ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 1, pp. 11–16. © Pleiades Publishing, Ltd., 2011.
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Catalytic and Inhibition Functions of Iron Ions in the Chain Oxidation of Acrylic Acid

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Received December 16, 2009

Abstract—The kinetics of acrylic acid oxidation in the presence of iron ions ($T = 333$ K, $p_{O_2} = 1$ atm) has been investigated by measuring the oxygen uptake. The reaction has an induction period τ, after which the O_2 uptake is described by the parabolic kinetic law $\Delta[O_2]^{0.5} = b(t - \tau)$. The parameter b characterizing the catalytic oxidation of acrylic acid has been calculated. Upon the introduction of an initiator (azobisisobutyronitrile), the oxidation has no induction period, but the autoacceleration of the reaction is still observed. A mechanism is suggested for the process. This mechanism includes initiation due to the interaction of the resulting peroxide and hydroperoxide groups with Fe^{2+} and Fe^{3+} ions and chain termination via the reaction $R^{\bullet} + Fe^{3+}$, where $R^{\bullet}$ is an acrylic acid macroradical.

DOI: 10.1134/S0023158411010137

Catalysis by variable-valence metals was described in detail for the oxidation of paraffins and alkylaromatic hydrocarbons, but it was poorly studied for the oxidation of vinyl monomers [1, 2]. This issue is especially important as regards acrylic acid, a large-tonnage monomer, because, as acrylic acid is stored and processed in a metallic vessel, the metal dissolves slowly, resulting in the accumulation of metal ions, mainly iron, in the acid. In our earlier work [3] we studied the initiated oxidation of acrylic acid and determined the kinetic parameters describing this process. The present study is devoted to the kinetics of acrylic acid oxidation with oxygen in the presence of iron ions.

EXPERIMENTAL

Chemicals

Acrylic acid (Aldrich, 99%, stabilized with 0.02% hydroquinone monomethyl ether) was purified by vacuum distillation (bp = 20 ± 1°C, 1.5 Torr) at a water bath temperature of 28 ± 1°C. During distillation, the receiver was cooled to 5–10°C. Purified acrylic acid was stored in the dark at a low temperature. Only freshly distilled portions of acrylic acid were used in experiments. The reagent oxidized as it was stored, so subsequent distillations of acrylic acid were carried out similarly, but in the presence of Irganox 1010 inhibitor at a concentration of 1.4×10^{-4} mol/l (0.017%). Azobisisobutyronitrile (AIBN, Aldrich) was used as the initiator. It purified by double recrystallization from methanol and benzene. Iron(III) stearate was synthesized by the replacement of the chloride ions in $FeCl_3$ with stearate anions [4]. *para*-Methoxyphenol (MQH, Aldrich) was purified according to the procedure described in [5].

Kinetic Measurements

Acrylic acid oxidation was studied at 333 K under atmospheric oxygen pressure ($p_{O_2} = 1$ atm). The oxygen uptake during acrylic acid oxidation was measured volumetrically using a standard manometric setup with automated pressure control [6]. The O_2 uptake rate was measured with a KM-6 cathetometer as the change in the level of mercury or *n*-decane (Δh, mm) in a temperature-controlled burette at a constant oxygen pressure. The temperature fluctuations for the contents of the measuring burette and reaction vessel during the experiment did not exceed 0.1 K. For a burette filled with mercury, and the error of volumetric measurements was at most 6×10^{-4} cm^3. When a burette was filled with *n*-decane, the error was 1.7×10^{-4} cm^3 or below. The concentration of absorbed oxygen (oxygen uptake, $\Delta[O_2]$, mol/l) was calculated using the following equation [3]:

$$\Delta[O_2] = \text{const} \times p V_1^{-1} T^{-1} \Delta h, \quad (1)$$

where const is the setup constant (3.255×10^{-5} (*n*-decane) or 1.1068×10^{-4} (Hg)), p is atmospheric pressure (Torr), $V_1 \approx 4.0$ cm^3 is the liquid volume in the reaction, and T is the temperature of the measuring burette (K). The shaking frequency of the glass reactor was 12 s^{-1}, which ensured fast dissolution of oxygen in the liquid phase and a kinetically-controlled regime of

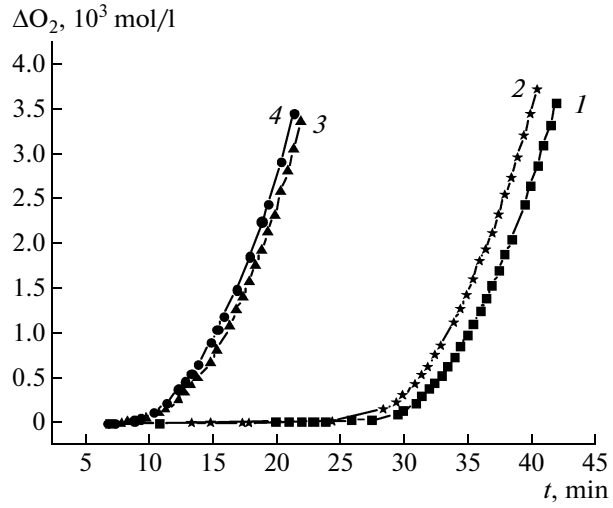


Fig. 1. Oxygen uptake kinetics in acrylic acid oxidation at 333 K and $p_{O_2} = 1$ atm. Reactor wall treatment: (*1*) washing with a $K_2Cr_2O_7 + H_2SO_4$ mixture and then with 3% HCl ($[FeSt_3] = 9.21 \times 10^{-4}$ mol/l), (*2*) washing with concentrated HNO_3 ($[FeSt_3] = 9.13 \times 10^{-4}$ mol/l), (*3*) washing with a $K_2Cr_2O_7 + H_2SO_4$ mixture ($[FeSt_3] = 9.24 \times 10^{-4}$ mol/l), and (*4*) reactor washed in the same way as in entry *3* ($[FeSt_3] = 9.09 \times 10^{-4}$ mol/l).

the reaction. The duration of an experiment on monomer oxidation ranged from 30 to 180 min. The concentrations of the reaction mixture components were calculated with the temperature dependence of the acrylic acid volume taken into account [3]. The acrylic acid concentration was 14.59 mol/l at 293 K and 14.02 mol/l at 333 K.

RESULTS AND DISCUSSION

The oxygen uptake kinetics in acrylic acid oxidation in the presence of trivalent iron ions is illustrated in Fig. 1. It can be seen that the reaction has an induction period, after which oxidation develops with autoacceleration. We demonstrated earlier [3] that acrylic acid oxidation both in the presence and in the absence of an initiator proceeds via a chain mechanism at a constant rate. The existence of an induction period in the presence of iron ions unambiguously indicates their inhibiting effect at the initial stages of the reaction (Fig. 1). The inhibition mechanism will be discussed below. The inhibition of the chain oxidation of acrylic acid is also indicated by the results of the experiments involving iron ions and the initiator at various concentrations: the rate of initiated acrylic acid oxidation decreases with an increasing concentration of iron ions (cf. entries 5 and 8, 6 and 9, and 7 and 10 in the table).

The kinetics of acrylic acid oxidation after the induction period is described by a parabolic function (Fig. 2):

$$\sqrt{\Delta[O_2]} = b(t - \tau), \qquad (2)$$

where τ is the induction period, b is the kinetic coefficient characterizing the autoacceleration of the reaction, and t is time.

The table lists the experimental conditions and kinetic characteristics of the oxidation reaction, namely, the initial oxidation rate v_0 in the presence of the initiator, the parameter b, and the induction period τ. The induction period was estimated from the dependence of $\Delta[O_2]^{0.5}$ on t. The error of the estimation of τ was ±20 s. The inconstancy of the induction period in entries 1–4 is due to the "memory" of the

Conditions and results of experiments on acrylic acid oxidation in the presence of iron ions at $T = 333$ K and $p_{O_2} = 10^5$ Pa

Entry	$[FeSt_3] \times 10^4$, mol/l	$[AIBN] \times 10^4$, mol/l	$v_i(AIBN) \times 10^7$, mol l^{-1} s^{-1}	$v_0 \times 10^6$, mol l^{-1} s^{-1}	$b \times 10^5$, $mol^{0.5}$ $l^{-0.5}$ s^{-1}	$\tau \times 10^{-3}$, s
1	9.21	0.0	0.0	–	6.58	1.98
2	9.13	0.0	0.0	–	6.77	1.98
3	9.24	0.0	0.0	–	7.32	0.78
4	9.09	0.0	0.0	–	6.88	0.84
5	9.25	0.85	0.88	13.1	6.77	–
6	8.93	1.89	1.95	12.3	7.50	–
7	8.96	3.07	3.16	11.6	8.31	–
8	28.03	0.85	0.88	5.19	–	–
9	28.33	1.91	1.97	6.22	–	–
10	28.12	3.16	3.25	7.60	–	–

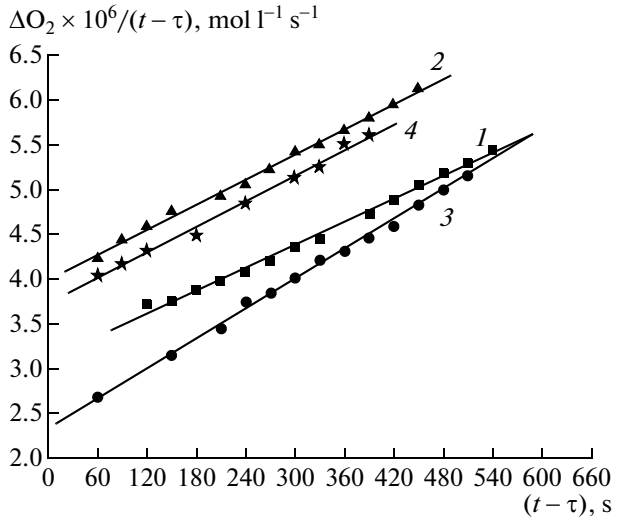


Fig. 2. Linearization of the kinetic curves presented in Fig. 1 in the $\Delta[O_2]/(t-\tau)$–$(t-\tau)$ coordinates.

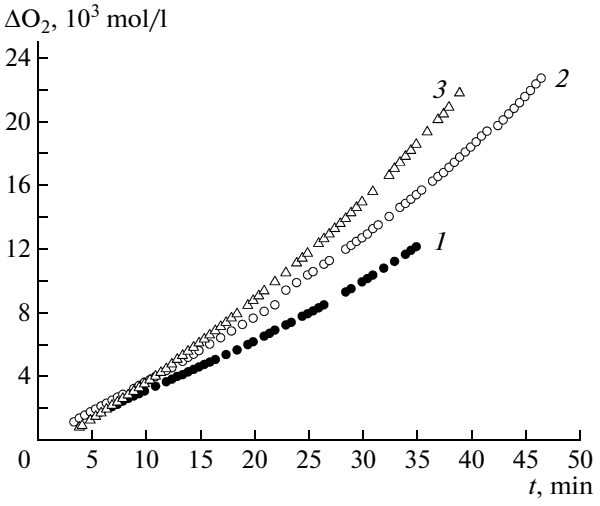


Fig. 3. Oxygen uptake kinetics in acrylic acid oxidation at 333 K, $p_{O_2} = 1$ atm, and the following AIBN and $FeSt_3$ concentrations (mol/l): (*1*) [AIBN] = 0.85×10^{-2}, [$FeSt_3$] = 2.80×10^{-3}; (*2*) [AIBN] = 1.91×10^{-2}, [$FeSt_3$] = 2.83×10^{-3}; (*3*) [AIBN] = 3.16×10^{-2}, [$FeSt_3$] = 2.81×10^{-3}.

reactor: the state of the reactor walls depends on the conditions of the previous experiment—so-called wall effect. As was demonstrated experimentally, the induction period depends on the method of preparation and washing of the reactor. This explains why τ in entries 1 and 2 differs from τ in entries 3 and 4. The shortest induction period is observed after washing the reactor with a mixture of $K_2Cr_2O_7$ and H_2SO_4 (entries 3 and 4). A longer induction period is observed for the reactor washed with nitric and hydrochloric acids. A possible cause of the inhibition effect is the formation of a polyacrylic acid film on the reactor wall. This film consists of iron ions absorbed during the previous experiment. No inhibition effect of the quartz vessel wall was observed in experiments on acrylic acid oxidation without iron ions [3]. As iron ions appear and accumulate, they catalyze peroxide decomposition into radicals, which results in the acceleration of the chain oxidation of acrylic acid.

In the AIBN-containing acrylic acid–Fe(III)–O_2 system, oxidation occurs without an induction period and at a higher rate (Fig. 3). Evidently, the initiator favors the quick establishment of the conditions necessary for the iron ions to execute their catalytic action.

The kinetics of acrylic acid oxidation in the presence of the AIBN initiator and MQH inhibitor is illustrated in Fig. 4. It can be seen that MQH inhibits acrylic acid oxidation both in the presence (Fig. 4, curve *2*) and in the absence (Fig. 4, curve *3*) of Fe(III), which is further evidence in favor of the chain mechanism of catalytic acrylic acid oxidation. A comparison between curves *2* and *3* shows that the induction period in the presence of Fe(III) is shorter ($\tau = 38$ min) than that in the absence of Fe(III) ($\tau = 60$ min). Therefore, the iron ions in the presence of the initiator ensure a higher initiation rate than the initiator alone. After the cessation of inhibition, the acrylic acid oxidation in the presence of both Fe(III) and AIBN proceeds more rapidly (oxidation rate of 1.09×10^{-5} mol l^{-1} s^{-1}) than the oxidation in the presence of the initiator alone (oxidation rate of 3.61×10^{-6} mol l^{-1} s^{-1}).

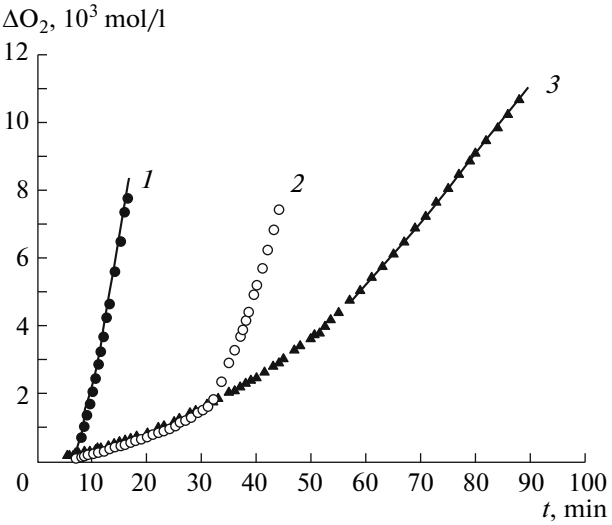


Fig. 4. Oxygen uptake kinetics in acrylic acid oxidation in the presence of the AIBN initiator at a concentration of 1.39×10^{-2} mol/l, $FeSt_3$, and the MQH inhibitor at 333 K and $p_{O_2} = 1$ atm: (*1*) [$FeSt_3$] = 9.24×10^{-4} mol/l, [MQH] = 0; (*2*) [$FeSt_3$] = 9.16×10^{-4} mol/l, [MQH] = 2.06×10^{-4} mol/l; (*3*) [$FeSt_3$] = 0, [MQH] = 2.19×10^{-4} mol/l.

As was shown in an earlier work [3], acrylic acid (AA) oxidation in the presence of an initiator proceeds via a chain mechanism and is described by the following kinetic scheme, supplemented with a catalysis step (the rate constants are given for $T = 333$ K) [1–3, 6]:

Initiation (here e is the probability of a radical escaping to the bulk)

$$\text{(i) AIBN} \longrightarrow 2e\text{r}^{\cdot} + \text{N}_2 \quad (k_\text{i} = 1.03 \times 10^{-5}\ \text{s}^{-1}),$$

$$\text{(01) r}^{\cdot} + \text{O}_2 \longrightarrow \text{rO}_2^{\cdot} \quad (k_{01} \approx 2 \times 10^9\ \text{l mol}^{-1}\ \text{s}^{-1}),$$

$$\text{(02) rO}_2^{\cdot} + \text{M} \longrightarrow \text{R}^{\cdot}.$$

Chain propagation

$$\text{(1) R}^{\cdot} + \text{O}_2 \longrightarrow \text{RO}_2^{\cdot} \quad (k_1 \approx 2 \times 10^9\ \text{l mol}^{-1}\ \text{s}^{-1}),$$

$$\text{(2) RO}_2^{\cdot} + \text{M} \longrightarrow \text{R}^{\cdot} \quad (k_2 \approx 2.84\ \text{l mol}^{-1}\ \text{s}^{-1}).$$

Catalysis

$$\text{(3) ROOR} + \text{Fe}^{2+} \longrightarrow \text{free radicals (see below).}$$

Chain termination

$$\text{(4) R}^{\cdot} + \text{R}^{\cdot} \longrightarrow \text{MOOM} \ (k_4 \approx 2.6 \times 10^8\ \text{l mol}^{-1}\ \text{s}^{-1}),$$

$$\text{(5) RO}_2^{\cdot} + \text{R}^{\cdot} \longrightarrow \text{RR} \ (k_5 \approx 10^9\ \text{l mol}^{-1}\ \text{s}^{-1}),$$

$$\text{(6) 2RO}_2^{\cdot} \longrightarrow \text{O}_2 + \text{molecules}$$

$$(2k_6 = 1.4 \times 10^7\ \text{l mol}^{-1}\ \text{s}^{-1}).$$

At fairly high p_{O_2} values and O_2 concentrations ($[\text{O}_2] > 10^{-6}$ mol/l), the concentration of peroxyl radicals $\text{RO}_2^{\cdot}$ in the oxidized monomer substantially exceeds the concentration of carbon-centered radicals $\text{R}^{\cdot}$. In this case, $v_6 \gg (v_4 + v_5)$. Then, according to the kinetic scheme, the chain oxidation rate v under quasi-steady-state conditions at a nearly constant initiator concentration ($[\text{AIBN}] \approx [\text{AIBN}]_0$) is

$$v = k_2(2k_6)^{-0.5}[\text{AA}]\, v_\text{i}^{0.5}, \qquad (3)$$

where $v_\text{i} = k_\text{i}[\text{AIBN}]$ is the initiation rate and $k_2(2k_6)^{-0.5} = 7.58 \times 10^{-4}\ \text{l}^{0.5}\ \text{mol}^{-0.5}\ \text{s}^{-0.5}$ at $T = 333$ K [3].

Note that, although the iron ions were introduced as iron stearate, they turned into ions surrounded by acrylic acid residues due to exchange with acrylic acid (whose concentration is four orders of magnitude higher than the concentration of FeSt_3). Therefore, they exert their inhibition and catalytic effect as iron acrylate. The introduction of iron ions leads to the situation such that the oligomeric acrylic acid radicals resulting from reaction (2) (see the above kinetic scheme) interact with Fe^{3+} ions with electron transfer from $\text{R}^{\cdot}$ to Fe^{3+}, which causes chain termination [7, 8] via the reaction

$$\text{(7) } \sim\text{CH}_2\text{C}^{\cdot}\text{H(COOH)} + \text{Fe}^{3+}$$

$$\longrightarrow \sim\text{CH}_2\text{C}^{+}\text{H(COOH)} + \text{Fe}^{2+},$$

$$\sim\text{CH}_2\text{C}^{+}\text{H(COOH)} + \text{CH}_2{=}\text{CHCOOH}$$

$$\longrightarrow \sim\text{CH}_2\text{CH(COOH)OC(O)CH}{=}\text{CH}_2 + \text{H}^{+}.$$

Reactions of this type occur in free-radical polymerizations of acrylic monomers and exert an inhibition effect. The rate of these processes is rather high. For example, for methyl methacrylate polymerization, the rate constant of the $\text{R}^{\cdot} + \text{Fe}^{3+}$ reaction is 5.0×10^3 l mol^{-1} s^{-1}. For methacrylonitrile polymerization in dimethylformamide at 333 K, the rate constant is 6.2×10^2 l mol^{-1} s^{-1} [8]. Fe^{3+} ions react still more rapidly with macroradicals in aqueous solution, where the rate constants of the reaction of $\sim\text{CH}_2\text{C}^{\cdot}\text{HCONH}_2$ with the iron ions at $T = 298$ K are as follows [7]:

Fe(III)	$\text{Fe}_{\text{aq}}^{3+}$	FeOH^{2+}	FeCl^{2+}
k, l mol^{-1} s^{-1}	2.0×10^3	2.1×10^4	8.1×10^4

The radicals are generated by oxidized hydrocarbons (RH) via the cyclic redox reaction of the resulting hydroperoxide with Fe^{2+} and Fe^{3+} ions [1, 6, 9, 10]:

$$\text{(3a) ROOH} + \text{Fe}^{2+} \longrightarrow \text{RO}^{\cdot} + \text{Fe}^{3+} + \text{OH}^{-},$$

$$\text{(3b) ROOH} + \text{Fe}^{3+} \longrightarrow \text{RO}_2^{\cdot} + \text{Fe}^{2+} + \text{H}^{+}.$$

Peroxides also react with Fe^{2+} ions:

$$\text{(3c) ROOR} + \text{Fe}^{2+} \longrightarrow \text{RO}^{\cdot} + \text{Fe}^{3+} + \text{RO}^{-}.$$

For example, the rate constant of the reaction between dibenzoyl peroxide and Fe^{2+} is 30.6 l mol^{-1} s^{-1} ($T =$ 333 K, ethanol) [7].

The oxidation of acrylic acid produces an oligomeric peroxide having terminal hydroperoxide groups resulting from the following reactions [6]:

$$\sim\text{CH}_2\text{CH(COOH)OO}^{\cdot} + \text{AA}$$

$$\longrightarrow \sim\text{CH}_2\text{CH(COOH)OOH} + \text{CH}_2{=}\text{CHCOO}^{\cdot},$$

$$\sim\text{CH}_2\text{CH(COOH)OO}^{\cdot} \longrightarrow \sim\text{CH}_2\text{CH(COO}^{\cdot}\text{)OOH}.$$

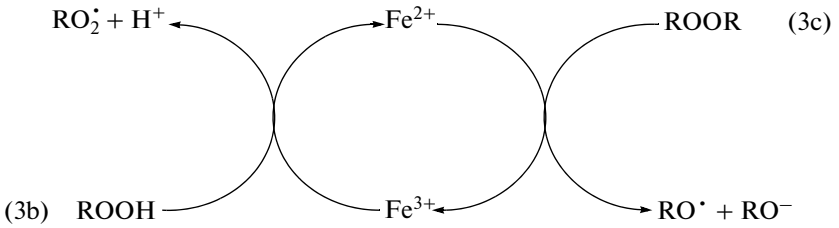
The possibility of slow hydrolysis (acidolysis) of the oligomeric peroxide cannot be excluded [11],

$$\text{ROOR} + \text{CH}_2{=}\text{CHCOOH}$$

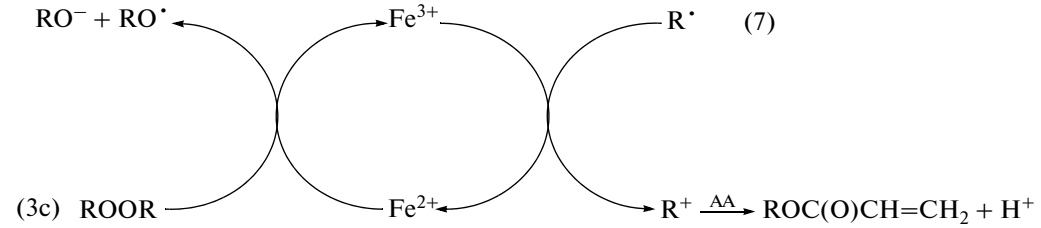
$$\rightleftharpoons \text{RO(H}^{+}\text{)OR} + \text{CH}_2{=}\text{CHCOO}^{-}$$

$$\longrightarrow \text{ROOH} + \text{ROC(O)CH}{=}\text{CH}_2.$$

Taking into account these data, we should accept the following mechanism of radical generation during catalytic acrylic acid oxidation:



In the presence of peroxide groups, one more cycle is observed, namely,



As a result of this cycle of reactions in the case of the reaction between Fe^{2+} and ROOR proceeding rapidly, the $R^{\bullet} + Fe^{3+}$ reaction (chain termination step (7)) turns into a chain propagation step and a dynamic equilibrium is established between the Fe^{2+} and Fe^{3+} concentrations. If the above cycles of the conversion of Fe^{2+} into Fe^{3+} take place, the rate of catalytic radical generation, v_{iFe}, will be

$$v_{iFe} = k_{3b}[ROOH][Fe^{3+}] = \alpha k_{3b}[ROOR][Fe^{3+}], \quad (4)$$

where $\alpha = [ROOH]/[ROOR]$. The reaction can be divided into the following two stages: an induction period, in which the peroxide concentration is low and chain termination via the $R^{\bullet} + Fe^{3+}$ reaction dominates, and accelerated catalytic oxidation of acrylic acid, in which the accumulated peroxide ensures rapid interaction between Fe^{3+} and ROOH and between Fe^{2+} and ROOR. During the induction period, the chains terminate via reactions (6) ($RO_2^{\bullet} + RO_2^{\bullet}$) and (7) ($R^{\bullet} + Fe^{3+}$). Once the peroxide ROOR is accumulated to such a concentration that the rate of the Fe^{2+} + ROOR reaction is higher than the rate of step (7), the latter stops being a chain termination step and, starting at the time $t \geq \tau$, acrylic acid is autocatalytically oxidized. In this oxidation regime, the chain initiation and termination rates at a quasi-steady-state concentration of peroxyl radicals are equal.

In the absence of an initiator, under quasi-steady-state oxidation conditions we have

$$v_{iO} + \alpha k_{3b}[ROOR][Fe^{3+}] = 2k_6[RO_2^{\bullet}]^2, \quad (5)$$

where v_{iO} is the rate of chain initiation due to the slow interaction of acrylic acid with oxygen [3]. Therefore, at $v_{iO} \ll \alpha k_{3b}[ROOR][Fe^{3+}]$ we obtain [1]

$$[ROOR]^{0.5} = \Delta[O_2]^{0.5} = b(t - \tau), \quad (6)$$

where $b = 0.5k_2[AA](2k_6)^{-0.5}(\alpha k_{3b}[Fe^{3+}])^{0.5}$. It is this parabolic dependence that was observed experimentally (Fig. 2).

In the presence of the initiator, the following equality is valid:

$$k_i[AIBN] + \alpha k_{3b}[ROOR][Fe^{3+}] = 2k_6[RO_2^{\bullet}]^2, \quad (7)$$

and the oxidation kinetics is described by the equation

$$\frac{\Delta[O_2]}{t} = \frac{k_2[AA]}{\sqrt{2k_6}}\sqrt{k_i[AIBN]} + b^2 t. \quad (8)$$

The values of the coefficient b calculated using Eqs. (2) and (8) are given in the table. As can be seen, the numerical values of this coefficient for the reaction in the presence and in the absence of the initiator are similar. This means that the scheme given above adequately describes the kinetics of acrylic acid oxidation catalyzed by iron ions both in the presence and in the absence of the initiator. The average value of b is $b = (7.16 \pm 0.56) \times 10^{-5}$ mol$^{0.5}$ l$^{-0.5}$ s^{-1}. Since $b = 0.5k_2[AA](\alpha k_{3b}[Fe^{3+}])^{0.5}/(2k_6)^{0.5}$, $k_2(2k_6)^{-0.5} = 7.58 \times 10^{-4}$ l$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ [3], and [AA] = 14.02 mol/l, we have $\alpha k_{3b} = 0.20 \pm 0.016$ l mol^{-1} s^{-1}.

Both the initiation function of the Fe^{2+} ions and the inhibition function of the Fe^{3+} ions are indicated by the results of the experiments on acrylic acid oxidation at various concentrations of iron ions in the presence of the initiator. Let us compare the rates of acrylic acid oxidation in experiments with mixed initiation (AIBN + Fe^{2+}/Fe^{3+}) and ordinary initiation (AIBN alone). In the case of mixed initiation, the oxidation rate is expressed as

$$v = \frac{k_2[AA]}{\sqrt{2k_6}}\sqrt{k_i[AIBN]} + b^2 t. \quad (9)$$

The rates of acrylic acid oxidation in both cases are given below, and the v_0(AIBN + Fe^{3+})/v(AIBN) ratio is given in parentheses:

[AIBN] × 10^2, mol/l	0.85	1.90	3.20
v (AIBN) × 10^6, mol l^{-1} s^{-1}	3.15	4.69	6.00
v_0 (AIBN + 9.0 × 10^{-4} [Fe^{3+}]) × 10^6, mol l^{-1} s^{-1}	13.1 (4.2)	12.3 (2.6)	11.6 (1.9)
v_0 (AIBN + 2.8 × 10^{-3} [Fe^{3+}]) × 10^6, mol l^{-1} s^{-1}	5.19 (1.6)	6.22 (1.3)	7.60 (1.3)

The rate of the reaction was estimated using the initial oxidation rate calculated via Eq. (9): $v = v_0$ at $t = 0$. Clearly, the oxidation rate v_0(AIBN + Fe^{3+}) is higher than v(AIBN). This indicates that additional initiation takes place in the presence of iron ions. However, the difference between the initiated and catalyzed oxidations decreases with an increase in the Fe^{3+} ion concentration (see the numbers in parentheses). Evidently, this is a consequence of the dual (accelerating and inhibiting) effect of the iron ions on acrylic acid oxidation, and the inhibiting effect strengthens as [Fe^{3+}] is increased.

Thus, a dual role of iron ions in the chain oxidation of acrylic acid was established. During the induction period, the Fe^{3+} ions inhibit oxidation by interacting with C-centered acrylic acid radicals, whereas they catalyze the process during developed oxidation due to the reactions between Fe^{2+} and ROOR and between Fe^{3+} and ROOH. The total catalytic activity of iron ions in the reaction was estimated from experimental data.

ACKNOWLEDGMENTS

This work was supported by the Division of Chemistry and Materials Science of the Russian Academy of Sciences (program no. 1 “Theoretical and Experimental Investigation of the Nature of the Chemical Bond and Mechanisms of the Most Important Chemical Reactions and Processes”).

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