

Use of Ionic Liquids in Cyclohexene Epoxidation with Hydrogen Peroxide

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Abstract—A comparative study of the reaction of catalytic epoxidation of cyclohexene with hydrogen peroxide in water and ionic liquids containing dihydrogen phosphate anions, such as trimethylammonium dihydrogen phosphate, diethylammonium dihydrogen phosphate, and *N*-methylpyrrolidonium dihydrogen phosphate has been performed. It has been shown that as high a cyclohexane epoxide yield as 80% with a selectivity close to quantitative can be obtained under optimum conditions by controlling the ratio of the ionic liquid components.

Keywords: ionic liquids, epoxidation, hydrogen peroxide, cyclohexene, hetero peroxocomplexes

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A key role in the implementation of the concept of sustainable development in chemistry is the design of catalytic processes that occur under mild conditions, do not require a large number of auxiliary procedures (separation, purification), and allow reactions to be run with a minimal yield of byproducts [1]. Catalytic oxidation processes play the major role in the petrochemical industry, accounting for 50% of production. They include heterogeneous catalytic processes for manufacturing of acrylic acid, adipic acid, ethylene oxide, and propylene oxide and the homogeneous catalytic processes of selective oxidation of unsaturated hydrocarbons (propylene, unsaturated carboxylic acids, cyclic olefins, higher alkenes) to epoxides, which form the basis for the synthesis of a wide range of oligomers and polymers (manufacturing of cyclohexene epoxide and other epoxides). Epoxidation of olefins is an important petrochemical process, since it opens a way of obtaining many valuable products widely used in organic synthesis. The widespread use of epoxides requires that they should be obtained with a maximal yield, a maximal selectivity, and the lowest consumption of the reactants.

For the epoxidation of unsaturated compounds with hydrogen peroxide in water and aqueous organic media, different types of catalyst systems, such as various molybdenum and tungsten peroxo compounds; polyoxometalates; and Mn, Fe, Cr, etc. porphyrin and imine complexes, can be used [2].

Polyoxometalates are cluster anions, whose acid and base properties can be controlled at the molecular level by both the type of substitution at the transition metal and the counterions. They have a relatively high resistance to oxidative degradation, are stable against

hydrolysis, and are multi-electron oxidants. The peroxo heteropoly species obtained from them are believed to be reactive epoxidation intermediates [3, 4].

Catalytic systems based on molybdenum and tungsten heteropoly acids with the ammonium or phosphonium counterion are widely used in the epoxidation of olefins with hydrogen peroxide, including that under the phase-transfer conditions [5–15].

Ionic liquids (ILs), in particular [C₄mim][X] (where X = PF₆, (CF₃SO₂)₂N, or BF₄), were examined in the epoxidation of a wide range of olefins with hydrogen peroxide in the presence of [bmim]₃PW₁₂O₄₀ as a catalyst [16]. The most active IL was the hydrophobic liquid with the [PF₆][−] anion. It was shown that active peroxo vanadate [PO₄(W(O)(O)₂)₄] is readily formed in the presence of IL. Catalysts of the same type based on phosphotungstates [Dopy]₃PW₁₂O₄₀ were tested in the epoxidation of *cis*-cyclooctene in a mixture of the [Bpy]BF₄ and [Dopy]BF₄ ILs ([Dopy] is *n*-dodecylpyridinium) [17].

In this paper, we report the results of a comparative study of the epoxidation reaction of cyclohexene with hydrogen peroxide in water and in an IL medium when a heteropoly anion is formed in situ. For this purpose, we used ionic liquids containing the dihydrogen phosphate anion.

EXPERIMENTAL

Oxidation of cyclohexene with aqueous H₂O₂ (35%) was run with continuous vigorous stirring at atmospheric pressure or in a tightly sealed thermostatted glass reactor with a magnetic stirrer. The desired

temperature (25–60°C) in the reactor was maintained by a thermostat accurate to within $\pm 0.5^\circ\text{C}$.

The reactor was charged with sodium tungstate, cyclohexene, phosphoric acid or a phosphorus compound, and a calculated amount of IL. Then, an aqueous solution of hydrogen peroxide was added. The reaction was conducted at a certain temperature for a preset time, after which the reactor was cooled to room temperature, the internal standard *n*-octane was added, and the organic phase was extracted with diethyl ether.

The organic layer was separated and analyzed by GLC on a ChromPack CP9001 chromatograph (with FID) using a capillary column of a 30 m length and a 0.2 mm internal diameter coated with the SE-30 stationary phase; the carrier gas was nitrogen.

^1H NMR spectra were recorded with a Varian-XR-400 spectrometer operating at a frequency of 400 MHz.

Procedures for Synthesis of Ionic Liquids

Synthesis of triethylammonium dihydrogen phosphate $[\text{Et}_3\text{NH}][[\text{H}_2\text{PO}_4]]$. A 10.1-g portion (0.1 mol) of triethylamine was placed in a flask equipped with a stirrer, a thermometer, and a reflux condenser. At 60°C, 8 mL (0.1 mol) of concentrated phosphoric acid was added dropwise within one hour. The reaction mixture was stirred further on a water bath for 2 h at 70°C. The water was removed by evaporation under vacuum at 80°C to a constant weight of the dry residue. The yield of $[\text{Et}_3\text{NH}][[\text{H}_2\text{PO}_4]]$ was 18 g (90%). Mp 93°C. ^1H NMR (DMSO-*d*₆): δ , ppm: 1.17 (t, 9H), 3.10 (m, 6H), 8.88 (s, 1H). Published data: mp 93°C; ^1H NMR (DMSO-*d*₆): δ , ppm: 1.18 (t, 9H), 3.10 (m, 6H), 8.89 (s, 1H) [18].

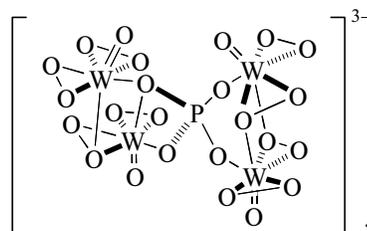
Synthesis of diethylammonium dihydrogen phosphate $[\text{Et}_2\text{NH}_2][[\text{H}_2\text{PO}_4]]$. The synthesis was carried out in the same manner as described for triethylammonium dihydrogen phosphate using 7.3 g (0.1 mol) of triethylamine and 6.8 mL (0.1 mol) of concentrated phosphoric acid. The product yield was 16.5 g (97%). Mp 148°C. ^1H NMR (DMSO-*d*₆): δ , ppm: 1.16 (m, 6H), 2.90 (m, 4H), 8.16 (s, 2H). Published data: mp 148°C; ^1H NMR (DMSO-*d*₆): δ , ppm: 1.16 (m, 6H), 2.92 (m, 4H), 8.18 (s, 2H) [18].

Synthesis of *N*-methylpyrrolidonium dihydrogen phosphate $[\text{NMP}][[\text{H}_2\text{PO}_4]]$. To 9.6 mL (0.1 mol) of cooled 1-methyl-2-pyrrolidone, the equimolar amount of concentrated phosphoric acid (6.8 mL) was added dropwise. After the addition, the reaction mixture was stirred at 80°C for 24 h. Then, water was evaporated under vacuum at 80°C until a constant weight of the residue. The resulting IL was a viscous yellow oil. Yield 18 g (91%). The product was characterized by ^1H NMR: (CDCl₃, δ , ppm): 1.85 (m, 2H), 2.17 (m, 2H), 2.64 (s, 3H), 3.30 (t, 2H). Published data: ^1H NMR (CDCl₃, δ , ppm): 1.87 (m, 2H), 2.15 (m, 2H), 2.66 (s, 3H), 3.29 (m, 2H) [19].

Synthesis of methyltrioctylammonium dihydrogen phosphate $[\text{A336}][[\text{H}_2\text{PO}_4]]$. In a flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser, 4 g (0.01 mol) of methyltrioctylammonium chloride (Aliquat 336) was placed. At 100°C, 1.35 g (0.01 mol) of potassium dihydrogen phosphate was slowly added to it. The mixture was stirred for 3 h and then cooled; after that, 10 mL of acetone was added. The resulting KCl precipitate was filtered off, and the filtrate was evaporated in a vacuum at 80°C to a constant weight. The resulting IL was a colorless viscous oil. Yield 4 g (80%). ^1H NMR (DMSO-*d*₆): δ , ppm: 0.83 (s, 9H), 1.2–1.3 (m, 30H), 1.61 (m, 6H), 3.15 (m, 6H), 2.94 (s, 3H). Published data: ^1H NMR (DMSO-*d*₆, δ , ppm): 0.85 (s, 9H), 1.2–1.3 (m, 30H), 1.58 (m, 6H), 3.16 (m, 6H), 2.92 (s, 3H) [20].

RESULTS AND DISCUSSION

In the case of epoxidation with tungsten compounds and hydrogen peroxide, we initially tested the sodium tungstate–surfactant–aminophosphonic acid catalyst system. The choice of the tungsten compounds was determined by the fact that tungsten(VI) complexes are the most suitable for the oxidation with H₂O₂. An oxidative intermediate in this case is in situ formed phosphorus polyoxotungstate:



As a result, the selective formation of epoxides in the reaction is possible. To accelerate the process, we used surfactants of various types as phase-transfer additives, which are components of the catalytic system (see below).

Among the phase-transfer agents used, the systems containing octyl (Aliquat) and dodecyl substituents showed the greatest activity. In this case, the conversion for 1 h was 10 to 20%, with the selectivity for epoxide being 90%. In other cases, the epoxide yield was significantly lower (Table 1). The reaction in the presence of Aliquat for 5 h gave the epoxide with a yield of 50% and an epoxide selectivity of 90%.

An increase in excess of hydrogen peroxide relative to the substrate leads to a drop in the selectivity: a portion of the epoxide transforms into ring-opening oxidation products, primarily, adipic acid and ketoglutaric acid.

Table 1. Epoxidation of cyclohexene in a biphasic system ($[C_6H_{10}]/[H_2O_2]/[Na_2WO_4]/[NH_2CH_2OP(OH)_2]/[phase\ transfer\ agent] = 100 : 150 : 2 : 1 : 1$; $[C_6H_{10}] = 4.35\ mol/L$; $60^\circ C$, 1 h)

Phase transfer agent	C_6H_{10} conversion, %	Yield of epoxide, %	Selectivity for epoxide, %
Aliquat	22	20	90
Aliquat (5 h)	55	50	90
CPC	6	6	100
BTEAB	4	4	100
DDDMAB	11	10	92
DTMAB	13	9	70
CTMAB	7	6	85
TEAB	6	4	66
Ph_3PPrSO_3	1	1	100
$[Ph_3PPrSO_3H]Br$	4	2	50
$[Ph_3PPrSO_3H]OTs$	1	1	100
$[BMIM]BF_4$	3	1	33
Et_3NPrSO_3	4	2	50

Aliquat is methyltriocetylammmonium chloride, CPC is cetylpyridinium chloride, BTEAB is benzyltriethylammmonium bromide, DDDMAB is didodecyldimethylammmonium bromide, DTMAB is dodecyltrimethylammmonium bromide, CTMAB is cetyltrimethylammmonium bromide, and TEAB is tetraethylammmonium bromide.

Table 2. Epoxidation of cyclohexene with various metal salts ($[C_6H_{10}]/[H_2O_2]/[metal\ compound]/[NH_2CH_2OP(OH)_2]/[phase\ transfer\ agent] = 100 : 150 : 2 : 1 : 1$; $[C_6H_{10}] = 4.35\ mol/L$; $60^\circ C$, 1 h)

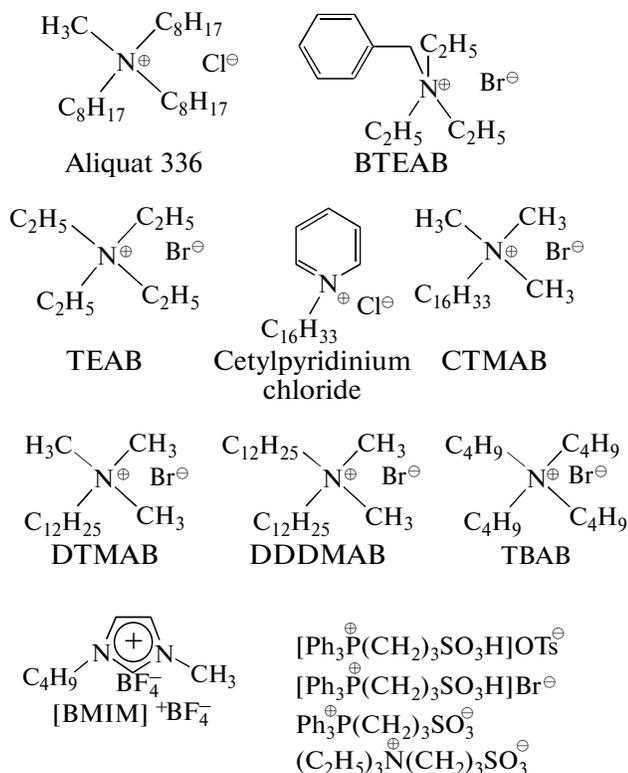
Phase-transfer agent	Salt	$NH_2CH_2OP(OH)_2$ admixture	Time, h	C_6H_{10} conversion, %	Epoxide yield, %	Selectivity for epoxide, %
Aliquat	Na_2WO_4	yes	1	22	20	90
Aliquat	Na_2MoO_4	yes	1	20	14	70
Aliquat	$Na_2MoO_4 + Na_2WO_4$	yes	1	36	30	83
Aliquat	Na_2WO_4	no	1	11	9	81
Aliquat	Na_2MoO_4	yes	2	13	2	12
CPC	Na_2WO_4	yes	1	6	16	100
CPC	Na_2MoO_4	yes	1	17	12	71

Table 3. Epoxidation of cyclohexene in the biphasic system ($[W] : [P] = 2 : 1$; $[H_3PO_4] = 0.043\ mmol/L$, $[C_6H_{10}] = 4.35\ mol/L$, $[H_2O_2] = 6.6\ mol/L$; $60^\circ C$)

Substrate/Aliquat	Time, min	Cyclohexene conversion, %	Selectivity for epoxide, %
100	60	38	64
67	60	38	64
50	60	38	66
40	60	37	71
33	60	33	75
29	60	33	77
25	60	24	92
20	60	25	93
20	30	20	95

Table 4. Epoxidation of cyclohexene in the biphasic system ([W] : [P] = 2 : 1; [H₃PO₄] = 0.043 mmol/L, [C₆H₁₀] = 4.35 mol/L, [H₂O₂] = 6.6 mol/L, [substrate]/[CH₃(*n*-C₈H₁₇)₃NCl] = 100; 60°C)

Time, min	Cyclohexene conversion, %	Epoxide yield, %
10	20	20
15	22	21
30	34	22
60	38	25
120	44	27

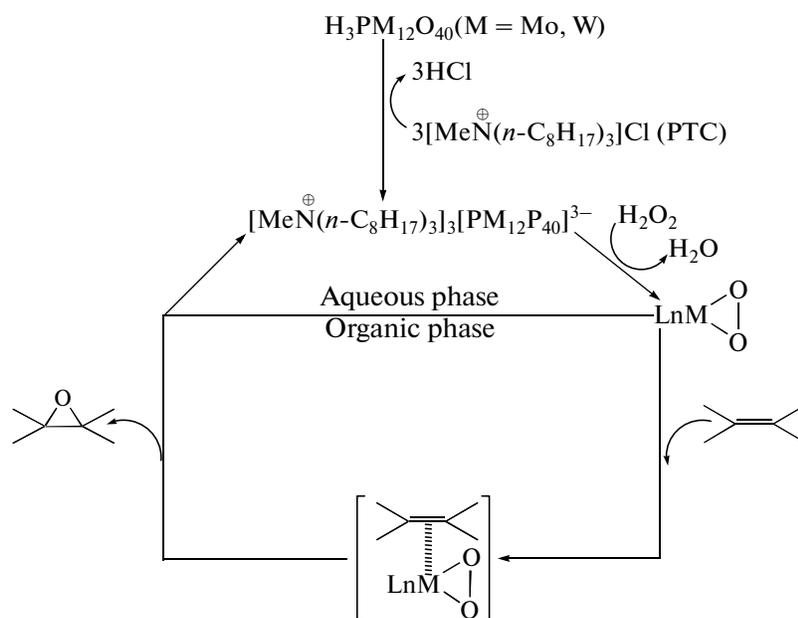
Phase transfer agents of various types**Table 5.** Epoxidation of cyclohexene in the biphasic system at different Na₂WO₄/H₃PO₄ ratios ([Na₂WO₄] = 0.086 mmol/L, [H₃PO₄] = 0.043 mmol/L, [C₆H₁₀] = 4.35 mol/L, [H₂O₂] = 6.6 mol/L, [substrate]/[CH₃(*n*-C₈H₁₇)₃NCl] = 100; 60 min; 60°C)

Na ₂ WO ₄ /H ₃ PO ₄	Cyclohexene conversion, %	Epoxide yield, %
4	25	17
2	38	25
2 (30 min)	34	22
1	69	31
0.5	92	1

Replacement of tungsten by molybdenum in the test process led to a reduction in the yield of the epoxide, apparently due to its hydrolysis during the process (Table 2). Note that the absence of aminomethylphosphonium acid additives leads to a sharp decrease in the epoxide yield (almost by half). The use of CPC together with the Mo complex leads to a significant increase in the epoxide yield compared to the system that contains the tungsten complex. It is also noteworthy that there is a synergistic effect when both the molybdenum and tungsten components are used simultaneously. Apparently, the process in this case proceeds through the formation of a mixed heteropoly acid from the aminomethylphosphonium compound. The mechanism involving the molybdenum and tungsten heteropoly acids can be represented as follows:

Table 6. Epoxidation of cyclohexene in the ionic liquid Et₃NH(H₂PO₄) ([C₆H₁₀] = 4.35 mol/L, [H₂O₂] = 6.6 mol/L, [substrate]/[CH₃(*n*-C₈H₁₇)₃NCl] = 20; 60°C; 130 min)

Et ₃ NH(H ₂ PO ₄) mol/L	CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ NCl mol/L	Substrate/Na ₂ WO ₄	Cyclohexene conversion, %	Epoxide yield, %
0.435	0	40	1	1
0.435	0 (1.5 h)	40	20	1
0.435	0	10	5	5
0.435	0.25	40	56	40
0.435	0.25 (1 h)	40	72	34
0.435	0.25	10	55	55
0.87	0.25	10	85	74
1.235	0.25	10	82	62



Scheme. Mechanism of epoxide formation mediated by molybdenum and tungsten heteropoly acids.

The key step in this process is the transfer of the resulting tungsten peroxocomplex to the organic phase by a phase-transfer agent, either Aliquat or cetylpyridinium chloride in the given case.

We have extensively studied the epoxidation of cyclohexene in the presence of the ionic liquid methyltrioctylammonium chloride $CH_3(n-C_8H_{17})_3NCl$ (Aliquat) and phosphoric acid (Table 3). The results obtained show that it is possible to manage without aminophosphonic acid as a source of phosphorus in this case.

It should be noted that at relatively low concentrations of surfactants, the process in the presence of phosphoric acid has a much lower selectivity than with aminophosphonic acid. A high selectivity is observed only at a 25-fold excess of the surfactant, but the conversion is as low as 20% in this case. Apparently, at low concentrations of Aliquat $CH_3(n-C_8H_{17})_3NCl$, the processes of epoxide hydrolysis and the subsequent oxidation of the diol occur at significantly higher rates than the formation of the epoxide. This assumption is confirmed by the data on the epoxide buildup kinetics: the reaction proceeds rapidly to reach a yield of 20% already within 10 min at $60^\circ C$ (Table 4). After 30 minutes, along with a very slow buildup of epoxycyclohexane and an increase in conversion, selectivity decline begins—of 16% of the substrate converted, the increment in the yield of the desired product makes only 4%.

We found that the selectivity and the reaction rate are also significantly affected by the tungstate anion: phosphoric acid (W : P) ratio. The selectivity was maximal at a fourfold excess of tungstate; the rate of the process was the highest at an excess of the acid, but the amount of epoxide became very small (Table 5). The

main products identified in this case are the corresponding acids and diol.

Thus, we can draw the general conclusion that the high acidity of the medium created by phosphoric acid used in large quantities does not allow for selective epoxidation and leads to the occurrence of deep oxidation processes.

To further increase the yield of epoxide, a new approach was used involving a combination of two solvent components, the acidic IL containing the dihydrogen phosphate anion and Aliquat $CH_3(n-C_8H_{17})_3NCl$ or its analogue having the dihydrogen phosphate anion in place of the chloride ($CH_3(n-C_8H_{17})_3N(H_2PO_4)$). The use of triethylammonium dihydrogen phosphate as a solvent for the catalyst system together with $CH_3(n-C_8H_{17})_3NCl$ can significantly increase the yield of the epoxide compared to standard systems (Table 6).

These data show that in order to achieve acceptable selectivity, it is important to take the optimal acid–hydrogen peroxide–produced epoxide combination formed by varying the component ratio in the IL.

The use of $CH_3(n-C_8H_{17})_3N(H_2PO_4)$ as a component of the catalyst system makes it possible to achieve acceptable results in combination with triethylammonium dihydrogen phosphate (Table 7).

Note that the presence of the triethylammonium IL is essential, since the reaction in its absence has a very low yield. The combination of the triethylammonium IL and $CH_3(n-C_8H_{17})_3N(H_2PO_4)$ can increase the yield of the epoxide to 70%, but an increase in the amount of the former component leads to a significant reduction in the activity of the system.

With the use of the diethylammonium dihydrogen phosphate IL $Et_2NH_2(H_2PO_4)$, the epoxide yield

Table 7. Epoxidation of cyclohexene in the mixture of the Et₃NH(H₂PO₄) IL and CH₃(*n*-C₈H₁₇)₃N(H₂PO₄) ([C₆H₁₀] = 4.35 mol/L, [H₂O₂] = 6.6 mol/L; 60°C; 30 min)

Et ₃ NH(H ₂ PO ₄) mol/L	CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ NCl, mol/L	CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ NH ₂ PO ₄ , mol/L	Substrate/Na ₂ WO ₄	Cyclohexene conversion, %	Epoxide yield, %
0.435	0.25	0	40	56	40
0.435	0.25 (1 h)	0	40	72	34
0.435	0	0.25	40	3	3
0	0	0.25	40	3	3
0.435	0	0.25	10	60	60
0	0.25	0.25	10	3	3
0	0.25	0.125	10	4	4
0.7	0	0.125	10	70	70
0.215	0	0.5	10	32	20

Table 8. Epoxidation of cyclohexene in the Et₂NH₂(H₂PO₄) IL ([C₆H₁₀] = 4.35 mol/L, 30 min)

H ₂ O ₂ , mol/L	NMP(H ₂ PO ₄), mol/L	CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ NCl, mol/L	<i>T</i> , °C	Time, min	Substrate/Na ₂ WO ₄ , %	Yield of epoxide, %
6.6	0.435	0	60	30	1	1
	0.435	0.25	60	30	99	1
	0.26	0.13	40	30	85	13
	0.26	0.13	30	30	68	28
	0.26	0.13	30	15	42	20
	0.26	0.13	30	90	98	1
	0.26	0.13	25	15	40	20
3.3	0.26	0.13	30	15	54	41
	0.35	0.07	30	15	46	14
	0.42	0.03	30	15	24	7
	0.13	0.36	30	15	46	46

could not be made greater than 40% within 1 h. Further running of the reaction did not lead to a significant increase in the substrate conversion or product yield. As in the case of the reaction in water alone, the rate of oxidation to acids turned out to be high. It should be noted that the selectivity of the process was quite high at conversions of up to 40% with a small amount of diethylammonium dihydrogen phosphate.

The system obtained with the use of *N*-methylpyrrolidonium dihydrogen phosphate NMP(H₂PO₄) as an IL exhibited the highest activity. At 60°C and in its combination with Aliquat CH₃(*n*-C₈H₁₇)₃NCl, the complete oxidation of cyclohexene to acids proceeded at a significant rate. A similar effect was observed at 40°C. The reaction could be stopped at the epoxide stage only at 30°C, with the epoxide yield under optimal conditions being about 48% within 15 min at the optimum Aliquat to IL ratio in the system and a

hydrogen peroxide deficiency. An increase in the reaction time did not appreciably affect the conversion and yield because of the complete consumption of the oxidant.

Thus, we have shown that the catalytic system based on acidic ionic liquids with the dihydrogen phosphate anion in combination with the methyltriocetyl anion are promising for the manufacturing of cyclohexane epoxide in two-phase epoxidation reactions with aqueous hydrogen peroxide.

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