Kinetics and Catalysis, Vol. 43, No. 6, 2002, pp. 778–784. Translated from Kinetika i Kataliz, Vol. 43, No. 6, 2002, pp. 835–842.
Original Russian Text Copyright © 2002 by Lysova, Kuzmin, Elizarova, Parmon.

Stationary Kinetics of Light Olefin Oxidation by Hydrogen Peroxide in Aqueous Alkali Solutions in the Presence of Fe(III) Oxide

A. A. Lysova[1, 2], A. O. Kuzmin[2], G. L. Elizarova[2], and V. N. Parmon[1, 2]
[1] *Novosibirsk State University, Novosibirsk, 630090 Russia*
[2] *Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

Received December 13, 2001

Abstract—The steady-state kinetics of ethylene and propylene oxidation by hydrogen peroxide in the presence of Fe(III) oxide in aqueous solutions with the permanent adding of H_2O_2 to the reaction medium was studied. The use of an original method for the study of the steady-state reaction kinetics with gas chromatographic detection of substrate consumption from the gas phase made it possible to estimate the apparent rate constants of ethylene oxidation, the ratio of the rate constants of propylene and ethylene oxidation, the reaction orders with respect to the substrate and oxidant concentration, the dependence of the apparent rate constant of ethylene oxidation on the catalyst weight and on the pH of solution, and the apparent activation energy of the process under condition of substrate distribution between the gas and liquid phases. It was found that the kinetic isotope effect in ethylene oxidation is almost absent when completely deuterated ethylene is used.

INTRODUCTION

The selective oxidation of light hydrocarbons under mild conditions has long attracted the attention of researchers in theoretical and applied catalysis. It has been shown in recent years that simple inorganic compounds, such as Cu(II) and Fe(III) oxides and hydroxides, can be efficient catalysts for the oxidation of several organic substrates (hydrazine derivatives, methane, ethane, ethylene, and benzene) by hydrogen peroxide in aqueous solutions with pH 7–11 at room temperature and atmospheric pressure [1–5]. It has been shown that oxidation occurs without the participation of free radicals under these conditions. The mechanism of oxidation in the presence of catalysts of this type is not yet clear, but it undoubtedly has some common features with the mechanisms of organic substrate oxidation in the presence of oxygenase enzymes. Kinetic studies may shed light on the mechanism of the new catalytic process.

In this work, we studied the steady-state kinetics of ethylene oxidation by hydrogen peroxide in aqueous alkali solutions in the presence of iron(III) oxide. Of course, this study cannot give answers to all the questions concerning the detailed reaction mechanism, but it allows one to approach understand the essence of the processes occurring and elucidate the role of free radicals in this reaction.

It is important that the study of the target reaction under our conditions is complicated by the occurrence of the side reaction of hydrogen peroxide decomposition and by the low substrate solubility in the liquid phase. In connection with this, we used a new variant of the kinetic distribution method to study the kinetics of gaseous substrate oxidation in aqueous solutions [6, 7], which makes it possible to study the processes occurring in the liquid phase by measuring the concentrations of the substrate in the gas phase.

EXPERIMENTAL

Reagents. The following reagents were used in this work: Fe(III) oxide hydrate (chemical purity grade, Reakhim), 30% H_2O_2 solution (extra purity grade), H_2SO_4 (extra purity grade), NaOH (*pro analysi*, Fluka), $TiCl_4$ (extra purity grade), $Ce(SO_4)_2 \cdot 4H_2O$ (analytical purity grade, Reakhim), metallic manganese Mg^0 (reagent purity grade, Vekton), $Na_2S_2O_3 \cdot 5H_2O$ (analytical purity grade, Reakhim), anhydrous Na_2CO_3 (analytical purity grade, Reakhim), KI (extra purity grade, Reakhim), $K_2Cr_2O_7$ (chemical purity grade, Reakhim), $FeSO_4 \cdot 7H_2O$ (chemical purity grade, Reakhim), *ortho*-phenanthroline (chemical purity grade, Reakhim), bromothymol blue (chemical purity grade, Reakhim), water-soluble starch for iodometry (chemical purity grade, Reakhim), and formic acid (chemical purity grade, Reakhim). The following standard titrants were used for the preparation of reference buffer solutions: a 0.05 mol/l solution of potassium tetraoxalate (pH 1.68), a 0.01 mol/l solution of sodium tetraborate acid salt (pH 9.18), and a 0.025 mol/l solution of monosubstituted sodium phosphate (pH 6.86) (AO EKROS, St. Petersburg). Solutions were prepared using water after a Milli-Q system for fine purification (Millipore, France). The following gases were used without additional purification: ethylene, propylene, methane,

0023-1584/02/4306-0778$27.00 © 2002 MAIK “Nauka / Interperiodica”

argon, and deuterated ethylene C_2D_4 (99.8% D) produced by ISOTOP (USSR).

Catalyst preparation. The catalyst was prepared by the calcination of Fe(III) oxide hydrate at 450°C for 5 h and characterized by XRD as α-Fe_2O_3 (S_{sp} = 20 m^2/g; the size of microcrystallites is ~400 Å). Before experiments, the catalyst was ground in a mortar to obtain particles with a size of 10 μm at most. To obtain a supernatant (a separate homogeneous liquid phase), the suspension of 1.15 g Fe_2O_3 and 115 ml of 0.01 mol/l solution of NaOH was intensively shaken in the reactor for 1 h, and the homogenous solution formed due to the mechanical destruction of the colloid was separated by centrifugation for 10 min with an intensity of 2800 rpm.

Equipment and instruments. To study the kinetics of oxygen evolution in the decomposition of H_2O_2, a volumetric setup was used. Optical spectra in the UV and visible regions were recorded using a Shimadzu UV 300 spectrophotometer (Japan). An MPW 340 centrifuge (Poland) was used for the centrifugation of sediments. Hydrogen peroxide was supplied to the reactor using a homemade syringe system for permanent adding of liquid reactants. An EV-74 ion meter (USSR) was used to control the pH of solutions.

The composition of the gas phase was studied using a Kristall 2000M chromatograph (Russia) equipped with a flame-ionization detector and a column packed with Paropak T. Argon was used as a carrier gas. Calibration curves were constructed for a detector temperature of 200°C; an evaporator temperature of 150°C; an argon flow rate of 30 ml/min; and a column temperature of 30°C for methane detection, 100°C for ethylene detection, and 140°C for propylene detection. Kinetic studies with the combined measurements of methane, ethylene, and propylene or simultaneous measurements of methane and ethylene were carried out in a temperature-programmed mode at a detector temperature of 200°C, an evaporator temperature of 150°C, and an argon flow rate of 30 ml/min. The column was kept at 30°C for 1.5 min, heated to 140°C at a rate of 30°C/min, and kept at this temperature for 5 min.

The products of ethylene and propylene oxidation by hydrogen peroxide was determined using chemical methods of analysis [6], by high performance liquid chromatography (HPLC) using a Millichrom 4 chromatograph (USSR), and by ^1H NMR spectroscopy using a Bruker MSL 400 spectrometer (FRG). To determine the ratio of concentrations of deuterated and nondeuterated ethylene in the study of the kinetic isotope effect (KIE), a Saturn GC/MS/MS instrument (USA) was used for chromatography coupled with mass spectrometry.

Methods of chemical analyses. The concentration of H_2O_2 in the solution after the reaction was determined by spectrophotometry by H_2O_2 absorption with Ti(IV) [4]. To this end, 2 ml of a catalyst suspension in water was added to a 2 ml solution of Ti(IV) in 4 mol/l H_2SO_4 (1 mg/ml) after a kinetic run. The liquid phase obtained by the addition of 2 ml of 4 mol/l H_2SO_4 to 2 ml of the reaction mixture and sediment separation by centrifugation was used as a reference solution. To calculate [H_2O_2], the extinction coefficient of the complex formed is used: ε = 700 l mol^{-1} cm^{-1} at λ = 405 nm.

The solutions of hydrogen peroxide were prepared by diluting the 30% solution of H_2O_2 with water. The exact concentration of H_2O_2 was determined by spectrophotometry using the reaction with Ti(IV) [8] or by titration with Ce(IV) [9].

The concentration of formic acid in the solution after the target reaction was determined using the reaction with chromotropic acid [10].

Kinetic experiment. Kinetic studies were carried out using a setup described in detail in [7, 11] and consisting of a catalytic flask, a mechanical rocker, a volumetric setup, a thermostat, and a system for permanent adding of liquid reactants.

Before an experiment, 115 ml of a Fe_2O_3 catalyst aqueous suspension with a required pH was supplied to a 152-ml reactor, and then the reactor was purged with argon for 15 min. Then, 2 (4, 8) ml of ethylene and 2 (4, 8) ml of methane were supplied to the reactor via a syringe and the reactor was shaken for 15 min. In the case of the simultaneous oxidation of ethylene and propylene, the reactor was simultaneously fed with ethylene, propylene, and methane (4 ml each). Then, a sample of the gas phase (0.5 ml) was withdrawn and the concentrations of oxidation substrate(s) and the nonoxidizable standard (methane) were determined using calibration curves obtained earlier. Then, the system for permanent adding of liquid reactants was attached to the setup and a 0.3 mol/l aqueous solution of H_2O_2 was continuously supplied to the reactor at a constant rate (0.82 ml/h) during the experiment.

In experiments on the determination of reaction orders with respect to hydrogen peroxide, [H_2O_2] in the solution supplied was varied from 0.3 to 1.2 mol/l. In the experiments on the determination of the dependence of the reaction rate on the catalyst amount, various catalyst loadings were used.

Gas-phase samples (~0.1 ml) were withdrawn every hour and the concentration ratio of the substrate and standard were determined. When the reaction was carried out in a suspension with initial pH 10, the first measurement was in 3 h rather than in 1 h as in the medium of 0.01 mol/l NaOH, when a constant pH was achieved (this was confirmed in a separate experiment). The subsequent measurements were performed every hour.

The steady-state concentration of H_2O_2 was determined upon the completion of the kinetic experiment using the reaction with Ti(IV).

Kinetic isotope effect measurements. To carry out the kinetic isotope effect (KIE) experiments, after purging the reactor with argon, 4 ml of ethylene and 4 ml of deuterated ethylene were supplied via syringe to the closed reactor containing 115 ml of an aqueous suspen-

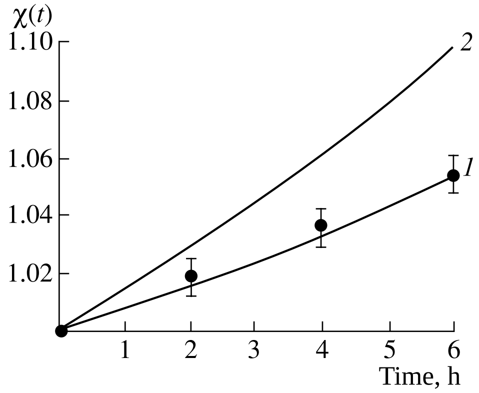


Fig. 1. Experimental and theoretical dependences of the $\chi(t)$ parameter for the oxidation of ethylene assuming the first order with respect to the substrate. ($T = 25°C$; $m_{cat} = 1.15$ g; pH 7; $V_g(0) = 37$ ml, $V_l(0) = 115$ ml; $\lambda = 0.29$; $\alpha_1 = 8.4$; $\alpha_2 = 67.2$; $W = 2.13$ ml/h; $\omega = 0.82$ ml/h; $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l, $[H_2O_2]_0 = 0.3$ mol/l): (*1*) theoretical curve with $k = 0.022$ h^{-1} and (*2*) theoretical curve with $k = 0$ (the reaction does not occur).

sion of the Fe_2O_3 catalyst (1.15 g sample) with pH 10 in a liquid phase and 37 ml of the gas phase. Then, the reactor was intensively shaken for 15 min and the system for permanent adding of liquid reactants was attached to it. The 0.3-mol/l aqueous solution of H_2O_2 was continuously supplied at a constant rate of 0.82 ml/h during the experiment. After 3 and 8 h (at the beginning and end of the reaction), 0.5-ml gas-phase samples were withdrawn via a syringe and transferred into flasks filled with argon. The ratio of concentrations of deuterated and nondeuterated substrates were determined by mass spectrometry assuming that this ratio is equal to the ratio of ion current intensities with masses of 28 for C_2D_4 and 26 for C_2H_4.

RESULTS AND DISCUSSION

Using the methods of chemical analysis and HPLC, we determined that the main product of ethylene and propylene oxidation under the experimental conditions is formic acid (formate ions). Acetic acid and formaldehyde were the other products. In contrast, ethylene oxidation by hydrogen peroxide in the presence of copper hydroxides led to the sole formation of formic acid [3, 4].

In this work, we did not carry out the quantitative determination of oxidation products and the selectivities of various channels depending on the reaction conditions.

The apparent rate constant of ethylene oxidation and the reaction order with respect to the substrate. To determine the apparent rate constant of the reaction and its order, we used the procedure described in [7].

For experimental data processing, a kinetic scheme was used, which included the following steps:

(1) Fast mass transfer between the gas and liquid phases (in a separate experiment, we found that the characteristic time of establishing the equilibrium between the gas and liquid phases was close to 7 min in the reactor used);

(2) Substrate oxidation in the liquid phase with the first order with respect to the substrate concentration;

(3) The dilution of gas-phase components due to oxygen formation in the side catalytic reaction of H_2O_2 decomposition.

Changes in the substrate concentration were measured relative to the concentration of the poorly oxidizable standard (methane).

When the liquid-phase oxidation reaction has the first order with respect to substrate, the apparent rate constant k can be found [7] by integrating the temporal dependence of the substrate concentration in the gas phase:

$$-\ln\left[\frac{X(t)}{X(0)}\right] - \ln\frac{[1+\alpha_1\lambda(t)][1+\alpha_2\lambda(0)]}{[1+\alpha_2\lambda(t)][1+\alpha_1\lambda(0)]} = k\int_0^t \frac{1}{1+\alpha_1\lambda(t)}\,dt + \int_0^t \frac{(\alpha_1-\alpha_2)(W+\omega)[1+\lambda(t)]}{V[1+\alpha_1\lambda(t)][1+\alpha_2\lambda(t)]}\,dt. \qquad (1)$$

Here t is time (h); V is the complete volume of the reactor (ml); $\lambda(t) = V_g(t)/V_l(t)$ at time t; $V_g(t)$ and $V_l(t)$ are the volumes of the gas and liquid phases (ml); $C_g(t)$ and $C_l(t)$ are the concentrations of the substrate in the gas and liquid phases, respectively (mol/l); $X(t) = C_{g1}(t)/C_{g2}(t)$ is the ratio of concentrations of substrate to the concentration of the standard in the gas phase; $\alpha = C_g/C_l$ is the equilibrium ratio of the hydrocarbon concentration in the gas and liquid phases determined by separate experiments; W is the rate of oxygen evolution in the system (ml/h); and ω is the flow rate of hydrogen peroxide solution dosing (ml/h). Subscripts 1 and 2 refer to the substrate and poorly oxidizable standard (methane), respectively.

In the experiment, we measured the value of $\chi(t) = \frac{X(t)}{X(0)}$ for certain times t ranging from 1 to 6 h.

Equation (1) can be integrated analytically and used to find k and the corresponding experimental errors [7] using the Mathematica 3 program package.

Figure 1 shows that the experimental points of $\chi(t) = \frac{X(t)}{X(0)}$ are well described (within the experimental accuracy) by a theoretical curve calculated using Eq. (1) by the method of maximal likelihood assuming the first order with respect to the substrate concentration. A real change in the ethylene concentration during the experiment is 25%. Thus, the reaction of ethylene oxidation by hydrogen peroxide in the presence of Fe_2O_3 has an order close to the first with respect to the ethylene concentration.

The value of the apparent reaction rate constant is 0.022 ± 0.005 h^{-1} at 25°C, $[H_2O_2]_{st} = 1.6 \times 10^{-3}$ mol/l, pH 7, and $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l. This value does not change when the initial concentration of the substrate in the gas phase changes by a factor of 4 in the interval $(1–4) \times 10^{-3}$ mol/l. This confirms the assumption of the first order with respect to ethylene concentration in the reaction of ethylene oxidation.

The ratio of propylene and ethylene oxidation rate constants. The relative reactivity of substrates is an important kinetic characteristic of the reaction. We studied the relative reactivity of propylene and ethylene in the reaction of oxidation by hydrogen peroxide in the presence of α-Fe_2O_3. With this goal, we carried out an experiment on the competitive oxidation of these substrates. Methane was used as a standard. The experiment was carried out at $T = 25$°C, $[H_2O_2]_{st} = 1.2 \times 10^{-3}$ mol/l, pH 7, and $[C_2H_4]_0 = [C_3H_6]_0 = 2 \times 10^{-3}$ mol/l. The ratio of the apparent rate constants of propylene and ethylene oxidation reactions is

$$k_{C_3H_6}/k_{C_2H_4} = 3.0 \pm 0.9.$$

Thus, propylene is much more reactive than ethylene in the reaction of oxidation by hydrogen peroxide in the presence of α-Fe_2O_3. Note that in the case of oxidation with the participation of OH radicals, the ratio of the rate constants for propane and ethane is close to 2 [6]. Unfortunately, we have found no data for propylene and ethylene oxidation by OH radicals.

Kinetic isotope effect in ethylene oxidation by hydrogen peroxide in the presence of Fe_2O_3. Study of the kinetic isotope effect is a method for determining the nature of the rate-limiting step. We measured the primary kinetic isotope effect in the reaction of ethylene oxidation by the competitive oxidation of C_2H_4 and C_2D_4. At 25°C and pH 7, KIE is close to unity. The absence of a noticeable kinetic isotope effect suggests that the rate-limiting step in catalytic ethylene oxidation is probably the step of C=C bond cleavage rather than C–H bond cleavage. This assumption agrees well with the fact that the main product of ethylene oxidation is formic acid. It is also possible that the rate-limiting step is the formation of peroxo complexes or the decomposition of the complex of product with the catalyst.

The order of ethylene oxidation reaction with respect to hydrogen peroxide. To determine the reaction order with respect to hydrogen peroxide concentration, the reaction was carried out under steady-state conditions in 0.01 mol/l NaOH at different concentrations of H_2O_2 supplied with the dosing system (0.3, 0.45, 0.6, and 1.2 mol/l). To calculate the apparent constants, Eq. (1) was used. The steady state concentration of hydrogen peroxide ($[H_2O_2]_{st}$) in the reactor was determined by spectrophotometry after the reaction.

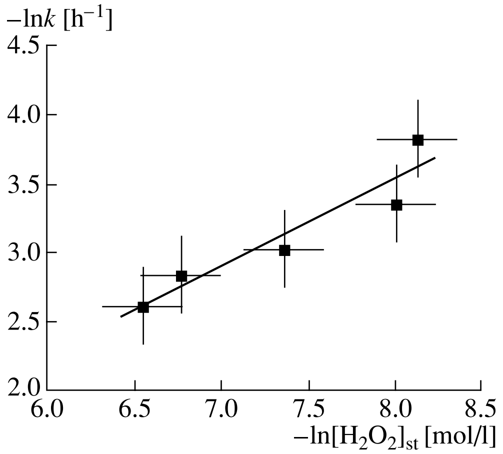


Fig. 2. A logarithmic plot of the apparent rate constant of ethylene oxidation on the steady-state concentration of hydrogen peroxide ($T = 25$°C, 0.01 mol/l NaOH; 1.15 g α-Fe_2O_3; $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l).

Figure 2 compares the apparent rate constants of ethylene oxidation and $[H_2O_2]_{st}$. Within the experimental accuracy, experimental points for ethylene oxidation are described by the linear dependence $\ln k = (0.6 \pm 0.2)\ln[H_2O_2]_{st} + 1.5$, which corresponds to a reaction order of ~0.5 with respect to hydrogen peroxide in the range of H_2O_2 concentrations. Nevertheless, we cannot exclude that this order is apparent because it may change to either zero or unity with an increase in the H_2O_2 concentration, as frequently happens in enzymatic systems. The range of H_2O_2 concentrations $(2.4 \times 10^{-4}–1.6 \times 10^{-3}$ mol/l) corresponds to the region with intermediate values of the reaction order.

Dependence of ethylene oxidation rate on the catalyst amount. To determine the dependence of the ethylene oxidation rate on the amount of the catalyst, the reaction was carried out under steady-state conditions in 0.01 mol/l NaOH at different Fe_2O_3 catalyst loadings (see table). The rate of H_2O_2 dosing was 0.82 ml/h at a H_2O_2 concentration of 0.3 mol/l as supplied by the dosing system. The steady-state concentration of hydrogen peroxide in the reactor was determined after the reaction.

Because the values of $[H_2O_2]_{st}$ were different in these experiments, the measured apparent rate constants were recalculated to $[H_2O_2]_{st} = 2.9 \times 10^{-4}$ mol/l, assuming that the reaction order is 0.5 with respect to hydrogen peroxide. The reaction was carried out at 25°C and $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l. The resulting rate constants k' thus obtained were the same within the experimental accuracy (see table).

The absence of the noticeable dependence of k' on the amount of the loaded catalyst suggests that most of the sites that are active in ethylene oxidation belong to

The values of the apparent rate constants in ethylene oxidation by H_2O_2 in the presence of α-Fe_2O_3 under different experimental conditions

No.	T, °C	pH	m_{cat}, g	$[H_2O_2]_{st} \times 10^4$, mol/l	k, h^{-1}	k', h^{-1}
1	25	7.0	1.5	6.3	0.031	0.031 ± 0.006
2	″	7.5	″	1.9	0.021	0.038 ± 0.008
3	″	10.7	″	2.2	0.020	0.034 ± 0.008
4	″	12	″	2.9	0.020	0.029 ± 0.006
5	″	0.1 M NaOH	″	2.9	0.020	0.022 ± 0.006
6	″	″	0.58	4.3	0.029	0.024 ± 0.006
7	″	″	0.29	4.6	0.019	0.015 ± 0.006
8	15	″	1.15	3.1	0.014	0.014 ± 0.011
9	20	″	″	2.3	0.008	0.009 ± 0.012
10	25	″	″	2.9	0.022	0.020 ± 0.006
11	30	″	″	1.1	0.025	0.041 ± 0.008
12	35	″	″	1.14	0.019	0.027 ± 0.010

Note: k' is the value of the apparent rate constant k recalculated to $[H_2O_2]_{st} = 6.3 \times 10^{-4}$ mol/l for runs 1–4 and to $[H_2O_2]_{st} = 2.9 \times 10^{-4}$ mol/l for other runs (see text); $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l.

the homogeneous part of the suspension. Indeed, we showed in [11] that the reaction of H_2O_2 decomposition in the absence of the substrate under the conditions studied occurs on both the solid particles of the Fe_2O_3 suspension and on the colloid consisting of the polymeric iron hydroxide molecules formed due to mechanical and probably chemical destruction of solid catalyst particles. These colloidal polymeric complexes are in equilibrium with the solid phase of the catalyst, and their concentration remains constant with a change in the amount of the solid phase and provides approximate constancy of the ethylene oxidation rate.

Indeed, after centrifugation, the supernatant (the homogeneous phase of spent reaction suspension) is a light yellow colloid, which is stable for a rather long time and which has a Fe(III) concentration of 6×10^{-5} mol/l and particle size of ~30 Å [11]. Experiments on ethylene oxidation in the presence of the supernatant obtained by intensive shaking of the Fe_2O_3 suspension in the 0.01 mol/l NaOH solution in the 152-ml reactor for an hour and the subsequent separation of the liquid phase showed that the supernatant has approximately the same activity in ethylene oxidation as the solid-phase catalyst.

Dependence of the ethylene oxidation rate on pH. To determine the dependence of ethylene oxidation rate on pH, the reaction was carried out at different pH (see table). The dosing rate of the H_2O_2 aqueous solution and the $[H_2O_2]_{st}$ concentration in these experiments were constant (0.82 ml/h and 0.3 mol/l, respectively). Nevertheless, because H_2O_2 decomposes more readily in an alkali medium, the values of $[H_2O_2]_{st}$ were different. Taking into account that the order of ethylene oxidation reaction with respect to hydrogen peroxide is 0.5, k was recalculated to the steady-state concentration of hydrogen peroxide equal to 6.3×10^{-4} mol/l to compare the values of apparent rate constants. The oxidation was carried out at 25°C, $m_{cat} = 1.15$ g, $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l, and $[CH_4]_0 = 2 \times 10^{-3}$ mol/l. The values of the apparent rate constant k' thus found were the same within the experimental accuracy (see table); that is, a change in the concentration of hydroxy ions by five orders of magnitude resulted in a small change in the apparent rate constant of the oxidation reaction.

The weak dependence of ethylene oxidation on pH is evidence for the nonradical or hidden radical mechanism of ethylene oxidation. Thus, if OH radicals participated in the reaction, changes in pH would drastically decrease the steady-state concentration of OH radicals. Therefore, the overall rate via the reaction channels with the participation of these radicals should increase with an increase in pH of the solution. If the reaction occurred via the radical mechanism with the participation of OH radicals, a noticeable decrease in the rate of ethylene oxidation with an increase in pH of the reaction medium would be observed.

Apparent activation energy of ethylene oxidation. To determine the apparent activation energy of ethylene oxidation, the process was carried out in the temperature range 15–35°C under steady-state conditions at a rate of hydrogen peroxide dosing of 0.82 ml/h and its concentration of 0.3 mol/l in a 0.01 mol/l NaOH solution. Because a change in the temperature results in a change in $[H_2O_2]_{st}$ in the system, even when the initial concentrations of H_2O_2 are the same, changes in k were recalculated to $[H_2O_2]_{st} = 2.9 \times 10^{-4}$ mol/l assuming that the reaction order with respect to hydrogen peroxide is 0.5. The corresponding data are shown in the table. The Arrhenius dependence of the apparent rate constants of ethylene oxidation thus obtained on the temperature is shown in Fig. 3, and the apparent activation energy is 43 ± 4 kJ/mol.

CONCLUSION

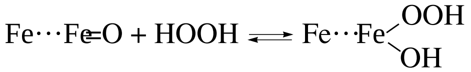
The method used in this work to study the oxidation kinetics of unsaturated hydrocarbons (ethylene and propylene) by hydrogen peroxide in aqueous solutions in the presence of Fe_2O_3 allowed us to determine a number of important regularities of the steady-state occurrence of this reaction, which is hard to study. Thus, we determined the reaction orders of ethylene oxidation by hydrogen peroxide in the presence of Fe_2O_3 with respect to all reactants. It is close to the first with respect to the substrate and to 0.5 with respect to H_2O_2. A substantial difference between the rate constants of propylene and ethylene oxidation ($k_{C_3H_6}/k_{C_2H_4} = 3.0 \pm 0.9$) points to the higher reactivity of propylene.

The absence of a noticeable KIE when deuterated ethylene is used suggests that the rate-limiting step is probably the cleavage of the C=C bond, the formation of peroxo complexes, or the decomposition of the complex of product and catalyst. The absence of a noticeable dependence of the rate of ethylene oxidation by hydrogen peroxide on the concentration of hydroxy ions at pH 7–11 points to the fact that the reaction occurs without the participation of free OH radicals. It is important that the apparent activation energy of ethylene oxidation by hydrogen peroxide in the presence of Fe_2O_3 at pH 12 is low (43 ± 4 kJ/mol) at $[H_2O_2]_{st} = 2.9 \times 10^{-4}$ mol/l.

The results obtained suggest a possible mechanism of ethylene oxidation in the presence of a hydroxide catalyst. As we showed in [2, 12], the interaction of H_2O_2 with Cu- or Fe-containing hydroxide catalyst begins with the formation of the terminal peroxo complex of the active ion:

$$M + HOOH \longleftrightarrow M{-}OOH + H^+. \qquad (I)$$

For simplicity, the coordination sphere of M is not shown. In the case of colloidal hydroxides, reaction (I) is accompanied by the considerable acidification of the reaction mixture. However, the large loading of the bulk iron oxide, in which the Fe(III) ions are largely surrounded by oxo ligands, may serve as a buffer for pH due to hydrogen peroxide addition to the oxo form of the iron cation:



$$Fe\cdots Fe{=}O + HOOH \rightleftarrows Fe\cdots Fe\begin{smallmatrix}OOH\\ OH\end{smallmatrix}$$

(II)

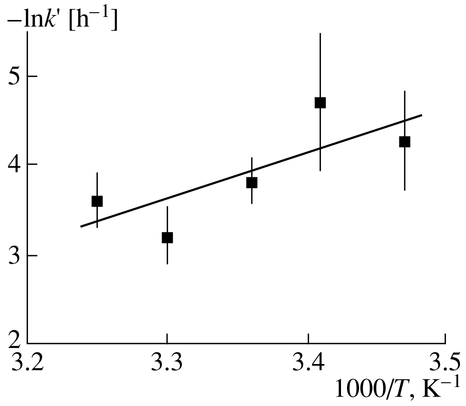
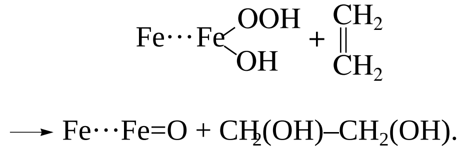


Fig. 3. The Arrhenius plot of the apparent rate constant of ethylene oxidation (0.01 mol/l NaOH; 1.15 g α-Fe_2O_3; $[C_2H_4]_0 = 2 \times 10^{-3}$ mol/l; $[H_2O_2]_{st} = 2.9 \times 10^{-3}$ mol/l).

We have found [13] that the terminal peroxo complex participates in the catalytic oxidation of biphenols and acetonitrile by hydrogen peroxide when copper hydroxide is used, which forms terminal and bridging peroxo groups. Therefore, we can assume that ethylene oxidation on both Cu- and Fe-containing hydroxide catalysts also occurs on a similar active site. As a result, in the case of the Fe-containing catalyst, the most probable first step of ethylene oxidation is the formation of ethylene glycol:



$$Fe\cdots Fe\begin{smallmatrix}OOH\\ OH\end{smallmatrix} + \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \longrightarrow Fe\cdots Fe{=}O + CH_2(OH){-}CH_2(OH).$$

(III)

This reaction can be viewed as the well-known oxidant addition to the double bond. Ethylene glycol formed at this stage may be oxidized further inside the coordination sphere of the catalyst. Reactions (II) and (III) explain the independence of the rate constant on pH over a wide range of pH found in the kinetic experiments and the absence of noticeable KIE.

An unexpected consequence of the results obtained is the fact that the oxidation of the hydrocarbon substrate occurs on the colloid formed due to the mechanical treatment of the solid catalyst in the course of the reaction rather than on the solid particles of the catalyst. However, this is not surprising because the surface of most oxides is hydroxylated in aqueous solutions, and intensive stirring may lead to their transformation to colloids of the corresponding hydroxides. This is very typical of iron oxides, and the catalyst indeed may exist in both bulk and colloidal states under the conditions studied. Moreover, the colloid has a much higher concentration of terminal iron ions than the bulk oxide. In our opinion, this is what in fact leads to the predominant occurrence of ethylene oxidation on the colloidal (hydroxide) portion of the catalyst.

In the well-known Gif-systems, the oxidation of alkanes to ketones by hydrogen peroxide in mixtures of pyridine and carboxylic acids [14], the catalyst is also hydrogen hydroxide. Therefore, the mechanisms of alkene oxidation in Gif-systems and in our systems should be very close. The formation of ethylene glycol instead of ethylene oxide can probably be explained by the occurrence of the reaction in water solutions, which is not the case of Gif-systems.

Formic acid, which is formed in a substantial amount, is a product of further oxidation of both free and coordinated ethylene glycol:

$$CH_2(OH)–CH_2(OH) + 3H_2O_2 \longrightarrow 2HCOOH + 4H_2O.$$

A similar scheme of the process is expected for the oxidation of the other studied alkene (propylene). In reaction (III), as in the oxidation of other substrates with a double C=C bond, the terminal peroxo complex most likely shows nucleophilic properties. For the oxidation of ethylene glycol and alkanes, which can also be oxidized in the systems under study, active sites with high electrophilicity are necessary. Bridging peroxides may play the role of such sites. In the case of iron hydroxide, the ions of iron in the high oxidation state can also be such sites. Because the standard oxidation potential of Fe(III) hydroxide is negative in weakly alkali media, the formation of ferryl ions under the action of such a strong oxidant as H_2O_2 is very probable.

We hope that further studies will provide experimental support for the formation of ethylene glycol as an intermediate product of oxidation, and the study of the system using physical and quantum chemical methods will suggest a more justified mechanism for the oxidation of light olefins on iron(III) hydroxides.

ACKNOWLEDGMENTS

We thank L.A. Kozhanova for the HPLC study of the reaction. This work was supported in part by the program Leading Scientific Schools (grant no. 00-15-97446).

REFERENCES

1. Pestunova, O.P., Elizarova, G.L., and Parmon, V.N., *Zh. Prikl. Khim.*, 1999, vol. 72, p. 1147.
2. Elizarova, G.L., Matvienko, L.G., and Parmon, V.N., *Kinet. Katal.*, 2000, vol. 41, no. 6, p. 839.
3. Kuzmin, A.O., Elizarova, G.L., Matvienko, G., Savinova, E.R., and Parmon, V.N., *Mendeleev Commun.*, 1998, no. 6, p. 210.
4. Elizarova, G.L., Matvienko, L.G., Kuz'min, A.O., Savinova, E.R., and Parmon, V.N., *Dokl. Akad. Nauk*, 1999, vol. 307, no. 5, p. 640.
5. Elizarova, G.L., Matvienko, L.G., Kuzmin, A.O., Savinova, E.R., and Parmon, V.N., *Mendeleev Commun.*, 2001, no. 1, p. 15.
6. Rudakov, E.S., *Reaktsii alkanov s okislitelyami, metallokompleksami i radikalami v rastvorakh* (Reactions of Alkanes with Oxidants, Metal Complexes, and Radicals in Solutions), Kiev: Naukova Dumka, 1985.
7. Kuzmin, A.O. and Parmon, V.N., *Kinet. Katal.*, 2002, vol. 43, no. 6, p. 831 [*Kinet. Catal*. (Engl. transl.), 2002, vol. 43, no. 6, p. 774].
8. Charlot, G., *Les methodes de la chimie analytique*, Paris: Masson, 1961.
9. Korostylev, P.P., *Reaktivy i rastvory v metallurgicheskom analize* (Reagents and Solutions in Metallurgical Analysis), Moscow: Metallurgiya, 1977.
10. Polyudek-Fabini, R. and Beirikh, T., *Organicheskii analiz* (Organic Analysis), Leningrad: Khimiya, 1981, p. 118.
11. Lysova, A.A., Kuz'min, A.O., and Parmon, V.N., *Kinet. Katal.*, 2003, vol. 44 (in press).
12. Elizarova, G.L., Matvienko, L.G., Ogorodnikova, O.L., and Parmon, V.N., *Kinet. Katal.*, 2000, vol. 41, no. 3, pp. 366.
13. Elizarova, G.L., Odegova, G.V., Matvienko, L.G., *et al.*, (in press).
14. Shilov, A.E., *Metal Complexes in Biomimetic Chemical Reactions*, New York: CRC, 1997, p. 101.