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Supramolecular calixarene-based catalytic systems in the Wacker-oxidation of higher alkenes

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Abstract

Biphasic Wacker-oxidation of a series of linear alkenes (from hexene-1 up to dodecene-1) and styrenes catalysed by water soluble calixarene-based systems has been studied. The substrate selectivity is shown to vary significantly depending on the calixarene used. The water soluble palladium(II) complexes with the calixarenes modified by the benzonitrile groups are shown to exhibit higher activity as compared to the same for similar catalytic systems containing a palladium salt and a water soluble calixarene.

Keywords: Biphasic catalysis; Supramolecular catalysis; Molecular recognition; Wacker-oxidation; Calixarenes

1. Introduction

Palladium and copper salt catalysed oxidation of alkenes by the oxygen in water-organic media is a convenient technique of ketone synthesis while the ethylene oxidation process (Wacker-process) is one of the major industrial methods of the acetaldehyde production [1]. Note that the rate of two-phase oxidation of higher alkenes is too low because of poor solubilities of substrates in water. We believe that problem can be solved by using of ligands based on molecular receptors such as cyclodextrins (cyclic oligosacharides consisting of six or more D-glucopyranose units), calixarenes (cyclic compounds containing phenol groups bridged by methylenes), urotropine-based macro-cycles, etc. [2–20]. Modified cyclodextrins and calixarenes can serve as efficient agents for the transport of non-polar substrates into the water phase due to formation of host–guest complexes with reactant [3–12,16–19]. The host molecule size governs the substrate selectivity of catalytic systems as it was shown by the example of the Wacker-oxidation [4–6,8] and the allylcarbonate decomposition [21,22].

Besides, due to substrate orientation, regio- and, in particular cases, stereoselectivity can be achieved. For example, the iron and copper complexes with modified cyclodextrins were active in selective hydroxylation of phenol to catechol [3,4]; the manganese complexes with cyclodextrin containing porphyrins exhibited high activity in selective hydroxylation of steroids [23–25]; the ruthenium complexes with the cyclodextrin modified porphyrins were used in selective oxidation of the isoprene fragment of the carotene [26–29].

In the present work, the Wacker-oxidation of a series of higher alkenes catalysed by supramolecular complexes containing the water soluble calixarenes (Fig. 1) has been studied. We suppose that such catalysts that combine in a single molecule properties of metal complex and phase transfer agent with molecular recognition ability provide substantial increase in catalytic activity and influence the selectivity due to the substrate orientation.

2. Experimental

p-Tetra-*tert*-butylcalix[4]arene and *p*-hexa-*tert*-butylcalix[6]arene were synthesised according to a procedure given in [30,31]. These were dealkylated to calix[4]arene and calix[6]arene as described in [32]. Potassium salts of calixarenes were obtained by the reaction of potassium *tert*-butylate with calixarenes according to the literature procedure [33].

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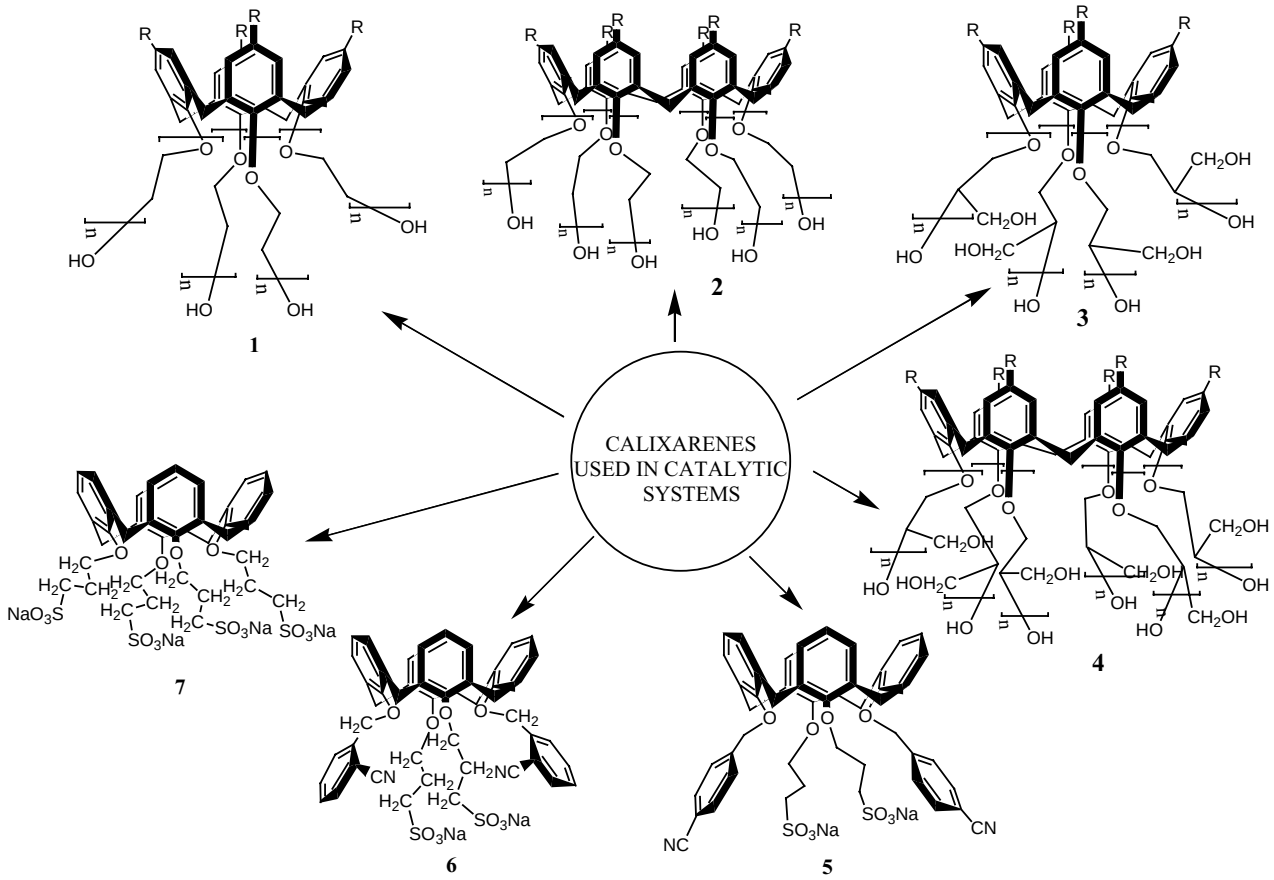

Fig. 1. Water soluble calixarenes.

NMR measurements were made with a VXR-400 Varian spectrometer operating at a frequency of 400 MHz. FTIR spectra were obtained with Perkin-Elmer 2000 spectrometer.

2.1. Preparation of oxyethylated calixarenes (*1*, *2*)

Potassium salt of calixarene (ca. 1 mmol) and ethylene carbonate (from 24 to 120 mol eq.) were dissolved in 25 ml of tetra-*N*-methylurea. The mixture was stirred at 150 °C under nitrogen for 4 h. Furthermore, after this period CO_2 evolution had ceased. The solvent was removed at 100 °C under reduced pressure. The crude product was dissolved in ethylacetate (10 ml) and all impurities were extracted by 5% solution of NaCl in water. By this methods compounds **1** ($n = 1.25$ and 3.25) and **2** ($n = 3$, $n = 4.5$) were synthesised.

2.1.1. Compound $\mathbf{1}_{n=1.25}$

^{1}H NMR ($CDCl_3$), δ, ppm: 1.0–1.4 (m, ArC(C**H**$_3$)$_3$); 6.8–7.3 (s, Ar**H**); 4.1 (t, ArOC**H**$_2$); 3.6 (t, ArOCH$_2$C**H**$_2$); 2.9 (broad line, ArOCH$_2$CH$_2$O(C**H**$_2$C**H**$_2$O)$_m$H).

^{13}C NMR ($CDCl_3$), δ, ppm: 123–124 (**C**Ar); 73 (**C**H$_2$CH$_2$OH); 61 (**C**H$_2$OH); 64 (ArO**C**H$_2$CH$_2$O); 69 (ArOCH$_2$**C**H$_2$O); 34 (Ar**C**(CH$_3$)$_3$); 31 (ArC(**C**H$_3$)$_3$); 70 (ArOCH$_2$CH$_2$O(**C**H$_2$**C**H$_2$O)CH$_2$CH$_2$OH).

2.1.2. Compound $\mathbf{1}_{n=3.25}$

^{1}H NMR ($CDCl_3$), δ, ppm: 1.0–1.5 (m, ArC(C**H**$_3$)$_3$); 7.3 (s, Ar**H**); 4.3 (t, ArOC**H**$_2$); 3.3 (t, ArOCH$_2$CH$_2$); 3.1 (broad line ArOCH$_2$CH$_2$O(C**H**$_2$C**H**$_2$O)$_m$H). ^{13}C NMR ($CDCl_3$), δ, ppm: 130–142 (**C**Ar); 73 (**C**H$_2$CH$_2$OH); 62 (**C**H$_2$OH); 67 (ArO**C**H$_2$CH$_2$O); 69 (ArOCH$_2$**C**H$_2$O); 34 (Ar**C**(CH$_3$)$_3$); 32 (ArC(**C**H$_3$)$_3$); 71 (ArOCH$_2$CH$_2$O(**C**H$_2$**C**H$_2$O)CH$_2$CH$_2$OH).

2.1.3. Compound $\mathbf{2}_{n=3}$

^{1}H NMR ($CDCl_3$), δ, ppm: 1.0–1.4 (m, ArC(C**H**$_3$)$_3$); 6.3–7.3 (s, Ar**H**); 4.1 (t, ArOC**H**$_2$); 3.6 (t, ArOCH$_2$C**H**$_2$); 2.85 (broad line, ArOCH$_2$CH$_2$O(C**H**$_2$C**H**$_2$O)$_m$H). ^{13}C NMR ($CDCl_3$), δ, ppm: 124–135 (**C**Ar); 73 (**C**H$_2$CH$_2$OH); 61 (**C**H$_2$OH); 64 (ArO**C**H$_2$CH$_2$O); 69 (ArOCH$_2$**C**H$_2$O); 34 (ArC(CH$_3$)$_3$); 31 (ArC(**C**H$_3$)$_3$); 70 (ArOCH$_2$CH$_2$O(**C**H$_2$**C**H$_2$O)CH$_2$CH$_2$OH).

2.1.4. Compound $\mathbf{2}_{n=4.5}$

^{1}H NMR ($CDCl_3$), δ, ppm: 1.0–1.5 (m, ArC(C**H**$_3$)$_3$); 7.3 (s, Ar**H**); 4.3 (t, ArOC**H**$_2$); 3.2 (t, ArOCH$_2$C**H**$_2$); 3.1 (broad line, ArOCH$_2$CH$_2$O(C**H**$_2$C**H**$_2$O)$_m$H). ^{13}C NMR ($CDCl_3$), δ, ppm: 130–140 (**C**Ar); 73 (**C**H$_2$CH$_2$OH); 62 (**C**H$_2$OH); 67 (ArO**C**H$_2$CH$_2$O); 69 (ArOCH$_2$**C**H$_2$O); 34 (Ar**C**(CH$_3$)$_3$); 31 (ArC(**C**H$_3$)$_3$);71 (ArOCH$_2$CH$_2$O(**C**H$_2$**C**H$_2$O)CH$_2$CH$_2$OH).

Table 1
Distribution of oxyethylated calixarenes from MALDI-TOF-MS data

Calixarene	Ratio ethylene carbonate/calixarene during synthesis	A number of ethylene oxide chains in one molecule	
		Range	Average number
$\mathbf{1}_{n=1.25}$	24	2–9	5
$\mathbf{1}_{n=3.25}$	80	4–20	13
$\mathbf{2}_{n=3}$	36	9–25	18
$\mathbf{2}_{n=4.5}$	120	14–35	27

The MALDI-TOF-MS spectra of calixarenes **1–2** were measured in reflecto-mol mode with MALDI-TOF-MS BRUKER spectrometer. Laser wavelength was 336 nm. 2,5-Dihydroxybenzoic acid was used as matrix.

Results are presented in Table 1.

2.2. Preparation of oligoglycerol-modified calixarenes (*3*, *4*)

Oligoglycerol-modified calixarenes were obtained by the following procedure. Glycidol (6 or 12 mmol) was added to potassium salt of calixarene (0.5 mmol) under stirring at 0 °C. The reaction was carried out at 25 °C for 30 h. The crude product was purified by recrystallisation from methanol/water mixture.

2.2.1. Compound $\mathbf{3}_{n=5}$

^{1}H NMR ($CDCl_3$) δ, ppm: 1.3 (s, (C**H**$_3$)$_3$CAr), 2.5–2.9 (broad s, ArO(CH$_2$C**H**(C**H**$_2$OH)O)$_n$H); 3.25–4 (broad s, ArO(CH$_2$C**H**(CH$_2$OH)O)$_n$H); 3.2, 4.2 (2d, ArCH$_2$Ar); 4.7 (t, ArO(C**H**$_2$CH(CH$_2$OH)O)$_n$H); 7.2 (s, ArH)).

2.2.2. Compound $\mathbf{4}_{n=5}$

^{1}H NMR ($CDCl_3$) δ, ppm: 1.3 (s, (C**H**$_3$)$_3$CAr); 2.5–2.9 (broad s, ArO(CH$_2$CH(C**H**$_2$OH)O)$_n$H); 3.25–4 (broad s, ArO(CH$_2$C**H**(CH$_2$OH)O)$_n$H); 3.2 (s, ArCH$_2$Ar); 4.7 (t, ArO(C**H**$_2$CH(CH$_2$OH)O)$_n$H); 7.2 (s, ArH).

Analysis of oligoglycerol-modified calixarenes by HPLC was conducted using column Diasorb-NH$_2$ (150 mm × 4 mm, 5 m km) with gradient elution (acetonitrile/water from 1/10 to 4/1 for 15 min) UV-detector (260 nm).

2.3. Preparation of calixarenes *5–7* (Fig. 2)

Calixarenes **8** and **9** for the synthesis of water soluble calyx[4]arenes 5 and 6 were synthesised as follows. A suspension of calix[4]arene (3 g, 7.1 mmol), anhydrous potassium carbonate (1.12 g, 8.1 mmol), and *p*-(bromomethyl)benzonitrile (for 8) or *o*-(bromomethyl)benzonitrile (for 9) in dry acetonitrile (100 ml) was refluxed for 12 h. After solvent evaporation, the residue was dissolved in chloroform (100 ml), twice washed with 1N HCl (25 ml), and then with a NaCl saturated solution (25 ml). The organic layer was dried over $MgSO_4$, and the solvent was removed by evaporation. The residue was washed with hot methanol. The product yield was 78%. HPLC analysis was carried out on a Diasorb-NH$_2$ column (250 mm × 4 mm, particle size of 5 m km) using the 2:1 chloroform–hexane solvent blend as an eluent. The purification was carried out on a column (400 mm × 10 mm) packed with the same sorbent using the 4:1 hexane–chloroform eluent. The compound obtained was characterized by NMR and MS techniques. MS spectra was obtained using Finnigan-MAT 1125 GC–MS system.

2.3.1. Compound *8*

^{1}H NMR ($CDCl_3$) δ, ppm: 3.3, 4.2 (2d, 8H, ArC**H**$_2$Ar); 5.2 (s, 4H, ArOC**H**$_2$ArCN); 6.7 (d, 4H, Ar**H**); 6.9 (d, 4H, ArH); 6.55 (t, 2H, Ar**H**); 6.65 (t, 2H, Ar**H**); 7.5 (d, 4H, **H**ArCN); 7.75 (d, 4H, **H**ArCN), *m/z* M($C_{44}H_{34}N_2O_4$) 654, 653, 539, 538, 521, 520, 444, 405; FTIR cm^{-1} (KBr) 2164 (CN).

2.3.2. Compound *9*

^{1}H NMR ($CDCl_3$), δ, ppm: 6.7 (d, 4H, Ar**H**); 6.9 (d, 4H, Ar**H**); 7.1 (d, 4H, Ar**H**); 3.4, 4.3 (dd, 8H, ArC**H**$_2$Ar); 5.3 (s, 4H, ArOC**H**$_2$ArCN); 7.2 (d, 2H, **H**ArCN); 7.5 (m, 4H, **H**ArCN); 8.3 (d, **H**ArCN); FTIR, cm^{-1} (KBr) 2164 (CN).

Calixarenes **5** and **6** were synthesised by the procedure given below. To calixarene **8** or **9** (0.7 g, 1.07 mmol) dissolved in absolute THF (75 ml), 0.25 g (22.5 mmol) of NaH (60% slurry in oil) was added under argon and the mixture was stirred until hydrogen evolution ceased. A solution of 1,3-propanesultone (1.01 g, 13.875 mmol) in THF (15 ml) was added dropwise, and the resultant mixture was stirred for 24 h at room temperature. After completion of the reaction, the residual NaH was decomposed with methanol, and the solvent was removed. The residue was dissolved in a small amount of hot water, and the product was precipitated by adding sodium acetate.

2.3.3. Compound *5*

^{1}H NMR (DMSO) δ, ppm 2.2 (4H, m, ArOCH$_2$C**H**$_2$CH$_2$SO$_3$Na); 2.6 (4H, t, ArOC**H**$_2$CH$_2$CH$_2$SO$_3$Na); 3.4, 4.35 (8H, 2d, ArCH$_2$Ar); 3.9 (4H, d, ArOCH$_2$CH$_2$C**H**$_2$SO$_3$Na); 5.2 (4H, s, ArOCH$_2$ArCN); 6.3–6.6. (12**H**, m, ArH); 7.4 (4H, d, HArCN); 7.65 (4H, d, HArCN).

^{13}C NMR (DMSO), δ, ppm: 25.1 (C**H**$_2$ calixarene); 30.1 (–CH$_2$C**H**$_2$CH$_2$SO$_3$Na); 48 (–CH$_2$CH$_2$C**H**$_2$SO$_3$Na); 74 (–C**H**$_2$CH$_2$CH$_2$SO$_3$Na); 87 (O–C**H**$_2$–Ar–CN); 112; 130, 140 (O–CH$_2$–Ar**H**–CN); 121–129, 151, 158 (CH$_2$–Ar**H**–CH$_2$) FTIR, cm^{-1} 2160 (CN); 1400; 1280 (SO_3^{2-}).

2.3.4. Compound *6*

^{1}H NMR (DMSO) δ, ppm 2.1 (4H, m, ArOC**H**$_2$CH$_2$ CH$_2$SO$_3$Na); 2.3 (4H, t, ArOCH$_2$CH$_2$C**H**$_2$SO$_3$Na); 3.1, 4.3 (8H, 2d, ArCH$_2$Ar); 4.0 (4H, t, ArOCH$_2$CH$_2$C**H**$_2$SO$_3$Na); 5.0 (4H, s, ArOCH$_2$ArCN); 6.4–7.1 (12H, m, ArH); 7.5 (2H, t, HArCN); 7.75 (2H, d, HArCN); 7.9 (2H, t, HArCN); 8.1 (2H, d, HArCN).

^{13}C NMR (DMSO), δ, ppm: 25.1 (C**H**$_2$ calixarene); 30.1 (–CH$_2$C**H**$_2$CH$_2$SO$_3$Na); 48 (–CH$_2$CH$_2$C**H**$_2$SO$_3$Na); 74

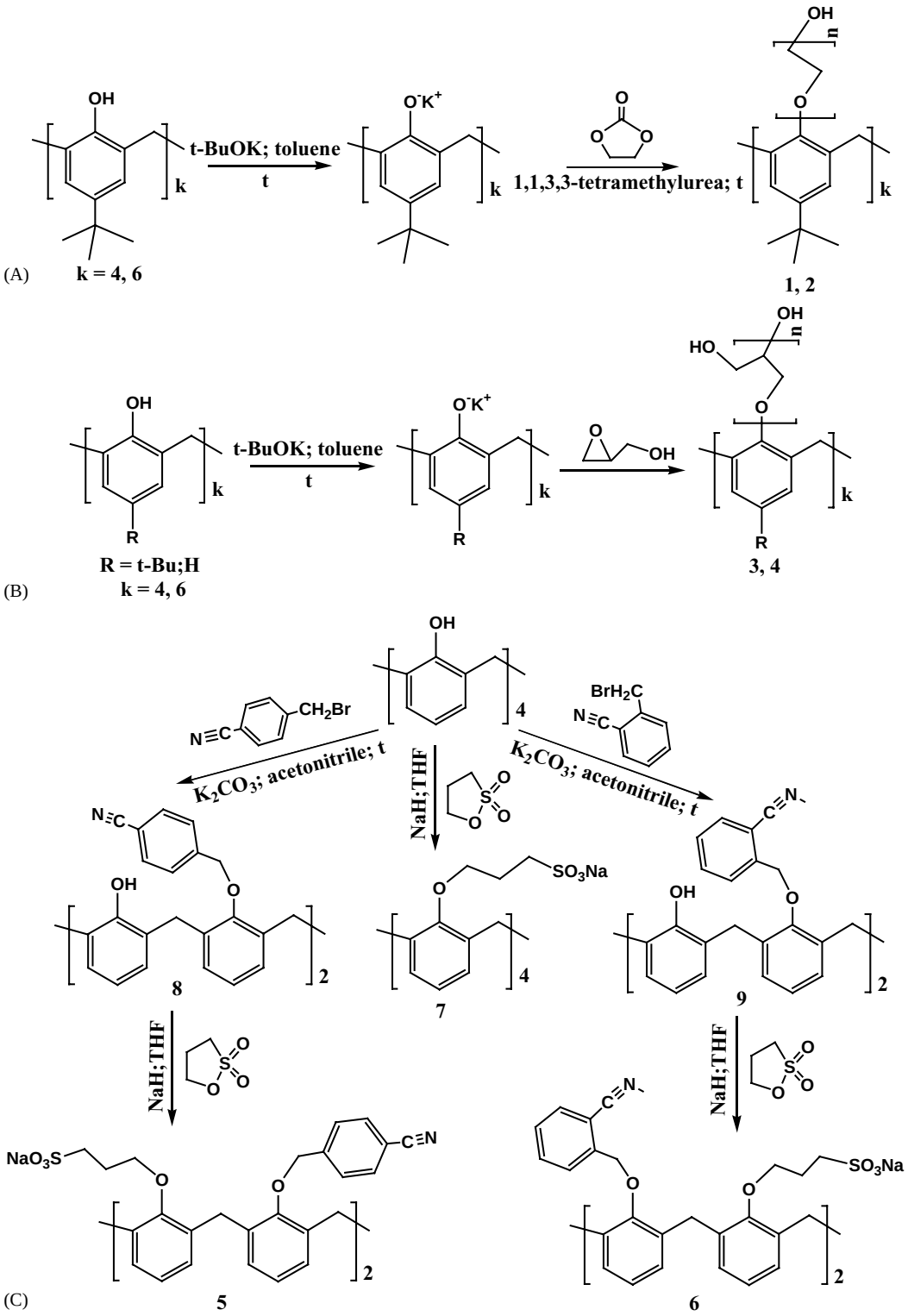

Fig. 2. Syntheses of modified water soluble calixarenes.

(–C**H**$_2$CH$_2$CH$_2$SO$_3$Na); 87 (O–C**H**$_2$–Ar–CN); 112; 133, 139 (O–CH$_2$–Ar**H**–CN); 121–129, 151, 158 (CH$_2$–Ar**H**–CH$_2$; O–CH$_2$–Ar**H**–CN) FTIR, cm^{-1} 2160 (CN); 1400; 1280 (SO$_3^{2-}$).

Compound **7** was synthesised by the procedure described in [32].

The palladium complex with ligands **5** and **6** was prepared by mixing palladium dichloride (188 mg) with 1 g of ligand

in an aqueous solution and heated to 60 °C. The mixture was intensively stirred for 2 h at this temperature; then, unreacted palladium dichloride was filtered off. Water was removed by distillation.

Palladium complexes were analysed by X-ray photoelectron spectroscopy (XPES) on a LAS-3000 (Riber) instrument equipped with an OPX-150 hemispherical photoelectron analyser. Photoelectrons were excited by aluminum anode (Al K α = 1486.6 eV) X-ray radiation at a tube voltage of 12 kV and an emission current of 20 mA. The palladium content of the supramolecular complexes obtained was determined by inductively coupled plasma atomic fluorescence spectrometry on a Barid AFS-2000 instrument with hollow-cathode lamp radiation (wavelength of 240.7–243.2 nm).

The Wacker-oxidation of unsaturated compounds was carried out in steel autoclaves at an oxygen pressure of 0.5 MPa for 2 and 8 h within the temperature range 30–80 °C under intensive stirring. The products were extracted with diethyl ether, the organic layer was analysed by gas–liquid chromatography using hexadecane as an internal standard. The analysis was conducted on a Chrompack CP9001 chromatograph with a SE-30 column (0.3 mm × 30 m).

The concentrations of oxyethylated calixarenes in water and alkene phase under 50 °C were determined by HPLC (Diasfer-C18 column (4 mm × 200 mm) water). The partition coefficients were evaluated with correction for difference of solvents volumes as ratio of the areas of calixarenes peaks with identical retention time.

3. Result and discussion

The oxyethylated calixarenes were produced via ethylene carbonate interaction with a potassium salt of *p-tert*-butylcalixarene (Fig. 2A). The oxyethylated calixarenes were characterized by NMR ^{1}H, ^{13}C and MALDI-TOF technique. According to the NMR spectroscopy, the reaction proceeds with participation of all calixarene hydroxyl groups. The MALDI-TOF data exhibit presence of a series of oligomers with various ethylenoxide group number (Table 1). Averaged value of the ethylenoxide group number per single aromatic fragment (the oxiethylation degree) was triple lower than the quantity added to the reaction.

The oligoglycerol-modified calixarenes were produced via glycidol interaction with a potassium derivative of calixarenes (Fig. 2B). The oligoglycerol-modified derivatives of calix[4]- and calix[6]arenes with and without *tert*-butyl groups were synthesised. The HPLC data show that in the case of calix[4]arenes products exhibit narrow molecular-mass distribution—two oligomers being predominant. In the case of calix[6]arenes the distribution is essentially wider and a product variety is obtained with different degree of the glycidol oligomerization. We used the NMR for calculation of averaged number of $CH(CH_2OH)CH_2O$-fragments per single phenol calixarene fragment. The calixarene derivatives containing five glycerol groups were used as catalysts component.

The ligands **5** and **6** were synthesised via modification of the hydroxyl groups by *p*- or *o*-bromomethylbenzonitrile and propanesultone (Fig. 2C). The di(*p*-methylenebenzonitrile) calix[4]arene and di(*o*-methylenebenzonitrile)calix[4]arene were separated using HPLC (column: C_{18}-amine, chloroform-hexane eluent). The ligand structure and purity were verified by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy. The methylene bridge CH_2-proton signal is evidence of the "cone" conformation of ligand produced (**5** and **6**). Along with the water soluble ligands **5** and **6**, the compounds **7** was synthesised using the technique described in [32].

By the reaction of **5** and **6** ligands reaction with the palladium chloride a complexes were obtained where one palladium ion and two chlorine anions fell on two calixarene molecules. In the XPES spectrum signals were present corresponding to the palladium(II).

The macromolecular ligands and palladium complexes obtained were investigated as catalysts for the Wacker-oxidation of alkene up to ketones in a two-phase water–substrate system; copper(II) salts were engaged as a palladium re-oxidant. The oxidation was performed in a steel autoclave at oxygen pressure of 0.5 MPa. Dependence of reaction rate from stirring was established. The stirring rate from kinetic region was used in all experiments to prevent mass-transfer limitation. The major reaction products were the corresponding methylketone (95–98%).

The effect of the substrate molecule size a on the catalytic system activity has been studied by using a series of alkenes-1 with different number of the carbon atoms. Adding to the system of both oligoglycerol-modified and oxiethylated calixarenes increases the product yield for particular alkenes. The oxidation product yield depends on the size of calixarene cavity and the modifying group nature. When using the oligoglycerol-modified calixarenes, the activity was highest in the case of hexene-1 for the calix[4]arenes and of octene-1 for the calix[6]arenes (Fig. 3). When using the oxyethylated calixarenes with low oxiethylation degree (1.25 for the calix[4]arene and 3 for the calix[6]arene), the maximal yields were obtained for the heptene-1. In this case, the calix[6]arene catalytic activity turns out to be higher in the case of the highest alkenes—octene-1, nonene-1 and decene-1. Increase of the oxiethylation degree in the same calixarenes up to 3.25 and 4.5 resulted in the catalytic activity increase in the case of octene-1 and nonene-1 oxidation (Figs. 4 and 5).

The results obtained can be explained as follows. Increase or decrease in the "guest" molecule size causes decrease in the stability of inclusion complexes which leads to reduction of catalytic activity. As a result, the transfer from the calix[4]arene to the calix[6]arene causes variation of the substrate selectivity: increase of the cavity size correlates with

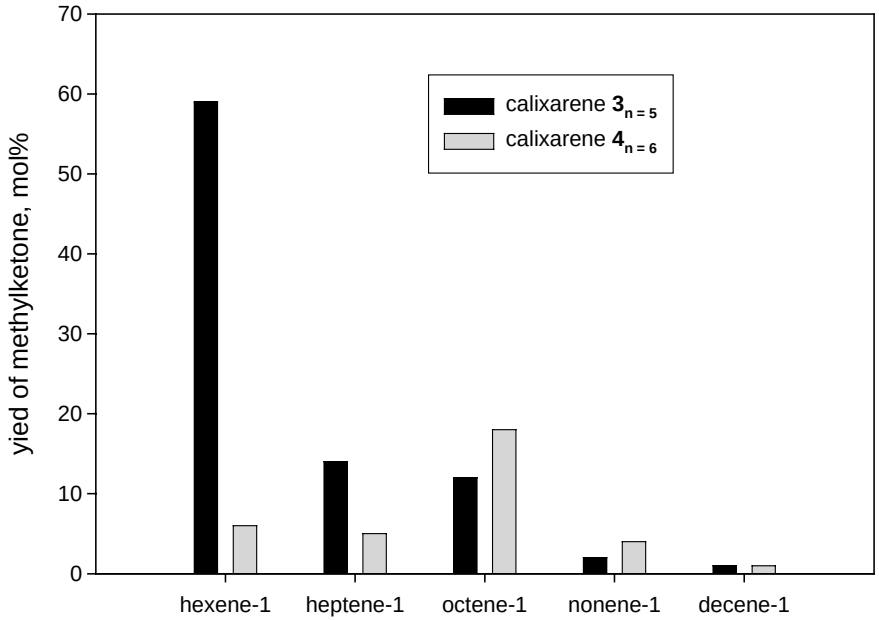

Fig. 3. Oxidation of 1-alkenes catalysed by the catalytic systems based on calixarenes **3** and **4** (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[1-alkene] = 1:10:2:50, 50 °C, 2 h).

higher oxidation rate of alkenes with larger carbon atom number.

Higher oxidation rates under use of oxyethylated calixarenes can be explained by the specificity of the substrate bounding into the host–guest complex. A part of the alkene-1 molecule is located inside the calixarene cavity and the other part is solubilized by the oligoethyleneoxide fragments. As a result, increase in the oxiethylation degree of the calixarenes used causes increase in the catalytic activity. This assumption is verified by the data of Table 2 which present comparison of the alkene-1 oxidation rate for two catalytic systems: one, containing the oxyethylated calixarenes (**1** or **2**), and the second, based on the polyethyleneoxide. The most significant rate increase is obtained for decene-1.

On the other hand the partial desolvation of oligoethyleneoxide fragments and partial solubilisation of the calixarene and Pd complex in the organic phase could be possible under high temperature. It was found that under 50 °C such effect is

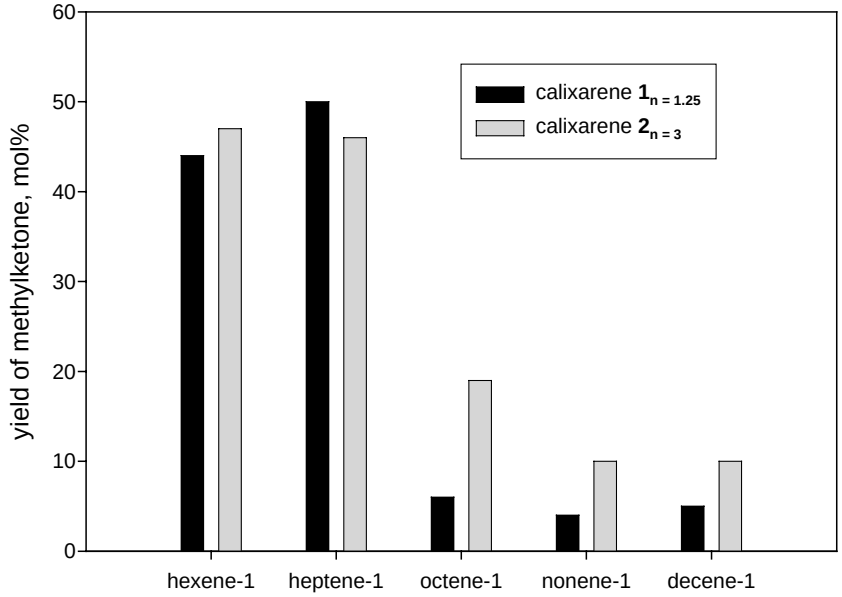

Fig. 4. Oxidation of 1-alkenes catalysed by the catalytic systems based on calixarenes $\mathbf{1}_{n=1.25}$ and $\mathbf{2}_{n=3}$ (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[1-alkene] = 1:10:2:50, 50 °C, 2 h).

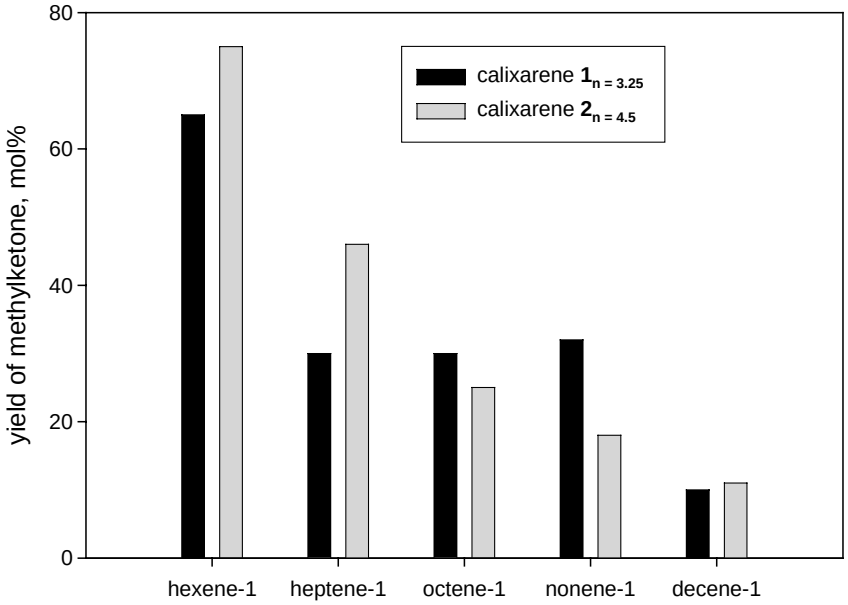

Fig. 5. Oxidation of 1-alkenes catalysed by the catalytic systems based on calixarenes $\mathbf{1}_{n=3.25}$ and $\mathbf{2}_{n=4.5}$ (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[1-alkene] = 1:10:2:50, 50 °C, 2 h).

insignificant. Partition coefficient of water soluble oxyethylated calixarenes in an aqueous–alkene mixture reaches 100 for low oxyethylated oligomers and exceeds 1000 for high oxyethylated oligomers.

Use of the palladium complexes with nitrile containing ligands **5** and **6** as catalysts shows that the optimum palladium/ligand ratio turned out to be 1:2. At the palladium concentration increase, the catalytic system activity did not vary essentially. The yields of ketones in reactions with preliminary synthesised complexes were virtually identical to those in the reactions with the "in situ" produced complexes. These facts is allowed to assume that the Pd complexes with calixarene/Pd ratio 2 acted as the catalyst. It seems likely that the second nitrile containing ligand is substituted by olefin at complex formation and stabilise the palladium during reoxidation.

The activity of the complexes with the ligands **5** and **6** was compared with the catalytic system containing palladium salt, copper salt, and water soluble calixarene **7**. The activity of the ligand **6**-based catalytic system for the hexene-1 oxidation turned out to be maximal. Yet, for the heptene-1 and octene-1 oxidation, the maximal activity was exhibited by the ligand **5**-based complex. The calixarene **7** containing system was the least active in all cases considered (Fig. 6).

Table 2
Oxidation of alkenes-1 catalysed by catalytic system containing calixarens $\mathbf{1}_{n=3.25}$ and $\mathbf{2}_{n=4.5}$ (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[styrene] = 1:10:2:50, 50 °C) TOF—mol ketone to mol Pd in h

Substrate	$TOF_{\text{with calixarene}\mathbf{1}}$/ $TOF_{\text{with PEG1500}}$	$TOF_{\text{with calixarene}\mathbf{2}}$/ $TOF_{\text{with PEG1500}}$
Hexene-1	1.3	1.5
Heptene-1	0.7	1.15
Octene-1	3.0	2.4
Nonene-1	3.2	1.8
Decene-1	10.0	11.0

The activity increase can be connected to the cooperative substrate bounding. Resulting from such bounding, the stability constant for the complex with the substrate should increase and the activation entropy should decrease; these two processes cause the reaction rate increase. Note that the calixarene **5** geometry is of this sort that the interaction between the substrate located in the host molecule cavity and the palladium ion coordinated with nitrile groups is unlikely for the hexene-1 case; the bounding probability increases with hydrocarbon length thus causing the rate increase for the heptene-1 (Fig. 7). As a result, the catalyst with the ligand **5** exhibited maximal activity for the heptene-1 oxidation and not for the hexene-1 as it took place under use of the calixarene **7** or calix[4]arene-*p*-tetrasulphonate as the phase-transfer catalysts [7].

Yet, in a complex with the ligand **6** the palladium is located closer to the calixarene cavity causing high activity for the hexene-1 oxidation and lower—for the heptene-1 oxidation. Thus, as for other "host" molecules—sulfocalixarene and cyclodextrins [3–10]—substrate selectivity took place depending substantially on the structure of the calixarene used.

Influence of the aromatic substrate size on the oxidation rate was investigated by the example of the substituted styrenes (Table 3). The palladium complexes with calixarenes **5** and **6** turned out to be essentially more active than the catalyst based on **7** or oxyethylated calixarenes. In the case of styrenes with substituents in *p*-position the catalyst activity was lower in comparison to styrene—the

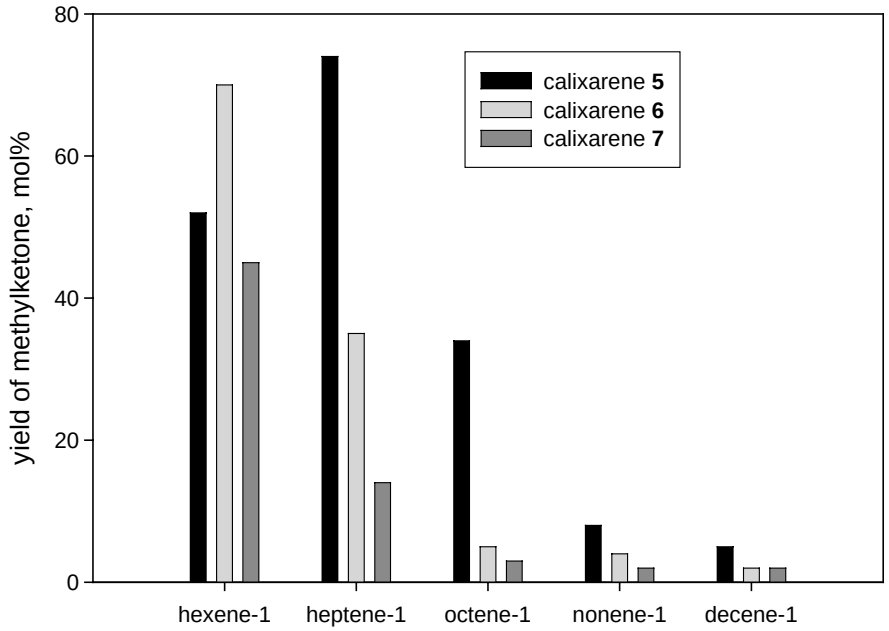

Fig. 6. Oxidation of 1-alkenes catalysed by the palladium complex with ligand **5** an **6** (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[1-alkene] = 1:10:2:50, 50 °C, 2 h).

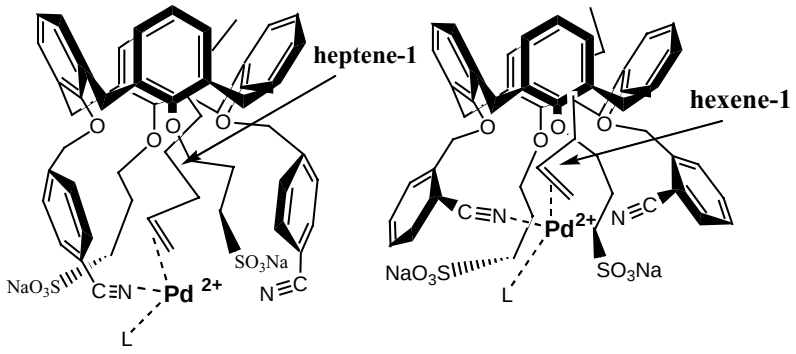

Fig. 7. Speculative scheme of coordination of substrate by palladium complexes with **5** (a) and **6** (b).

Table 3
Oxidation of styrenes with calixarenes-based catalytic systems (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[styrene]= 1:10:2:50, 50 °C)

Macroligand	Ketone yield (%)		
	From styrene	From *p*-methylstyrene	From *p-tert*-butylstyrene
1$_{n=1.25}$	17	19	<1
1$_{n=3.25}$	67	14	3
2$_{n=3}$	10	10	<1
2$_{n=4.5}$	20	28	7
5	60	16	<1
6	45	27	<1
7	5	<1	<1
PEG1500	10	5	<1

fact can be connected with the discordance between the substrate size and the calixarene cavity for the substituted styrenes. Note that yield of the reaction products grows with increase of the oxiethylation degree in the case of the oxyethylated calixarenes.

Recycling experiments were performed using palladium complexes containing ligands **5** and **6**. Catalysts can be efficiently recycled several times without significant drop of product yields.

Apparent activation energies were obtained for the heptene-1 and styrene oxidation catalysed by the complexes with ligands **5**, **6** and **7** (Table 4). The changing in activation energies can be attributed to changing in mode formation of host–guest complexes. Complexes of water soluble calixarenes (sulfocalixarens or calixarene **7**) with molecules containing alkyl chain are stabilised by hydrophobic effect because of difference between accessible hydrophobic

Table 4
Activation energies of oxidation of olefins with calixarenes-based catalytic systems (P_{O_2} = 0.5 MPa, $[Pd^{2+}]$ = 26 mmol/l, $[Pd^{2+}]$:$[CuCl_2]$:[calixarene]:[olefin] = 1:10:2:50)

Substrate	E_A (kJ/mol)		
	Calixarene **5**	Calixarene **6**	Calixarene **7**
Heptene-1	20	69	35
Styrene	88	63	175
p-Methylstyrene	56	74	93

surface area of the host–guest complex and that of the separate host and guest molecule. It is generally attributed in large part to entropic effect [34–36]. For Pd catalysts with ligands **5** and **6** host–guest complexes and transition state of the reaction can be stabilised additionally by interaction of palladium ion with alkene-1 double bond. Furthermore during complexation the olefinic function is in close vicinity to the catalytically active Pd-center making Wacker-oxidation entropically favourable. If the first factor is dominant, the activation energy decreases by comparison with less active catalytic system based on calixarene **7**. If the main factor is entropy changes the activation energy increases. The activation energy in the case of heptene-1 for the complex with ligand **6** turned to be higher and for the complex with ligand **5**—lower than the same for calixarene **7**. Thus, for the first case, increase in the rate of the heptene-1 oxidation reaction is governed primarily by the entropy factors.

In the case of aromatic compounds the π–π stacking interactions between the benzene ring of the guest and the aromatic surface of the host play the main role in formation of inclusion complexes. The influence of hydrophobic interaction is poor [37,38]. The additional bounding of styrene molecule by coordinated Pd ion may lead to stabilisation of host–guest complexes and transition state. Indeed, the activation energies for the palladium complexes with ligands **5** and **6** in styrene and *p*-methylstyrene oxidation in comparison with calixarene **7** decrease.

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