyst.

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* The system was prepared by the addition of a stoichiometric amount of an aqueous solution of $[C_5H_5NC_{16}H_{33}]Cl$ to an aqueous solution of $H_3PW_{12}O_{40}$—H_2O_2, where $[H_2O_2] : [H_3PW_{12}O_{40}] = 2$. The precipitated crystals of $[C_5H_5NC_{16}H_{33}]_3(PW_{12}O_{40}) \cdot 2H_2O$ were filtered off, washed with water, and dissolved in $CHCl_3$. The number of peroxo groups was determined iodometrically.

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