Liquid-Phase Catalytic Oxidation of Alkenyl and Cycloalkenyl Aromatic Hydrocarbons with Hydrogen Peroxide

T.A. Valiyeva [*], E.S. Musayeva, H.M. Alimardanov, A.A. Mammadov,
N.I. Garibov

Y.H. Mamedaliyev Institute of Petrochemical Processes Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan
tahminavaliyeva1@gmail.com

Abstract. The reaction of liquid-phase catalytic oxidation of alkenyl and cycloalkeyl aromatic hydrocarbons with hydrogen peroxide with the participation of a heteropoly acid of the Keggin series modified with compounds of rare earth elements was studied. The dependences of the main factors of the oxidation reaction of alkenyl and cycloalkeyl aromatic hydrocarbons on temperature, duration, amount of catalyst, and the molar ratio of hydrocarbon: hydrogen peroxide were determined. For alkenyl aromatic compounds they are as follows: reaction temperature 50-80°C, duration 5-8 hours, molar ratio of alpha methyl styrene: hydrogen peroxide 1:2, catalyst $GdPO_4 + H_3[PMo_{12}O_{40}] \cdot nH_2O$ 1-5% of the mass of the reaction mixture, under these conditions the conversion of alpha methyl styrene is about 55%, for hydrogen peroxide 52%. For alkenyl aromatic compounds they are as follows: reaction temperature 50-80°C, duration 5-8 hours, molar ratio of alpha methyl styrene: hydrogen peroxide 1:2, catalyst $GdPO_4 + H_3[PMo_{12}O_{40}] \cdot nH_2O$ 1-5% of the mass of the reaction mixture, under these conditions the conversion of alpha methyl styrene is about 55%, for hydrogen peroxide 52%. The selectivity for 2-phenylpropanal is 56.8%, for epoxide 30.2%, for diol 11.3%, for phenylacetone 2.0%. Higher results for alkenyl aromatic oxidation with hydrogen peroxide were achieved with the participation of the $TbPO_4+H_3[PMo_{12}O_{40}] \cdot nH2O$ catalyst, and deeper oxidation of the diol to alpha oxyketone isomers was also achieved. The double bond in 1.2-norbornene compounds, as well as in those with the cyclohexenyl derivative, is quite strained and reacts rapidly with the addition of an oxygen group. At temperatures of 50-700°C, the glycol yield reaches 68-70%.

Keywords: Alicyclic unsaturated hydrocarbons, liquid phase, catalytic oxidation, alkenyL aromatic compounds, hydrogen peroxide, multiple bond

1. Introduction

Oxygen functionalization of alkenyl and cycloalkenyl aromatic hydrocarbons, i.e., the introduction of epoxy, hydroxyl, carbonyl, carboxyl, and ether functional

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groups into their composition, is one of the main areas of development in modern petrochemistry.

Hydrocarbons with the listed functional groups are valuable products of petrochemical synthesis and are used in the pharmaceutical industry in the production of medicines, and in the field of perfumery products as aromatic substances [1]. There is extensive material in the literature concerning the liquid-phase catalytic oxidation of styrene and its methyl derivative α-methyl styrene into the corresponding oxygen-containing compounds, but these materials mainly relate to oxidation with atmospheric oxygen [2]. It is known that during the oxidation of unsaturated hydrocarbons by atmospheric oxygen, the primary stable product is hydroperoxide [3]. The further direction of oxidation depends on the decomposition of hydra peroxide, which can be hemolytic, with the division of an electron pair (CO\OH) or heterolytic C\OOH, COO\H with the formation of positive and negative charged particles. It should be noted, however, that oxidation processes with atmospheric oxygen are not highly selective. Chromatographic analysis of the oxidate composition reveals the formation of at least a dozen corresponding oxygen-containing compounds. In this regard and also taking into account modern environmental requirements for chemical processes, we used a 30–35% aqueous solution of hydrogen peroxide as an oxidizing agent, which also meets the criteria of green chemistry [4]. The catalytic system used in the work was synthesized on the basis of phosphorus molybdenum heteropoly acid modified with Tb^{3+} and Gd^{3+} cations. The aim of the presented work is to study the reaction of liquid-phase catalytic oxidation of alkenyl aromatic hydrocarbons (styrene and α-methyl styrene) and cycloalkenyl aromatic derivatives of norbornene and cyclohexenyl with hydrogen peroxide using the synthesized catalytic system of polyoxophosphorus-molybdic acid $H_3[PMo_{12}O_{40}]$ modified with Tb^{3+}, Gd^{3+} cations. [5]

2 Experimental Section

The starting hydrocarbons used in this study are styrene, alpha-methyl styrene, norbornene, and its aromatic derivatives. Styrene and alpha-methyl styrene used in the oxidation reaction are produced as chemical reagents according to GOST TU 6-09-3999-78 [6]. They can also be obtained from pyrocondensate with a fraction boiling point in the range of 130-190°C. A 30-35% H_2O_2 solution was used as the oxidizing agent. Technical conditions for the production of hydrogen peroxide comply with GOST 177-88. Stabilized norbornene, 99% purity (Thermo Scientific, Product of Germany, CAS: 498-66-8) [7].

3 Results and Discussion

According to literature [8], the primary product of styrene oxidation is phenyl oxirane. However, it is also known that, regardless of the oxidizing agent, the oxidate consists of benzaldehyde, phenyl acetaldehyde, phenylethane-1.2-diol, and benzoic acid. Increasing the duration and temperature of the oxidation reaction significantly increases feedstock conversion and the depth of oxidation. The accumulation of water in the system hydrolyzes the accumulated oxirane into a diol, which subsequently isomerizes into phenyl acetaldehyde and acetophenone. It should be noted that the oxidation of α-methyl styrene occurs without the formation of its oxidative oligomerization products. The oxidation products include the corresponding epoxide, diol, and aldehyde [10].

Table 1. Effect of reaction duration on the conversion and selectivity of α-methyl styrene transformation t=70°C, molar ratio α-methyl styrene: hydrogen peroxide=1:2, 35% H_2O_2

Duration, hours	Conversion, %		Oxidate composition, %			
	α-Mct	H_2O_2	Epoxide	2-Phenylpropane	Phenyl methylethane diol	Phenyl acetone
$GdPO_4 + H_3[PMo_{12}O_{40}] \cdot n\ H_2O$						
3	11.9	14.5	39.2	39.5	-	-
7	50.3	53.9	31.7	49.8	15.1	5.9
10	58.9	62.1	26.3	60.1	8.9	8.8
$TbPO_4+H_3[PMo_{12}O_{40}] \cdot n\ H_2O$						
5	36.1	37.9	49.5	41.2	3.9	8.9
7	49.4	60.8	36.1	49.4	3.5	9.1
10	59.9	68.7	30.3	56.5	7.1	11.0

The table shows the effects of oxidant concentration, duration, and catalyst type. Increasing the oxidation duration by 2–3 hours increase α-methyl styrene conversion by 15–20%. The table shows that the heteropolyphosphoromolybdate $H_3[PMo_{12}O_{40}]$ catalytic system modified with the rare earth element Tb performs a more profound oxidation compared to other catalyst samples. Temperature changes have an even greater effect on the oxidant composition.

Table 2. shows the results of the influence of temperature on the conversion of the feedstock and on the selectivity for oxyproducts.

The use of hydroperite in the oxidation of α-methyl styrene involves formic or acetic acid. The use of one of these acids creates an acidic environment in the reaction medium, without which oxidation cannot occur. Although acetic acid is inferior in activity to formic acid, when using polyoxophosphomolybdic acid or its rare earth salt, the equilibrium concentration of the transition complex is easily achieved, and the reaction proceeds selectively with the formation of the corresponding products - oxirane and aldehyde (phenylpropanal):

When using formic acid, oxidation is non-selective; along with the aldehyde and ketone, 2-phenylpropanoic and benzoic acids are formed during the oxidation process. Under more severe conditions (80°C, 8 hours), their amounts reach 15.0-20.0% [11].

As can be seen from Table 2, the transformation of α-MCt in the presence of the above-mentioned catalytic complex with the participation of acetic acid, the reaction up to 40°C proceeds with a clearly expressed induction period. At 40°C and a run time of 7 hours, the conversion of the starting reagent is only 18.6%. Under these conditions, the ratio of epoxide to 2-phenylpropanal in the catalysate is 1:1. As the temperature increases in the range of 50-80°C, the induction period decreases sharply, and substrate conversion reaches 76.2%. The ratio of epoxide to aldehyde changes dramatically. The amount of epoxide decreases from 54.7 to 5.4%, while that of 2-phenylpropanal increases from 47.7 to 89.7%. Accumulation of the oxirane rearrangement product, phenylacetone, is also observed in the catalyst [12].

Table 2. The effect of temperature on the conversion of α-methyl styrene and the composition of the oxidate when using hydroperite (an adduct of urea and hydrogen peroxide) as an oxidizing agent: α-MST: $CH_3COOH:H_2O_2$ = 1:0.2:1, T = 7 H, $TBPO_4$ + [$\cdot PMO_{12}O_{40}$] $\cdot NH_2O$/MUM - 15 g/l.

Temperature °C	Conversion,%		Oxidate composition, % mol			
	α-MCт	H_2O_2	Epoxide	2-phenyl propana	Phenyl acetone	1 Phenyl 1methyl-1.2 ethanediol
40	20.1	22.5	56.8	45.3	-	-
50	31.0	39.3	39.3	59.1	1.6	-
60	54.2	23.8	23.8	72.9	1.9	1.4
70	68.5	11.2	11.2	81.9	4.2	2.7
80	76.2	5.4	5.4	89.7	5.1	4.2

Under the above temperature conditions, the direction of oxidation of α-methylstyrene also depends on the nature, in particular, the polarity of the solvent used. Table 3 shows that when using weakly polar solvents (toluene, xylene, dioxane), the oxidation of α-methylstyrene proceeds more selectively toward the accumulation of compounds with a carbonyl group—2-phenylpropanal and phenylacetone. The overall selectivity for these compounds reaches 86.1–90.2%. With increasing polarity of the solvents in the catalysate, the content of epoxide and the product of its hydrolysis, the diol of the corresponding structure, increases [13].

After filtering the catalyst, the organic layer was separated from the aqueous layer, and the aqueous layer was extracted with toluene. The extract was combined with the organic layer and subjected to atmospheric vacuum distillation.

Fraction 100-101°C/1.33 kPa, d_4^{20}= 1.008, n_D^{20}=1.5092 according to GLC analysis consists of 95.0% 2-phenylpropanal and 5.0% 1-phenylpropanone and has a pleasant smell of greenery, hyacinth.

Thus, we have established that the main products of the liquid-phase oxidation of α-methylstyrene with hydrogen peroxide (or hydroperite) are the corresponding aldehyde and ketone. The maximum yield of these compounds is achieved at a temperature of 70-80°C, a reaction time of 7 hours, and a molar ratio of α-MSt:H_2O_2 = 1:2.

Table 3. Dependence of α-methylstyrene conversion and oxidate composition on the solvent used in the presence of hydroperite (kat-P $CEPO_4 \cdot PW_{12}O_{41} \cdot NH_2O$/MUM mole ratio α-MST: CH_3COOH: $H_2O_2[CO(NH_2)_2]$ = 1:0.2:2, T = 70°C, T = 7H)

Solvent	Conversion,%	Oxidate Composition, Mol%			
		Epoxide	2-Phenyl Propanal	Feni-Propanone	1-Methyl-1-Phenylethanediol
toluene	68.5	11.2	81.9	4.2	2.7
m-xylene	59.0	9.2	83.6	6.1	1.1
dioxane	56.4	8.8	86.2	4.0	1.0
ethanol	73.5	12.6	74.5	3.2	9.7
2-propanol	76.4	14.1	74.1	3.8	8.0
2-methylpropanol	80.2	13.7	76.4	6.1	3.8
dimethyl formamide	83.7	8.4	72.2	8.2	11.2
toluene + 2-propanol	77.9	12.5	80.5	4.2	2.8

In the case of using hydroperite, oxidation is carried out in the presence of acetic acid, at a molator ratio of α-MCt: CH_3COOH: H_2O_2 = 1:0.2:1. under these conditions, the yield of the above-mentioned compounds is reached 59.0-66.0%.

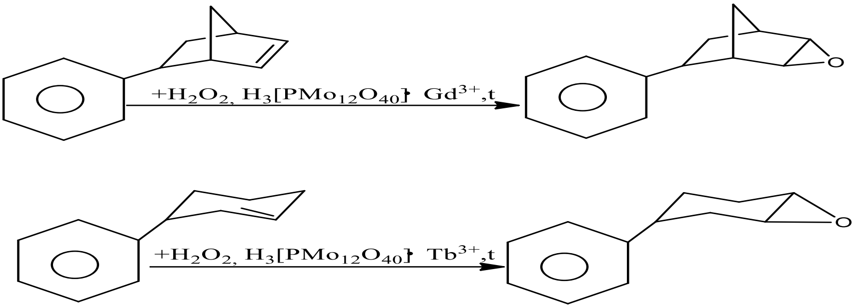

Fig.1. Catalytic Epoxidation of Alkenes with Hydrogen Peroxide in the Presence of $H_3[PMo_{12}O_{40}]$–Lanthanide(III) Complexes

The multiple bonds in the 1.2-scheme compounds with the norbornene and cyclohexenyl moieties are more strained and readily undergoes electrophilic addition of the oxygen moiety. At low temperatures (10–30°C), the oxidation reactions of these compounds yield 8–12% feedstock conversion, and the qualitative and quantitative composition of the oxidate is nearly identical in both cases. With increasing temperature in the range of 50–70°C, the oxidation rate increases, as does the degree of dihydroxylation, and the glycol yield reaches 68–70%. Further increases in temperature lead to deeper oxidation of the diol to α-hydroxyketone isomers and then to the dicarboxylic acid.

4 Conclusion

The conducted studies on the liquid-phase catalytic oxidation of alkenyl aromatic and cycloalkenyl aromatic hydrocarbons with hydrogen peroxide using a phosphomolybdic heteropoly acid of the Keggin series modified with rare earth metal cations Gd^{3+} and Tb^{3+} show that, under identical oxidation reaction conditions, terbium cations exhibit higher activity and perform deeper oxidation.

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