CATALYSIS

Kinetic Relationships of Liquid-Phase Oxidation of Styrene with Hydrogen Peroxide in the Presence of Polyoxotungstate Modified with Cerium Cations

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Abstract—Liquid-phase oxidation of styrene with hydrogen peroxide in the presence of a catalytic system based on $(NH_4)_{10}W_{12}O_{41} + Ce(NO_3)_3 + H_3PO_4$, supported on a microstructured carbon material and treated with an aqueous H_2O_2 solution, was studied. The major reaction products are phenyloxirane and benzaldehyde, with phenylacetaldehyde, 1-phenylethane-1,2-diol, and benzoic acid also present. The kinetic relationships of the process were studied, and a kinetic model according to which phenyloxirane is the primary reaction product was suggested. Aldehydes are accumulated by parallel routes: oxidation of phenyloxirane and of its hydrolysis product, 1-phenylethane-1,2-diol. With an increase in the styrene: H_2O_2 molar ratio, oxidation of 1-phenylethane-1,2-diol becomes the major pathway of the aldehyde formation.

Keywords: oxidation, styrene, hydrogen peroxide, phenyloxirane, benzaldehyde, cerium polyoxotungstate, kinetic model

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Oxidative functionalization of unsaturated hydrocarbons with hydrogen peroxide is one of priority directions of organic and petrochemic al synthesis [1, 2]. The oxidation products (epoxides, alcohols, ketones, aldehydes, ethers, esters) are used for producing pharmaceuticals, perfumes, biologically active compounds, epoxy resins, and plasticizers.

Epoxidation of olefins on the commercial scale is performed either with molecular oxygen in the presence of a catalyst containing silver oxide nanoparticles [3] or with organic hydroperoxides with the participation of various molybdenum and tungsten compounds [4, 5]. Epoxidation of styrene (St) and its derivatives in the presence of various homogeneous and heterogeneous catalytic systems is performed using such oxidants as hydrogen peroxide [6–8], NaClO [9], and NaIO₄ [10]. Tungsten or molybdenum polyoxo complexes show high activity and selectivity in oxidation of unsaturated hydrocarbons [11, 12]. The peroxotungstates or peroxomolybdates formed from these complexes are active intermediates in introduction of oxygencontaining fragments into the starting molecules.

Only a few studies deal with the kinetic relationships of the oxidation of styrene and its derivatives; molecular oxygen or NaIO₄ is used in these studies as an oxidant [10, 13]. It should be noted, however, that the mechanism of the oxidation of this substrate with hydrogen peroxide differs essentially from the mechanism of its oxidation with molecular oxygen.

This study was aimed at determining the kinetic relationships of the liquid-phase oxidation of styrene with hydrogen peroxide in the presence of polyoxotungstate modified with cerium cations and at developing a kinetic model of the multiple-route process.

EXPERIMENTAL

The liquid-phase oxidation of styrene was performed using a catalytic system (CS) prepared by mixing and boiling for 2 h aqueous solutions of $(NH_4)_{10}W_{12}O_{41}$ and

(b) (a) 22 Z, nm 904 18 Intensity, % 31 14 8000 10 6000 6 Y, nm 4000 8000 2 2006000 4000 50 70 2000 10 30 X, nmZ, nm

Fig. 1. (a) 3D image and (b) surface histogram of the synthesized carbon material, taken with an atomic force microscope.

Ce(NO₃)₃ (Sigma–Aldrich, 99.9%), 85% H₃PO₄, and a microstructured carbon material. The resulting mixture was evaporated, and the solid residue was dried at 100–120°C and heat-treated at 180–200°C [14]. A carbon material prepared by stirring aluminum metal turning with excess CCl₄ at 75–76°C [15],

$$2Al + 3CCl_4 \rightarrow 2AlCl_3 + C_2Cl_6 + C,$$

$$2Al + C_2Cl_6 \rightarrow 2AlCl_3 + 2C,$$

was used as a support. The reaction was performed for 3-4 h until the aluminum was completely consumed. The resulting carbon material was separated by filtration, washed with CCl₄, dried in a nitrogen stream at 80–120°C, and heat-treated at 200–250°C until the HCl evolution and AlCl₃ sublimation ceased (Fig. 1).

Prior to use in styrene oxidation, the catalytic system was kept in a 35% H₂O₂ solution at the ratio CS : H₂O₂ = 1 : 200 (Fig. 2). According to [11, 12], such catalytic system consists of various peroxo complexes of the general formula $[P_k W_m O_n (O_2)_p]_x$.

The styrene oxidation was performed in a temperature-controlled 50-mL glass reactor equipped with a thermometer, a magnetic stirrer, a reflux condenser, dropping funnels, and a unit for sampling at 60–80°C. The reactor was charged simultaneously with styrene (0.1–0.15 mol), hydrogen peroxide (35% aqueous solution, 0.1–0.3 mol), catalyst, and toluene (10 mL). A solution of H₃BO₃ in *n*-butanol or α -naphthol (0.5% relative to the reaction mixture) was added to the reaction mixture to prevent oxidative oligomerization of styrene. After the reaction completion, the organic layer was separated, the aqueous layer was extracted

with ethyl acetate, and the ester extracts were combined with the organic layer. After distilling the solvent off, the oxidation products were analyzed.

The styrene oxidation products were identified using gas–liquid chromatography, mass spectrometry, and IR spectroscopy.

Efficient separation of styrene oxidation products was reached on a Tsvet-100 m chromatograph under the following conditions: thermal conductivity detector, carrier gas helium, 1 m × 2 mm column, stationary phase Apiezon L (15 wt % on Chromaton N-AW-HMDS). The IR spectra of the oxidation products and catalyst were recorded with an Alpha Fourier IR spectrometer in the range 400–4000 cm⁻¹ or with a Vertex spectrometer (Bruker) in the range 100–700 cm⁻¹. The absorption bands were assigned in accordance with the reference data. Elemental analysis was performed with a TruSpes Micro analyzer (LECO Corporation, the United States).

Images of cerium polyoxotungstate and cerium polyoxoperoxotungstate samples were taken with an Oxford Instruments Nano Analysis (OINA) 5-3400N scanning electron microscope (SEM).

The surface relief of the microstructured carbon material was examined with an NC-AMF scanning atomic force microscope.

Analysis by gas chromatography–mass spectrometry (GC–MS) was performed with a GC 7890A-MSD5975C device (Agilent Technologies) under the following conditions: HP5-MS column, programmed heating in the range 40–280°C, carrier gas helium.

In the IR spectra of the catalyst samples, the absorption bands at 406, 486, 566, 587, 603, 620, and

 $(a) 100 \ \mu m$

Fig. 2. Electron microscopic images of the surface of Ce peroxotungstate samples treated with (a) phosphoric acid and (b) hydrogen peroxide.

775 cm⁻¹ characterize the -O-Ce-O fragment. The bands at 980, 925, 880, and 871 cm⁻¹ belong to stretching vibrations of WO⁴⁺ and W=O fragments. The bands at 1015, 1030, and 1065 cm⁻¹ in the Fourier IR spectrum of the polyoxophosphotungstate complex characterize the PO₄³⁻ stretching vibrations. The reaction of these catalyst samples with a 35% aqueous H₂O₂ solution yields a mixture of at least two peroxo complexes of golden yellow color. The absorption bands at 890, 680, 589, and 561 cm⁻¹ belong to stretching vibrations of the peroxide bond W 1. The IR spectra of the heterogenized samples contain all the above-indicated absorption bands. As shown by SEM (Fig. 2) and X-ray diffraction analysis, the crystalline structure of the sample undergoes amorphization on treatment with H₂O₂.

The elemental composition of the catalyst is as follows: C 24.58, Ce 3.55, P 1.57, W 56.0, and O 18.3 wt %, which corresponds to C 53.0, Ce 0.77, P 1.56, W 9.4, and O 35.3 at. %.

RESULTS AND DISCUSSION

Recentpublisheddataconcerningthestyreneoxidation with hydrogen peroxide are quite contradictory, which is caused by the use of different catalytic systems [6–8, 16–18]. Taking this fact into account, we first performed experiments without catalyst. A mixture of 0.05 mol of styrene, 6 g of 35% H_2O_2 , and 30 mL of toluene was stirred at 80°C for 3 h. The styrene conversion was 4.0%; i.e., without a catalyst styrene is not noticeably oxidized.

When using the peroxopolytungstate catalytic system, the styrene conversion and oxidate composition vary in a wide range depending on the reaction temperature and stirring rate. Because variation of the stirring rate in the range 700–900 rpm (Fig. 3) does not influence the styrene conversion, the kinetic studies were performed at 700 rpm. Under these conditions, there is no external diffusion hindrance.

The degree of styrene oxidation and the composition of reaction products significantly differ depending on the polyoxotungstate modification (Table 1). For example, when using unmodified polyoxotungstate under the conditions chosen as standard (80°C, 5 h, styrene : H_2O_2 molar ratio 1 : 1.2), the styrene



Fig. 3. Styrene conversion as a function of the rate of stirring the reaction mixture at 70°C (St : H_2O_2 molar ratio 1, solvent toluene).

Oxidate composition, wt % Styrene Catalyst conversion, benzphenylphenylphenylethanebenzoic oligomeric styrene % aldehyde acetaldehyde acid products oxirane diol $(NH_4)_{10}W_{12}O_{41} \cdot nH_2O(I)$ 29.5 67.3 17.7 2.6 3.0 9.4 $(NH_4)_{10}W_{12}O_{41} + H_3PO_4$ 32.6 4.4 14.5 6.2 4.0 8.2 1.7 1.0 (II) $(NH_4)_{10}W_{12}O_{41} +$ 42.7 4.5 14.4 8.8 6.0 9.3 4.1 2.9 $Ce(NO_3)_3 + H_3PO_4$ (III) Catalyst III + carbon 45.0 1.9 18.4 8.7 6.9 10.4 2.0 1.7 material (IV) Catalyst $IV + H_2O_2(V)$ 54.0 3.2 27.3 9.8 4.7 3.7 3.5 7.8

Table 1. Results of catalytic oxidation of styrene with hydrogen peroxide in the presence of various forms of polyoxotungstate ($T = 80^{\circ}$ C, $\tau = 5$ h, styrene : H₂O₂ = 1 : 1.2)

conversion is 29.5%, and the major reaction products are phenyloxirane and 1-phenylethane-1,2-diol. With unsupported cerium polyoxotungstate, the styrene conversion reaches 42.7%, and the amount of aldehydes in the oxidate increases (Table 1). The use of the catalyst supported on the carbon material increases the styrene conversion to 45.0% with higher selectivity of phenyloxirane and benzaldehyde formation. However, the highest conversion of styrene is reached in the presence of the catalytic system preliminarily treated with hydrogen peroxide (Table 1).

In kinetic studies of styrene oxidation in the presence of heterogeneous catalysts, the internal diffusion hindrance is revealed by varying the catalyst particle size. According to the SEM data, the particle size of the catalyst used is $1-3 \mu m$, which does not allow revealing the effect of the internal diffusion hindrance on the reaction rate. Sarbak and Lewandowski [19] suggest



Fig. 4. Influence of the catalyst concentration on the styrene oxidation rate.

the following formula for evaluating the effect of the internal diffusion:

$$\Phi = \frac{rd_{\rm p}^2}{4c_{\rm s}D_{\rm e}} < 1/[n]$$

where *r* is the reaction rate (mol $g_{kg} L^{-1} \min^{-1}$); d_p , catalyst particle size (cm); c_s , substrate concentration (M); and D_e , diffusion coefficient of the starting compound in the solvent (cm² min⁻¹). According to published data, at $\Phi < 1/[n]$ the effect of diffusion on the reaction order *n* can be neglected.

With an increase in the initial concentrations of styrene, hydrogen peroxide (Table 2), and catalyst (Fig. 4) at constant concentrations of the other components, accumulation of oxidation products linearly increases. The styrene oxidation rate (r_{St}) was determined using the formula

$$r_{\rm St} = \frac{c_1^0 - c_1^0}{\tau} = \frac{c_1^0 K_{\rm c1}}{\tau},$$

where $r_{\rm St}$ is the styrene transformation rate (mol L⁻¹ h⁻¹); c_1^0 , initial styrene concentration (M); c_1^{τ} , styrene concentration after the experiment (M); K_{c_1} , styrene conversion (rel. units); and τ , experiment time (h).

Without catalyst, the reaction rate is low. With an increase in the catalyst concentration from 0 to 11.0 g L^{-1} , the reaction order with respect to the catalyst approaches unity (Fig. 4). In the interval $11.0-12.5 \text{ g L}^{-1}$, this parameter varies from zero to unity, and above 12.5 g L^{-1} it is equal to zero. The catalysts supported on the carbon material preserve their activity for a long time (Fig. 5).

Fable 2. V _é	ariation of t	the runn	ning concentrat	tions of oxi	dation pro	ducts with va	riation of the ini	tial concentrations	of styrene and h	ıydrogen peroxi	de
Q	Ĩ		Styrene					c_i, M			
<i>c</i> °,	IVI	τ, h	conversion,	c_1	c_2	c ₃ (phenvl-	c ₄ (benz-	<i>c</i> ₅ (phenvlacetal-	c ₆ (phenvlethane	<i>c</i> ₇	c ₈ (oligomeric
styrene	$\mathrm{H}_{2}\mathrm{O}_{2}$		2	(styrene)	(H ₂ O ₂)	oxirane)	aldehyde)	dehyde)	diol)	(benzoic acid)	products)
						9	50°C				
1.2	1.2	7	8.4	1.099	0.9830	0.0760	0.0150	0.0062	I	I	I
1.2	1.2	б	12.3	1.0524	0.9600	0.1055	0.0320	0.0074	Ι	I	Ι
1.2	1.2	5	21.5	0.942	0.9200	0.1421	0.0510	0.01635	I	I	I
1.2	1.2	7	27.4	0.8712	0.8254	0.1644	0.0986	0.02959	I	I	Ι
						6	70°C				
1.2	1.2	0	17.0	0.996	0.9470	0.1360	0.0320	0.0160	0.010	I	0.006
1.2	1.2	б	24.7	0.9036	0.8164	0.1632	0.0565	0.0243	0.0190	0.0065	0.0235
1.2	1.2	5	33.6	0.7968	0.735	0.180	0.0950	0.0480	0.0235	0.0110	0.0430
1.2	1.2	7	44.0	0.672	0.600	0.264	0.1267	0.0528	0.0264	0.0130	0.0451
						6	10°C				
1.2	0.6	0	7.6	1.1088	0.4061	0.0765	0.0110	0.0037	I	I	I
1.2	0.6	б	14.0	1.032	0.365	0.1200	0.0245	0.0115	Ι	I	0.0120
1.2	0.6	5	23.0	0.9240	0.270	0.1740	0.0451	0.0200	0.0100	I	0.0269
1.2	0.6	7	28.6	0.8568	0.186	0.2063	0.06128	0.0317	0.0126	I	0.019
						6	10°C				
1.2	1.8	7	19.2	0.9696	1.4584	01200	0.0510	0.0247	0.0095		0.021
1.2	1.8	б	28.0	0.864	1.3862	0.1745	0.0790	0.0334	0.0126	I	0.027
1.2	1.8	S	39.2	0.7296	1.2835	0.2384	0.0930	0.0510	0.0314	I	0.046
1.2	1.8	7	49.7	0.6037	1.1863	0.2845	0.1321	0.0664	0.0476	I	0.0531
						2	70°C				
1.2	2.4	0	20.4	0.9552	2.1135	0.1450	0.0642	0.0268	0.0098	I	I
1.2	2.4	e	31.7	0.8196	1.9839	0.2075	0.0926	0.0360	0.0103	0.010	0.024
1.2	2.4	5	45.2	0.6576	1.8076	0.3082	0.1420	0.0580	0.0156	0.013	0.0056
1.2	2.4	2	52.6	0.5688	1.7388	0.3621	0.1638	0.0640	0.0184	0.013	0.01
						6	15°C				
1.2	1.2	0	21.7	0.9396	0.9016	0.1510	0.0441	0.0210	0.015	0.01	0.0193
1.2	1.2	б	31.8	0.8184	0.7516	0.1921	0.0786	0.0430	0.021	0.018	0.0289
1.2	1.2	5	47.0	0.636	0.5927	0.2562	0.124	0.0745	0.032	0.031	0.0463
1.2	1.2	7	54.5	0.546	0.5165	0.3348	0.136	0.0824	0.036	0.0218	0.043
						×	30°C				
1.2	1.2	7	26.5	0.882	0.8412	0.1645	0.0482	0.0284	0.021	0.022	0.0339
1.2	1.2	ŝ	43.1	0.6828	0.6341	0.2147	0.1080	0.0648	0.046	0.0427	0.0410
1.2	1.2	ν t	54.0	0.552	0.5270	0.3041	0.1283	0.0830	0.046	0.0416	0.0450
1.2	1.2	_	68.7	00.270	0.3524	0.3726	0.1927	0.1028	0.00	0.0483	0.0520

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Fig. 5. Variation of the activity of catalyst V in the course of repeated runs (time of each run 5 h). (1) Styrene conversion and (2) selectivity with respect to the sum of oxidation products.

In the examined range of the initial concentrations of styrene and hydrogen peroxide, the rate of their consumption is a linear function of the concentration of the starting components. Hence, the formal reaction rate is determined by the formula

$$W_{\rm St} = k[c_1][c_2 \times {\rm CAT}],$$

where W_{St} is the formal rate of styrene transformation (mol L⁻¹ h⁻¹); k, rate constant (L mol⁻¹ h⁻¹); c_1 and c_2 ,

styrene and hydrogen peroxide concentrations (M); and CAT, catalyst amount (g L^{-1}).

Based on the experimental data (Table 2), we suggest two schemes of the oxidative transformation of styrene and accumulation of reaction products (Schemes 1, 2).

Oxidation of unsaturated hydrocarbons with hydrogen peroxide occurs along multiple routes via formation of the corresponding epoxide. Hence, it can be assumed that the reaction occurs in successive steps involving further transformations of the peroxides

Scheme 1.

I
$$C_{6}H_{5}$$
 + $H_{2}O_{2}$ $\xrightarrow{K_{1}}$ $C_{6}H_{5}$ + $H_{2}O_{7}$
II $C_{6}H_{5}$ \xrightarrow{O} $\xrightarrow{K_{2}}$ $C_{6}H_{5}$ \xrightarrow{O} (or C $_{6}H_{5}$),
III $C_{6}H_{5}$ + $2H_{2}O_{2}$ $\xrightarrow{K_{3}}$ $C_{6}H_{5}$ \xrightarrow{O} H + $CH_{2}O$ + $2H_{2}O_{7}$

IV
$$C_6H_5 \xrightarrow{O}_H + H_2O_2 \xrightarrow{K_4} C_6H_5 \xrightarrow{O}_{OH} + H_2O,$$

V
$$C_6H_5 \xrightarrow{O} + H_2O_2 \xrightarrow{K_5} C_6H_5 \xrightarrow{O} OH + CH_2O + H_2O,$$

VI
$$C_6H_5 \xrightarrow{O} +H_2O \xrightarrow{K_6} C_6H_5 \xrightarrow{OH},$$

- VII C_6H_5 + $H_2O_2 \xrightarrow{K_7} C_6H_5$ $H_1 + H_2O_1$
- VIII C_6H_5 + $H_2O_2 \xrightarrow{K_8}$ oxidative oligomerization products

Scheme 2.



formed. To check this version, we plotted the styrene conversion curves (Fig. 6) in the *S*–*K* coordinates (*S* is the selectivity with respect to epoxide, and *K* is the styrene conversion). Phenyloxirane at $K \rightarrow 0$ is not the only product of styrene oxidation (found by extrapolation of the curves at different temperatures) (Fig. 6).

Phenylacetaldehyde, benzaldehyde, and phenylethane-1,2-diol are formed along with the epoxide. The results of the studies show that the reaction occurs via parallel-consecutive transformations of styrene and oxidation products. This pattern is probably caused by the formation of tungsten peroxo complexes of different structures, exhibiting different activity in this reaction. The assumption that such styrene oxidation products as benzaldehyde, phenylacetaldehyde, and phenylethane-1,2-diol are formed exclusively via transformation of the epoxy intermediate is groundless. Such products can also be formed directly by the oxidation of styrene itself.

The first step in both schemes of the process is directly the styrene epoxidation. However, whereas in the first scheme reactions II, V, and VI illustrate the transformation of the oxirane formed into benzaldehyde, phenylacetaldehyde, and phenylethane-1,2-diol, in the second scheme the above aldehydes are formed from phenylethane-1,2-diol and phenyloxirane by reactions IV, V, and VII. Both the first (reactions III, VII) and the second (reaction III) schemes include the styrene oxidation to aldehydes in one step.

According to published data [20, 21], vanadiumsubstituted heteropolymolybdic acidexhibits high activity in benzene hydroxylation to phenol [21, 22], and the heteropoly compound $(NH_4)_8[La(PMo_9V_2O_{39})]\cdot 6H_2O$ is highly active in phenol oxidation to hydroquinone [22]. It is assumed that these systems operate in hydrocarbon oxidation similarly to Fenton's reagent (Fe²⁺ + H₂O₂) [23, 24]. Taking these facts into account, we assumed



Fig. 6. Reaction selectivity with respect to phenyloxirane as a function of the styrene conversion at (1) 50, (2) 70, (3) 75, and (4) 80°C.

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ω_i , mol L ⁻¹ h ⁻¹											
-ω ₁ (styrene)	$-\omega_2(\mathrm{H}_2\mathrm{O}_2)$	ω ₃ (phenyloxirane)	ω ₄ (benzaldehyde)	ω ₅ (phenylacetaldehyde)	ω ₆ (phenylethanediol)	ω ₇ (benzoic acid)	ω ₈ (oligomeric products)				
		1		60°C							
5.05	10.85	3.8	0.75	0.31	_	_	_				
4.92	8.0	3.5	1.067	0.247	_	_	_				
5.16	5.6	2.842	1.02	0.327	_	_	_				
4.70	5.35	2.35	1.408	0.410	_	_	_				
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1											
4.56	9.695	3.825	0.55	0.185	_	_	_				
5.60	7.833	4.00	0.817	0.383	_	_	0.4				
5.52	6.60	3.48	0.902	0.400	0.20	_	0.538				
4.90	5.91	2.947	0.875	0.452	0.18	_	0.271				
	I	I	I	70°C							
10.2	12.65	6.50	1.60	0.80	0.5	_	0.3				
9.88	12.78	5.44	1.883	0.81	0.633	0.217	0.783				
8.064	9.30	3.60	1.90	0.96	0.47	0.220	0.86				
7.543	8.57	3.77	1.81	0.754	0.377	0.186	0.644				
	I	I	I	70°C	1	I I					
11.52	17.08	6.00	2.55	1.235	0.475	0.21	0.105				
11.20	13.79	5.82	2.63	1.113	0.420	0.32	0.90				
9.408	10.33	4.77	1.86	1.02	0.628	0.21	0.92				
8.52	8.77	4.06	1.89	0.95	0.68	0.18	0.76				
70°C											
12.24	14.325	7.25	3.21	1.29	0.49	—	_				
12.68	13.87	6.91	3.09	1.20	0.34	0.33	0.8				
10.848	11.85	6.16	2.84	1.16	0.31	0.26	0.112				
9.017	9.446	5.17	2.34	0.91	0.26	0.19	0.143				
75°C											
13.02	14.92	7.55	2.205	1.05	0.75	0.5	0.665				
12.72	14.95	6.40	2.62	1.43	0.70	0.6	0.963				
11.28	12.146	5.12	2.48	1.49	0.64	0.62	0.926				
9.34	9.76	4.78	1.94	1.18	0.51	0.31	0.61				
				80°C							
15.9	17.94	8.225	2.41	1.42	1.05	1.10	1.695				
17.24	18.86	7.157	3.60	2.16	1.53	1.42	1.367				
12.96	13.46	6.082	2.57	1.66	0.92	0.83	0.90				
11.78	12.11	5.323	2.75	1.47	0.80	0.69	0.742				

Table 3. Observed rate of accumulation of key substances in styrene oxidation with hydrogen peroxide at various temperatures

Scheme 3.

$$Ce^{3+} + H_2O_2 \longrightarrow Ce^{4+} + OH^- + \dot{O}H,$$

$$Ce^{4+} + H_2O_2 \longrightarrow Ce^{3+} + \dot{O}_2H + \dot{H}^+,$$

$$[WO]^{4+} + O_2H + \dot{O}H \longrightarrow \begin{bmatrix} O \\ - \\ O \end{bmatrix}^{2+} + H_2O,$$

$$C_6H_5^-CH = CH_2 + \begin{bmatrix} O \\ - \\ O \end{bmatrix}^{2+} \longrightarrow C_6H_5 - CH - CH_2 + [WO]^{4+}.$$

that Ce^{3+} cations participate in generation of \dot{O}_2H radicals in accordance with the Scheme 3.

To refine the kinetic relationships, we performed experiments with the binary mixtures styrene + phenyloxirane, styrene + benzaldehyde, styrene + phenylacetaldehyde, and styrene + benzoic acid in various ratios. At the degree of the styrene oxidation no higher than 40–45%, the above products do not inhibit the styrene oxidation, except benzoic acid, which is incorporated into the ligand surrounding of the catalyst, cerium-containing polyoxotungstate, decreasing its activity. However, benzoic acid is formed under harder conditions; therefore, its effect on the mechanism of the liquid-phase oxidation of styrene was not considered.

The closest agreement between the calculated and experimental data (Table 3) is reached when using the following kinetic equations constructed taking into account the independent reactions in Scheme 2:

$$r_1 = k_1[c_1][c_2] \tag{1}$$

$$r_2 = k_2[c_3] \tag{2}$$

$$r_3 = k_3[c_1][c_2]^2 \tag{3}$$

$$r_4 = k_4[c_6] \tag{4}$$

$$r_5 = k_5[c_3] \tag{5}$$

$$r_6 = k_6[c_2][c_4] \tag{6}$$

$$r_7 = k_7[c_2][c_6] \tag{7}$$

$$r_8 = k_8[c_1][c_2] \tag{8}$$

where k_1 - k_8 are the rate constants of reactions I–VIII; r_1 - r_8 , rates of product accumulation in accordance with the corresponding stoichiometric equations; and c_1 - c_6 , compound concentrations (M) (Table 2).

The rates of transformation/accumulation of styrene and oxidation products formed in reactions I–VIII were calculated using the following equations:

$$\omega_1 = r_1 - r_3 - r_8, \tag{9}$$

$$\omega_2 = r_1 - 2r_3 - r_6 - r_7, \tag{10}$$

$$\omega_3 = r_1 - r_2 - r_5, \tag{11}$$

$$\omega_4 = r_2 - r_5 + r_5 \tag{12}$$

$$\omega_4 = r_4 + r_5. \tag{12}$$

$$\omega_6 = r_2 - r_4 - r_7,$$
 (14)

$$\omega_7 = r_6,$$
 (15)

$$\omega_8 = r_8, \tag{16}$$

where ω_1 and ω_2 are the experimentally determined rates of consumption of styrene and available oxygen in hydrogen peroxide, and $\omega_3-\omega_8$ are the rates of accumulation of phenyloxirane, benzald-ehyde, phenylacetaldehyde, phenylethane-1,2-diol, benzoic acid, and oxidative oligomerization product, respectively (Table 3).

The rate constants were calculated using the modified fourth-order Runge–Kutta method with the Matlab-6.5 program. The experimental rate constants were determined graphically using the method of initial rates and refined by minimization of the rms deviations of the calculated data for Eqs. (9)–(16) from the observed values.

Table 4. Calculated values of the preexponential factor k_{0i} and activation energy E_i for the rate constants of oxidative transformation of styrene (reactions I–VIII, Scheme 2)

Rate constant	k _{0i}	E_i , J mol ⁻¹
k_1 , L mol ⁻¹ h ⁻¹	1.02×10^{9}	74200
k_2, h^{-1}	1.16×10^{8}	44724
k_3 , L mol ⁻¹ h ⁻¹	1.41×10^{8}	55788
k_4, h^{-1}	1.96×10^{7}	40802
k_5, h^{-1}	3.32×10^{6}	25939
k_6 , L mol ⁻¹ h ⁻¹	6.76×10^{6}	42751
k_7 , L mol ⁻¹ h ⁻¹	3.32	16488
k_8 , L mol ⁻¹ h ⁻¹	2.25	26988

No.	o. Step equation ^a			Stoichiometric coefficient of the step in indicated reaction								
		Ι	II	III	IV	V	VI	VII	VIII			
1	$C_6H_5 \rightarrow ZO_{n+1} \rightarrow C_6H_5 \rightarrow ZO_n$	1	0	1	0	0	0	0	0			
2	$C_6H_5 \xrightarrow{O} ZO_n \rightarrow C_6H_5 \xrightarrow{O} ZO_n$	1	0	1	0	0	0	0	0			
3	$C_6H_5 \xrightarrow{O} + ZO_n + H_2O \longrightarrow C_6H_5 \xrightarrow{OH} ZO_n$	0	1	1	0	1	0	1	0			
4	$C_6H_5 \xrightarrow{OH} C_6H_5 \xrightarrow{OH} C_6H_5 \xrightarrow{OH} ZO_n$	0	1	1	0	1	0	1	0			
5	$C_{6}H_{5} \xrightarrow{OH} + ZO_{n+1} \longrightarrow C_{6}H_{5} - CHO \cdot ZO_{n} + CH_{2}O + H_{2}O$	0	0	1	0	0	0	1	0			
6	C_6H_5 -CHO·ZO _n \rightarrow C_6H_5 -CHO + ZO _n	0	0	1	0	0	0	1	0			
7	$C_6H_5 \xrightarrow{OH} OH + ZO_n \rightarrow C_6H_5 \xrightarrow{O} ZO_n + H_2O$	0	0	0	1	1	0	0	0			
8	$C_6H_5 \xrightarrow{O}_H C_6H_5 \xrightarrow{O}_H ZO_n$	0	0	0	1	1	0	0	0			
9	$C_6H_5 \xrightarrow{O} + ZO_{n+1} \longrightarrow C_6H_5 \xrightarrow{O} ZO_{n+1}$	0	0	0	0	1	0	0	0			
10	$C_6H_5 \xrightarrow{O}_H C_6H_5 \xrightarrow{O}_H ZO_n$	0	0	0	0	1	0	0	0			
11	$C_{6}H_{5}-CHO + ZO_{n+1} + H_{2}O_{2} \longrightarrow C_{6}H_{5}COOH \cdot ZO_{n+1} + H_{2}O$	0	0	0	0	0	1	0	0			
12	$C_6H_5COOH \cdot ZO_{n+1} \longrightarrow C_6H_5COOH + ZO_{n+1}$	0	0	0	0	0	1	0	0			
13	$C_6H_5 \longrightarrow H_2O_2 \rightarrow$ intermediate oxidized oligomer	0	0	0	0	0	0	0	1			
14	$ZO_n + H_2O_2 \longrightarrow ZO_{n+1} + H_2O$	1	0	2	0	0	0	1	0			

Table 5. Step scheme of styrene oxidation with hydrogen peroxide in the presence of CePO₄·PW₁₂O₄₁·nH₂O/carbon material

^a ZO_n and ZO_{n+1} are oxo- and peroxotungstates containing Ce^{n+} cations.

The calculated rate constants of reactions I-VIII (Table 4) agree with the experimental data. The rms deviation of the calculated rate constants from the experimental values was 9.2-11.4% for the main reactions I-IV and 14.6-18.0% for the side reactions V-VIII. The other models of styrene oxidation lead to considerably larger discrepancies.

The results obtained allow the liquid-phase oxidation of styrene to be described by a set of steps given in Table 5. The step involving the interaction of styrene with the catalytic complex formed is chosen as the limiting step. The other steps are assumed to be fast or equilibrium. According to Horiuti's rule [25], the

number of stoichiometric pathways (P) corresponding to the step scheme is determined by the equation P =S - J = 8, where S is the number of steps and J is the number of intermediates forming a complex with the catalyst. Thus, the suggested scheme completely describes the diversity of reactions occurring in the system [25].

The developed kinetic model of liquid-phase oxidation of styrene with hydrogen peroxide in the presence of polyoxotungstate can be used for mathematical modeling and optimization of the process, and also in studying kinetic relationships of other multiple-route oxidative processes.

CONCLUSIONS

The kinetic relationships and mechanism of the liquidphase oxidation of styrene with hydrogen peroxide in the presence of polyoxotungstate modified with cerium cations were studied. The styrene oxidation follows a complex scheme with the predominant formation of a mixture of phenyloxirane and benzaldehyde. The rate equations of the accumulation of reaction products were constructed, the kinetic parameters were calculated, and the model including the main reaction routes was suggested. According to the suggested model, the primary product of styrene oxidation is phenyloxirane, which then undergoes hydrolysis, isomerization, and oxidation following a consecutive-parallel scheme. The ratio of the epoxide and aldehydes can be varied by varying the temperature and substrate : oxidant molar ratio.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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