Catalytic oxidation of olefins and alcohols with hydrogen peroxide in a two-phase system giving mono- and dicarboxylic acids

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The present study considered the influence of various factors on the catalytic activity of systems based on a combination of tetrakis(oxodiperoxotungsto)phosphate(3–) with quaternary ammonium cations, for example, with methyltri-*n*-octylammonium [Me(n-C₈H₁₇)₃N]⁺. The catalysts were tested in oxidation of cycloolefins (cyclohexene and cyclooctene), alcohols (octan-1-ol and phenylmethanol), and unsaturated fatty acids (*cis*-9-octadecenoic and 12-hydroxy-9*Z*-octadecenoic acids) with a 30% hydrogen peroxide solution. These reactions proceed under mild conditions (atmospheric pressure, 80–90 °C) to give carboxylic acids. The catalytic systems were characterized by vibrational (IR and Raman) spectroscopy. The state of the systems formed from various precursors, *viz.*, polyoxometallates and phase-transfer catalysts, was studied. It was demonstrated for the first time that the structure formation of peroxo complexes depends on the nature of the halide anion of the quaternary ammonium salt used. The melting points of individual catalytic complexes were determined. The optimal conditions for oxidation were found.

Key words: phase-transfer catalysis, peroxopolyoxotungstates, oxidation, cycloalkenes, alcohols, unsaturated fatty acids, carboxylic acids.

Mono- and dicarboxylic acids are of interest as products of large-scale industry (adipic, suberic, benzoic, *etc.* acids) or intermediates in the synthesis of biologically active compounds.

Carboxylic acids can be prepared by oxidation of olefins with ozone or oxometallic reagents, such as potassium permanganate. Ruthenium tetroxide is used, as a rule, together with NaOCl₄ or NaOI₄, organic hydroperoxides, or peracids. The selectivity of these reactions with respect to the target carboxylic acid is at most 40–50% due to formation of a large amount of by-products and partial oxidation of hydrocarbons to CO₂ and H₂O. For this reason, a two-step method is used for the industrial production of carboxylic acids, for example, adipic acid (Scheme 1). This process includes initial oxidation of cyclohexane with atmospheric oxygen yielding a mixture of cyclohexanol and cyclohexanone followed by oxidation with nitric acid to give adipic acid.¹

The second step affords 6,6-nitrohydroxyiminohexanoic acid as one of the main intermediates, whose concentration in the reaction mixture has a substantial effect on the yield of adipic acid. In addition to 6,6-nitrohydroxyiminohexanoic acid, the reaction gives other intermediates, which are transformed into lower dicarboxyScheme 1



lic acids (glutaric, succinic, and oxalic).² The addition of the steps of separation and purification of the final product to the technological process is associated with investments in plants for the production of adipic acid. Besides, the use of nitric acid as an oxidizer results in the formation of toxic nitrogen oxides. The above-mentioned drawbacks are typical also of other technological methods for the synthesis of mono- and dicarboxylic acids.

The synthesis of carboxylic acids by direct catalytic oxidation of unsaturated hydrocarbons (Scheme 2) is of great interest. An aqueous hydrogen peroxide solution is among the most suitable oxidizers.

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Cat is a catalyst

The advantages of this method are that the process occurs in one step, is efficient and ecologically safe, and requires inexpensive reagents.

Systems based on peroxopolyoxometallates combined with phase-transfer catalysts, *viz.*, quaternary ammonium salts, are recognized as the most efficient catalysts for oxidative cleavage of unsaturated hydrocarbons in a two-phase medium.^{3–7}

To use peroxopolyoxometallate-based multicomponent systems, it is necessary to study in detail both the formation of active catalytic complexes and the mechanism of oxidation reactions of organic substrates.

The aim of the present study was to synthesize peroxopolyoxotungstophosphate complexes combined with quaternary ammonium cations and to use these complexes for oxidation of various organic substrates.

Experimental

Cyclohexene (99%), cyclooctene (98%, Acros), benzyl alcohol (high-purity grade), octan-1-ol (reagent grade), *cis*-9-octadecenoic (oleic) acid (high-purity grade), and dichloromethane (analytical grade) were used. 12-Hydroxy-9*Z*-octadecenoic (ricinoleic) acid was isolated from castor oil: triglycerides were subjected to alkaline hydrolysis (saponification) to prepare a mixture of unsaturated fatty acids, which were separated by chromatography on a column with silica gel⁸ (L100/160 μ m, Merck, hexane—ethyl acetate, 7 : 2, as the eluent, ricinoleic acid, $R_{\rm f}$ 0.12). The structure of the resulting compound was confirmed by ¹H and ¹³C NMR and IR spectroscopy. The concentration of hydrogen peroxide (special purity grade) in an aqueous solution was determined by iodometric titration.

Table 2. Catalytic complexes $Q_3{PO_4[WO(O_2)_2]_4}$ (2 and 3)

Table 1. Quaternary ammonium salts $Q \cdot X \cdot nH_2O(1)$ used in the synthesis of the catalytic complexes

| Salt ^a | Q ⁺ | X- | n | Manufacturer (concentration; m.p. ^b /°C) |
|-------------------|-----------------------------|-----|---|---|
| 1Aa | $Bu^{n}_{4}N^{+}$ | F- | 3 | Fluka Chemie (>98%; 58—60) |
| 1Ab | Bun_4N^+ | Cl- | 0 | Acros (95%; 70) |
| 1Bb | $C_5H_5N(n-C_{16}H_{33})^+$ | Cl- | 1 | Acros (98%; 83-86) |
| 1Cb | $MeN(n-C_8H_{17})_3^+$ | Cl- | 0 | Acros (Aliquat® 336) |
| 1Bc | $C_5H_5N(n-C_{16}H_{33})^+$ | Br- | 1 | Aldrich or |
| | | | | Lancaster (98%; 67-71) |

^{*a*} Hereinafter, The letters **A**, **B**, and **C** in the notations of the compounds correspond to different Q⁺, the letters **a**, **b**, and **c** correspond to the F⁻, Cl⁻, and Br⁻ anions, respectively. ^{*b*} www.acros.be.

Quaternary ammonium halides (QAH) 1 listed in Table 1 and $H_3PW_{12}O_{40}$ (reagent grade) or $Na_2WO_4 \cdot 2H_2O$ (reagent grade) with H_3PO_4 (reagent grade) were used in experiments.

Tungstophosphoric heteropolyacid (HPA) was additionally purified by recrystallization from water. The purity of HPA was checked by ³¹P NMR spectroscopy. The number of water molecules in crystal hydrates of HPA was determined gravimetrically; the calcination temperature was 500 °C. Sodium tungstate was transformed into H₂WO₄ by treating an aqueous Na₂WO₄ solution with concentrated HCl (stirring for 30 min). The resulting yellow gel-like compound was washed with water until the reaction for Cl⁻ became negative and then centrifuged. The precipitate was separated on a glass filter and dried in air at room temperature. According to the results of IR spectroscopic analysis, the finely dispersed precipitate thus obtained corresponded to H₂WO₄.

Synthesis of catalytic complexes. Compounds 2Aa, 2Ab, 2Bb, and 2Bc (Tables 2 and 3) were synthesized according to a known procedure.⁹ A 25% H_2O_2 solution (34 mL, 250 mmol) was added to a solution of $H_3PW_{12}O_{40} \cdot 15.4 \cdot H_2O$ (4.0101 g, 1.27 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 0.5 h, and then salt 1 (3.81 mmol) was added portionwise as dry salt 1Bc (1.5334 g) or solutions of salts 1Aa

| Com- | Value of Q | Precursors | | Characteristics of the sample (m.p./°C) | |
|--------------------|--|--|------------|--|--|
| pound ^a | in the complex | Oxometallate | QAH | | |
| 2Aa 2Ab | $[Bu^{n}_{4}N]_{3}^{+}$ (A) $[Bu^{n}_{4}N]_{3}^{+}$ (A) | $H_{3}PW_{12}O_{40} \cdot 15.4H_{2}O$ $H_{3}PW_{12}O_{40} \cdot 15.4H_{2}O$ | 1Aa 1Ab | White crystalline compound (129–130) White crystalline compound (127–128) | |
| 2Bb | $[C_5H_5N(n-C_{16}H_{33})]_3^+$ (B) | $H_{3}PW_{12}O_{40} \cdot 15.4H_{2}O$ | 1Bb | White crystalline compound (130–131) | |
| 2Bc | $[C_5H_5N(n-C_{16}H_{33})]_3^+$ (B) | $H_{3}PW_{12}O_{40} \cdot 15.4H_{2}O$ | 1Bc | Bright yellow crystalline compound (65–68) | |
| 2Cb | $[Me(n-C_8H_{17})_3N]_3^+ (C)^b$ | $H_2WO_4^c + H_3PO_4$ | 1Cb | Yellowish syrup-like substance | |
| 3Cb | $[\mathrm{Me}(n-\mathrm{C}_{8}\mathrm{H}_{17})_{3}\mathrm{N}]_{3}^{+}(\mathrm{C})$ | $H_2WO_4 + H_3PO_4$ | 1Cb | Yellowish syrup-like substance | |

^{*a*} The letters A, B, and C in the notations of compounds 2 and 3 correspond to different Q^+ , the letters a, b, and c correspond to the F^- , Cl^- , and Br^- anions, respectively.

^b According to the results of IR spectroscopy, the composition of the catalyst is partially inconsistent with this formula.

^c The catalyst was prepared with the use of colloidal H_2WO_4 .

(1.2022 g), **1Ab** (1.060 g), and **1Bb** (1.3640 g) in water (2 mL). The solid precipitate was filtered off on a glass filter, washed with a small amount of water, and dried in air.

Compounds **2Cb** and **3Cb** (see Table 2) were synthesized according to a procedure published earlier.¹⁰ The procedures for the synthesis of compounds **2Cb** and **3Cb** differ in that colloidal H_2WO_4 was used in the synthesis of **2Cb**, whereas solid H_2WO_4 was used in the synthesis of **3Cb**. A mixture of 25% H_2O_2 (3.8 mL, 28.1 mmol) and H_2WO_4 (4.55 mmol) was vigorously stirred in a temperature-controlled glass reactor at 60 °C until the solution turned completely colorless and cooled to room temperature. Then an H_3PO_4 solution (1.143 mmol) was added with vigorous stirring and cooling ($T \le 20$ °C). Salt **1Cb** (0.9215 g, 2.28 mmol) dissolved in CH_2Cl_2 (18.2 mL) was added with stirring to the resulting solution for 2 min. The reaction mixture was stirred for 15 min. Then the organic phase was separated, dried over Na₂SO₄ (~15 h), filtered, and concentrated at 40–50 °C to obtain a yellowish syrup-like substance.

The IR spectra of the samples as Nujol mulls or in KBr pellets were recorded on a Bomem MB-102 Fourier-transform IR (FTIR) spectrometer in the 400–4000 cm⁻¹ region. The Raman spectra were measured on a Bruker 100/S Fourier-transform spectrometer in the 100–1200 cm⁻¹ cm⁻¹ with the use of a Nd-YAG laser ($\lambda = 1.06 \mu m$, power was 100 mW) as the radiation source.

Catalytic oxidation of organic substrates. Selective catalytic oxidation of cycloalkenes, alcohols, and unsaturated fatty acids was carried out in a shaken (≥600 rpm) "catalytic duck" reactor¹¹ or in a temperature-controlled conical flask equipped with a reflux condenser with the use of a magnetic stirrer (600 rpm). The temperature of 80–90 °C was maintained with an accuracy of ± 0.1 °C using a water thermostat. The reaction mixture was prepared as follows: a weighed sample of the catalyst was placed in the reactor, the substrate was added, the reaction mixture was stirred, 30% H₂O₂ was added, and heating was switched on. The conversion of unsaturated hydrocarbons and alcohols was determined by GLC on a Tsvet-500 chromatograph equipped with a flame ionization detector and a 3 m \times 2 mm steel column (0.4% OV-225 on graphitized thermal carbon black, nitrogen as the carrier gas, the evaporator temperature was 150 or 180 °C, the column temperature was 100 or 140 °C, the detector temperature was 120 °C). The conversion of unsaturated fatty acids was monitored by TLC on Silufol plates (Chemapol) using a 3 : 2 hexane-ethyl acetate mixture as the eluent. In some experiments, oxidation products were analyzed by GLC on a Tsyet-500 chromatograph equipped with a flame ionization detector and a $1 \text{ m} \times 3 \text{ mm}$ stainless steel column (SKTFT 15% on Inerton AW-DMCS as the stationary phase, the column temperature was varied in the range of 100-325 °C, the rate of temperature rise was 15 K min⁻¹, the evaporator temperature was 300 °C, helium as the carrier gas). The component contents were determined by internal normalization; the accuracy of measurements was 10 rel. %.

Procedures for isolation of carboxylic acids from the reaction mixture. To quantitatively extract adipic, suberic, and benzoic acids, the reaction mixture was cooled to room temperature, a 10% NaHCO₃ solution (30 mL) was added, the mixture was transferred to a separating funnel, CH_2Cl_2 (30 mL) was added, and the reaction mixture was stirred. The organic layer was separated from the aqueous layer by washing 2–3 times with a saturated NaHCO₃ solution. Hydrochloric acid was added

dropwise with stirring to the aqueous phase (1 : 1) to pH 3 and the reaction mixture was kept at 8–10 °C for ~10 h. The crystalline precipitate that formed was filtered off, washed with a small amount of cold water (\leq 5 °C), and dried in air. The identification was carried out by IR spectroscopy.

n-Octanoic acid was isolated from the reaction mixture by extraction with CH_2Cl_2 (1×10 mL and 3×5 mL). The extract was concentrated on a water bath to obtain an oily liquid, which was dried in a desiccator over $CaCl_2$ (n^{24} 1.4290).

Results and Discussion

Catalytic complexes. In our earlier investigations¹¹ and studies by other authors,^{3-5,9,10} the *in situ* synthesis of the catalyst has been demonstrated to give mixtures of structurally different peroxo complexes, for example, the tungsten peroxo complexes $Q_3\{PO_4[WO(O_2)_2]_4\}$, $Q_2[W_2O_3(O_2)_4(H_2O)_2]$, and $Q_2\{HPO_4[WO(O_2)_2]_2\}$. The complex anion $\{PO_4[WO(O_2)_2]_4\}^3$ shows the highest catalytic activity. Hence, when developing procedures for the synthesis, we sought to prepare a catalytic system involving this anion (see Table 2, Fig. 1) using QAH with



Fig. 1. IR spectra of complexes 2Aa (*a*), 2Ab (*b*), 2Bb (*c*), and 2Bc (*d*) prepared by the reactions of $H_3PW_{12}O_{40}$, H_2O_2 , and correspondingly QAH 1Aa, 1Ab, 1Bb, and 1Bc.

various anions (**1Aa** with F⁻, **1Ab**, **1Bb**, and **1Cb** with Cl⁻, and **1Bc** with Br⁻). As can be seen from Table 2 and Fig. 1, the absorption bands in the IR spectra of complex compounds **2Aa**, **2Ab**, and **2Bb** prepared with the use of quaternary ammonium fluoride (QAF) or chloride (QAC) correspond to the { $PO_4[WO(O_2)_2]_4$ }³⁻ anion and agree well with our results¹¹ and the published data.^{3,4,10}

The IR spectrum of complex compound **2Aa** (see Fig. 1) shows absorption bands of the PO_4^{3-} ion (1085, 1052, and 1038 (sh) cm⁻¹), the W=O bond (971 cm⁻¹), the O–O bond (856 and 845 cm⁻¹), and antisymmetric and symmetric vibrations of W–O–O (590 and 521 cm⁻¹). The spectrum also has other absorption bands (722, 736, 651, 577, and 550 cm⁻¹) associated with absorption of the cation.

The IR spectrum of complex compound **2Ab** shows absorption bands of the PO_4^{3-} ion (1082, 1051, and 1036 (sh) cm⁻¹), the W=O bond (970 cm⁻¹), the O–O bond (855, 844 cm⁻¹), antisymmetric and symmetric vibrations of W–O–O (591 and 521 cm⁻¹), and absorption bands at 721, 735, 650, 574, and 549 cm⁻¹ characterizing the cation.

The IR spectrum of compound **2Bb** has absorption bands of the PO_4^{3-} ion (1088, 1061, and 1038 (sh) cm⁻¹), the W=O bond (988 and 961 cm⁻¹), the O–O bond (856 and 844 cm⁻¹), antisymmetric and symmetric vibrations of W–O–O (591 and 526 cm⁻¹), and absorption bands at 722, 650, 571, and 548 cm⁻¹.

The Raman spectra (Fig. 2) were recorded for catalyst **2Aa** and the complex salt, which was prepared from the filtrate after isolation of **2Aa** according to the procedure described earlier.¹¹ The spectra *a* and *b* (see Fig. 2) corre-



Fig. 2. Raman spectra of the catalysts based on peroxopolyoxometallates: $K_2[W_2O_3(O_2)_4(H_2O)_2]$ (a) and $[Bu^n_4N]_3\{PO_4[WO(O_2)_2]_4\}$ (b).

spond to the $K_2[W_2O_3(O_2)_4(H_2O)_2]$ (956, 851, 619, 568, 558, 331, and 318 cm⁻¹) and $[Bu_4N]_3\{PO_4[WO(O_2)_2]_4\}$ (980, 860, 591, 578, 534, 330, 298, and 259 cm⁻¹) compounds and are consistent with the results of the study.⁹

In the synthesis of complex **2Bc** with the use of quaternary ammonium bromide (QAB) **1Bc**, the reaction mixture warmed up and vigorous foaming occurred in the step of precipitation of the peroxo complex. These phenomena were not observed in reactions with the use of QAF and QAC. In the IR spectrum of the yellow crystalline compound (**2Bc**) prepared by precipitation of the peroxo complex with QAB (**1Bc**), the absorption bands of the PO₄³⁻ ion (1089, 1069, and 1032 (sh) cm⁻¹) only partially consistent with the published data.^{9,10} Other absorption bands in the spectrum do not correspond to the catalyst $[C_5H_5N(CH_2)_{15}Me]_3\{PO_4[WO(O_2)_2]_4\}$ (see Fig. 1, *d*).

The observed influence of QAB (1Bc) on decomposition of the peroxo complex can be attributed to the higher reducing power of the bromine salts compared to QAF and QAC (QBr > QCl > QF), which is also true for the series of halogens $F_2 > Cl_2 > Br_2$, whose standard redox potentials $(E^{\circ})^{12}$ are 2.87, 1.359, and 1.065 V, respectively. Apparently, the redox reactions $W_2O_5 + 2 Br^- + 2 H^+ \rightarrow Br_2 + 2 WO_2 + H_2O$ resulting in decomposition of tungsten peroxo complexes can occur in solution upon the addition of QAB.

This assumption is also supported by the characteristic features encountered by mixing with KBr and compacting into wafers for measurements of IR spectra. As can be seen from Fig. 3, the spectra of catalysts 2Aa and 2Bb, which were synthesized with the use of OAF (1Aa) and QAC (1Bb), respectively, recorded in KBr pellets (a, c)differ from the spectra measured as Nujol mulls (b, d). The spectra b and d correspond to the structures of the complexes synthesized, whereas the absorption bands in the spectra *a* and *c* are inconsistent with these structures, which can be associated with decomposition of the complexes due to interaction of the Br- ions with the peroxide groups. The longer the time from the preparation of the sample to the onset of exposure, the larger discrepancies observed in the spectra. An analogous situation is also characteristic of the tungsten peroxo complexes $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. The IR spectra of the potassium salt of this complex are shown in Fig. 4.

Attempts to change the conditions of the synthesis in the step of addition of QAH (variations in the temperature (5–30 °C) and pH, the addition of either dry QAH or QAH predissolved in water) were unsuccessful. Therefore, regardless of the nature of the quaternary cation, QAB do not allow one to perform the synthesis of catalytic systems of the desired composition including tungsten peroxo complexes.

Of all the complexes synthesized (see Table 2), tetra*n*-butylammonium tetra(diperoxotungsto)phosphate (**2Aa**



Fig. 3. IR spectra of the catalytic complexes $Q_3\{PO_4[WO(O_2)_2]_4\}$: $[Bu^n_4N]_3\{PO_4[WO(O_2)_2]_4\}$ **2Aa** and **2Ab** (a, b) and $[C_5H_5N(CH_2)_{15}CH_3]_3\{PO_4[WO(O_2)_2]_4\}$ **2Bb** and **2Bc** (c, d); *a* and *c*, in KBr pellets; *b* and *d*, as Nujol mulls.

and **2Ab**) is most stable on storage. This complex can be kept at room temperature for one month. The changes in the IR spectrum of methyl-tri-*n*-octylammonium di(diperoxotungsto)hydrophosphate (**3Cb**) characterized by absorption bands at 1264, 1088, 1056, 1033 (sh), 973, 892, 855, 846, 741, 733, 702, 651, 625, 591, 576, 549, and 523 cm⁻¹ are observed after three days. The *N*-hexadecylpyridinium tetra(diperoxotungsto)phosphate complex (**2Bb**) is less stable. This complex remains unchanged for only one day. Therefore, the order of decreasing stability for the above complexes is as follows: $K_2[W_2O_3(O_2)_4(H_2O)_2] > [Bu^n_4N]_3[PO_4[WO(O_2)_2]_4]$ (**2Aa**, **2Ab**) > [Me(*n*-C₈H₁₇)₃N]₂{HPO₄[WO(O_2)_2]₂} (**3Cb**) > [C₅H₅N(CH₂)₁₅Me]₃{PO₄[WO(O₂)₂]₄ (**2Bb**)

The fact that we synthesized individual complex compounds 2Aa, 2Ab, 2Bb, and 3Cb rather than mixtures of compounds, for example, 2Aa + 1Aa is supported not only by the data from IR and Raman spectroscopy but also by the melting points (see Table 2), which differ substantially from the melting points of QAH (see Table 1). It is not inconceivable that the resulting compounds contain halide ions as impurities, because the complexes were not thoroughly washed off from F⁻ and Cl⁻ ions.

Oxidation of organic substrates. Experiments on oxidation of various organic substrates with 30% H₂O₂ showed that the use of a "catalytic duck" reactor allows one to prepare products in the highest yields at a given

rocking speed (m) > 500 rpm, *i.e.*, the observed plot of the reaction rate vs. the rocking speed is characterized by the presence of a plateau. At the same time, a plateau was achieved already at m = 300 rpm when the reaction was performed in a conical flask with magnetic stirring of a two-phase solution. It should also be noted that the volume of the reaction mixture for the reactors under consideration was $\sim 1/3$ of the reactor volume. An interesting result was obtained when we performed parallel experiments on oxidation of benzyl alcohol with the use of the above-described reactors at m = 600 rpm, all other factors being the same. It was found that the degree of conversion of the alcohol (a peak at 120 °C) in a "catalytic duck" after 1.5 h (Fig. 5, a, b) is higher than that in a conical flask equipped with a stirrer. Moreover, the conversion of the alcohol in a "catalytic duck" after 3 h (see Fig. 5, a' and b') was 100%, and by-products were virtually absent (a'). The yield of the target product, viz., PhCO₂H, was 98-99%, whereas large amounts of by-products, including benzyl benzoate (peak at 210 °C), were present in the organic phase prepared by the reaction in a reactor equipped with a stirrer (b') in spite of a rather high degree of conversion of the alcohol (a peak at 120 °C), the yield of PhCO₂H being 60%. Therefore, the above experimental data suggest that not only the reaction rate but also the reaction mechanism depend substantially on the mode of stirring of a two-phase mixture. This is consistent with the



Fig. 4. IR spectra of the salt $K_2[W_2O_3(O_2)_4(H_2O)_2]$: in KBr pellets (*a*), as Nujol mulls immediately after mixing (*b*) and after storage at 6.5 °C for 1.5 months (*c*).

conclusions drawn in the study¹³ that the use of reactors equipped with a stirrer can give rise to an effect of the socalled slipping of the stirrer. In this case, in spite of an increase in the rotational speed of the stirrer, the rate of stirring and, consequently, the surface area of the inter-



Fig. 5. Chromatograms of the organic phase of the reaction mixture prepared by oxidation of benzyl alcohol: a, a "catalytic duck"; b, a conical flask equipped with a stirrer; the reaction time was 1.5 (a, b) and 3.0 h (a', b'); solvents: 1, (EtOH); 2, PhCH₂OH; 3, PhCHO.

face are not increased. In this connection, the observed rates of the same reaction, which are obtained by mixing two-phase solutions in different hydrodynamic modes, can hardly be expected to have a good convergence. For the above reasons, the data on oxidation of alcohols and cycloolefins reported in the studies,^{3,4,14,15} are difficult to compare with each other. The conditions of mixing of nonviscous liquids can be standardized by performing reactions in a rocking "catalytic duck" reactor placed on a high-speed rocking platform.

Study of oxidation of various organic substrates (Table 3) demonstrated that oxidation accompanied by

Table 3. Catalytic oxidation of olefinic compounds and alcohols with hydrogen peroxide

| Substrate | Catalyst | <i>T</i> /°C | $[H_2O_2]/[Sub]$ | Resulting acid | Yield (mol.%) |
|------------------------------|---------------|--------------|------------------|-----------------------------------|---------------|
| Cyclohexene ^a | 3Cb | 90 | 2 | Hexane-1,6-dioic | 72 |
| Cyclooctene ^a | 2Aa | 85 | 8 | Octane-1,8-dioic | 60 |
| Octan-1-ol ^a | 3Cb | 90 | 2 | <i>n</i> -Octanoic | 80 |
| | 2Ab | 90 | 6 | <i>n</i> -Octanoic | 81 |
| Benzyl | 2Bb | 90 | 2 | Benzoic | 67 |
| alcohol ^a | 3Cb 90 | 2 | Benzoic | 81 | |
| | | | 5 | Benzoic | 98 |
| Oleic acid ^b | 2Bb | 80 | 4 | Nonane-1,9-dioic | 86 |
| | | | | <i>n</i> -Nonanoic | 82 |
| | | | | cis-9,10-Epoxyoctadecanoic | ≤ 2 |
| Ricinoleic acid ^b | 2Bb | 80 | 4 | Nonane-1,9-dioic | 84 |
| | | | | 3-Hydroxynonanoic | 84 |
| | | | | 12-Hydroxy-9,10-epoxyoctadecanoic | ~4 |

^{*a*} The reaction conditions: the reaction time was 3 h; [Sub]/[Cat] = 200.

^{*b*} The reaction time was 1 h, [Sub]/[Cat] = 50.

double bond cleavage occurs at temperatures higher than 80 °C to give mono- and dicarboxylic acids in high yields. Oxidation of cycloolefins for 3 h affords adipic acid in yields of up to 72% (70% after 24 h in the study⁴), and the yield of suberic acid is no lower than 60%, the conversion of cyclohexene and cyclooctene being 85%.

Oxidation of linear alcohols with hydrogen peroxide was investigated using oxidation of octan-1-ol at [Sub]/[Cat] = 200 (Sub is the substrate) at 90 °C as an example. After 3 h, the reaction afforded octanoic acid in 80% yield (in the study,³ the yield was 85% after 6 h). Oxidation of benzyl alcohol at 83 °C gave PhCO₂H in 98–99% yield (85% at 90 °C in the study³) due to a more thorough choice of the optimal ratio [H₂O₂]/[Sub] = 3. In spite of the fact that, according to the stoichiometry of the reaction

 $PhCH_2OH + 2 H_2O_2 \rightarrow PhCOOH + 3 H_2O,$

this ratio is 2, an excess of H_2O_2 is required to achieve more complete oxidation.

The dependence of the yield of benzoic acid on the $[H_2O_2]/[Sub]$ ratio (Fig. 6) is indicative of the presence of a transition region in the range from 1.8 to 3.0. In this connection, the portionwise addition of a hydrogen peroxide solution to the reaction mixture (three equal portions during the reaction) used in the study¹⁴ was, apparently, reasonable. Since decomposition of H_2O_2 is excluded or, at least, is reduced to a minimum, the $[H_2O_2]/[Sub]$ ratio would be expected to be close to the stoichiometric value.

Our experiments demonstrated that the oxidative cleavage of unsaturated fatty acids at 80 °C in the presence of *N*-hexadecylpyridinium tetra(diperoxotungsto)phosphate (**2Bb**) gave rise to di- and monocarboxylic acids. In addition, the reaction mixture contained a small amount (~5%) of the partial oxidation product, *viz.*, epoxide. Ac-



Fig. 6. The yield of benzoic acid as a function of the $[H_2O_2]/[Sub]$ molar ratio in oxidation of benzyl alcohol. The reaction conditions: $[Me(n-C_8H_{17})_3N]_3$ {PO₄[WO(O₂)₂]₄} (**3Cb**) as the catalyst, $[Sub]/[Cat] = 200, 83 \degree C, 3 h.$

cording to the results of our study (see Table 3), oxidation of oleic acid affords nonane-1,9-dioic and *n*-nonanoic acids with selectivity of 82-86%, as well as *cis*-9,10-epoxyoctadecanoic acid ($\leq 2\%$), the conversion of oleic acid being 95% (Scheme 3).

Scheme 3



i. 30% H₂O₂ (4 equiv.), 2Bb (2 mol.%), 80 °C, 1 h.

The above-mentioned yields are substantially higher than the yields of the acids reported in the study,⁶ where oxidation of oleic acid was performed under analogous conditions but at 90 °C. The total yield of azelainic and nonanoic acids was 57 and 64% after 5 and 10 h, respectively.

Under the conditions of oxidation of oleic acid, ricinoleic acid is converted into nonane-1,9-dioic and 3-hydroxynonanoic acids with selectivity of 84%(Scheme 4). In addition, the reaction produces 12-hydroxy-9,10-epoxyoctadecanoic acid (~4%) (see Table 3).

Scheme 4



To conclude, our experimental data allow the optimization of the procedure for the synthesis of promising catalytic complexes based on tungsten peroxo complexes combined with phase-transfer catalysts for oxidation in two-phase solutions. In addition, we refined the reaction conditions for oxidation of various organic substrates for the preparation of industrially important mono- and dicarboxylic acids.

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