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Kinetics and Mechanism of the Oxidation of Acrylic Acid and Methyl Methacrylate

N. N. Pozdeeva and E. T. Denisov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: det@icp.ac.ru

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Abstract—The kinetics of the initiated oxidation of acrylic acid and methyl methacrylate in the liquid phase were studied volumetrically by measuring oxygen uptake during the reaction. Both processes proceed via the chain mechanism with quadratic-law chain termination. The oxidation rate is described by the equation $w = k_2/(2k_6)^{1/2}[\text{monomer}]w_i^{1/2}$, where w_i is the initiation rate and k_2 and k_6 are the rate constants of chain propagation and termination. The parameter $k_2/(2k_6)^{1/2}$ is 7.58×10^{-4} $(\text{l mol}^{-1}\ \text{s}^{-1})^{1/2}$ for acrylic acid oxidation and 2.09×10^{-3} $(\text{l mol}^{-1}\ \text{s}^{-1})^{1/2}$ for the oxidation of methyl methacrylate ($T = 333$ K). For the oxidation of acrylic acid, $k_2 = 2.84$ l mol^{-1} s^{-1} ($T = 333$ K) and the activation energy is $E_2 = 54.5$ kJ/mol; for methyl methacrylate oxidation, $k_2 = 2.96$ l mol^{-1} s^{-1} ($T = 333$ K) and $E_2 = 54.4$ kJ/mol. The enthalpies of the reactions of $RO_2^{\bullet}$ with acrylic acid and methyl methacrylate were calculated, and their activation energies were determined by the intersecting parabolas method. The contribution from the polar interaction to the activation energy was determined by comparing experimental and calculated E_2 values: $\Delta E_{\mu} = 5.7$ kJ/mol for the reaction of $RO_2^{\bullet}$ with acrylic acid and $\Delta E_{\mu} = 0.9$ kJ/mol for the reaction of $RO_2^{\bullet}$ with methyl methacrylate. Experiments on the spontaneous oxidation of acrylic acid provided an estimate of the rate of chain initiation via the reaction of oxygen with the monomer: $w_{i,0} = (3.51 \pm 0.85) \times 10^{-11}$ mol l^{-1} s^{-1} ($T = 333$ K).

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Acrylic acid (AA) is the largest tonnage acrylic monomer. At the same time, the oxidation of AA remains almost unstudied [1, 2], although information on its oxidizability is important for the technology of storage and processing of this monomer. The theoretical aspect of AA oxidation is also interesting. A comparison between the kinetic characteristics of the oxidation of AA and those of other acrylic monomers suggests that the carboxyl group in the AA monomer affects its reactivity in the reaction with peroxyl radicals. In the present work, we describe the oxidation and reactivity of AA. The kinetics of methyl methacrylate (MMA) oxidation was studied in parallel under the same conditions to correctly compare the kinetic characteristics. In addition to the experimental study, theoretical calculation of the activation energies of the reactions of peroxyl radicals with AA and MMA was performed. The model of radical addition as a superposition of three parabolic potential curves was used as the computational method [3].

EXPERIMENTAL

Chemicals

Methyl methacrylate (reagent grade) stabilized with hydroquinone was purified to remove the inhibitor by multiply washing it with an aqueous solution of NaOH until the formation of a colorless aqueous layer. During washing, the vessel with the reagent was continuously saturated with a bubbling inert gas to prevent hydroquinone oxidation. Next, MMA was washed to neutral reaction with H_2O, with a 3% solution of HCl, and then again with H_2O and was dried with anhydrous Na_2SO_4. Then the reagent was distilled in vacuo. Thereafter, the reagent was twice passed through a column packed with specially prepared layers of freshly calcined Al_2O_3, SiO_2, and Na_2SO_4 and was distilled again ($T_b = 54.5$°C/14.5 Torr).

Acrylic acid (Aldrich, 99%, stabilized by 0.02% monomethyl ether of hydroquinone) was purified by vacuum distillation ($T_b = (20 \pm 1)$°C/1.5 Torr) at a water bath temperature of (28 ± 1)°C. During distillation the receivers were cooled to $T \cong (5–10)$°C. The purified reagent was stored at a low temperature. Only freshly distilled portions of the monomer were used in experiments. As the reagent was oxidized, the subsequent distillations of AA were carried out by the same method, adding the Irganox 1010 inhibitor (1.4×10^{-4} mol/l, 0.017%) into the distillation flask.

Chlorobenzene and the initiator (azobisisobutyronitrile, AIBN) were purified by standard methods.

Table 1. Addition of $RO_2^{\bullet}$ to olefins: parameter br_e (Eq. (4)), enthalpy ΔH, and activation energy E of the reactions [6]

Olefin	$-\Delta H$, kJ/mol	E, kJ/mol	br_e, (kJ/mol)$^{1/2}$
$CH_2{=}CH_2$	19.1	63.4	17.69
$CH_2{=}CHMe$	16.9	60.8	17.29
$CH_2{=}CHEt$	18.2	53.8	16.54
E-MeCH=CHMe	16.5	59.2	16.98
$CH_2{=}CMe_2$	21.8	56.9	17.24
$MeCH{=}CMe_2$	25.5	55.8	17.47
$CH_2{=}CH(CH_2)_3Me$	17.3	58.4	16.97
$CH_2{=}CHCMe_3$	29.3	55.9	17.84
	Average: $br_e = 17.25 \pm 0.39$		

Kinetic Measurements

The oxidation reactions of AA and MMA were studied under the following conditions: AIBN as the initiator, chlorobenzene as the solvent, 333 K, atmospheric pressure of oxygen or air (P_{O_2} = 1.0 atm or P_{O_2} = 0.21 atm (air)). Oxygen uptake was measured during monomer oxidation by the volumetric method. A standard manometric setup with automated atmospheric pressure control was used [4]. The O_2 uptake rate was measured with a KM-6 cathetometer as the change in the level of Hg or n-decane (Δh, mm) in a temperature-controlled burette at a constant oxygen or air pressure. Variations of the temperature of the measuring burette and reaction vessel during the experiment did not exceed 0.1 K. The error of volumetric measurements using the mercury burette was $\leq 6 \times 10^{-4}$ cm^3, and that for the burette filled with n-decane was $\leq 1.7 \times 10^{-4}$ cm^3. The concentration of absorbed oxygen $\Delta[O_2]$ was calculated as

$$\Delta[O_2]\ (\text{mol/l}) = \text{const} \times P \times V_l^{-1} T^{-1} \Delta h, \qquad (1)$$

where const is the instrument constant, which is 3.255×10^{-5} for n-decane and 1.1068×10^{-4} for Hg, P (Torr) is atmospheric pressure, $V_l \cong 4.0$ cm^3 is the volume of the liquid in the reactor, and T (K) is the measuring burette temperature. The shaking frequency of the glass reactor was 12 s^{-1}, which ensured fast oxygen dissolution in the liquid phase and kinetic control of the reaction. The duration of experiments on monomer oxidation ranged from 30 to 50 min. The oxygen uptake curves were straight lines in the t–$\Delta[O_2]$ coordinates. Their slope ratio was used to determine the oxygen uptake rate. The setup makes it possible to measure oxidation rates (w) from 2×10^{-8} to 5×10^{-5} mol l^{-1} s^{-1}. In the calculation of component concentrations in the reaction mixture, it was taken into account that the volumes of MMA, AA, and chlorobenzene (V_T) depend on temperature as

$$V_T = V_{293}(1 + \beta \Delta T), \qquad (2)$$

where V_T is the liquid volume at the experimental temperature, V_{293} is the volume at 293 K, ΔT = 40 K, and β is the volumetric thermal expansion coefficient equal to 1.00×10^{-3} for AA and chlorobenzene and 1.125×10^{-3} for MMA. The concentrations of the individual substances were as follows: [AA] = 14.59 (293 K) and 14.02 (333 K) mol/l; [MMA] = 9.39 (293 K) and 8.98 (333 K) mol/l [5].

COMPUTATIONAL PROCEDURE

The activation energy of the addition of peroxyl radicals to the monomers was calculated using the model of radical addition reaction as a superposition of three potential parabolic curves [3]. One of them describes the stretching vibrations of the forming C–O bond, and the superposition of the two other curves describes the transformation of the double π bond into the ordinary σ bond. The addition reaction is characterized by the following parameters: classical enthalpy, ΔH_e; classical potential barrier, E_e; algebraic sum of the extensions of the reacting bonds, $r_e = \Delta r_{C-C} - \Delta r_{C=C} + \Delta r_{C-O}$; force constant of the attacked π bond, $2b^2$; coefficients $\alpha = \nu_{C=C}/\nu_{C-O}$ and $\gamma = (\nu_{C=C} - \nu_{C-C})/\nu_{C-O}$, where ν are the stretching frequencies of the corresponding bonds; preexponential factor, $A = 10^9$ l mol^{-1} s^{-1} for the given class of reactions. The classical enthalpy of the reaction, ΔH_e, is related to the enthalpy of the reaction, ΔH, by the simple expression

$$\begin{aligned}\Delta H_e &= \Delta H + 0.5hN_A(\nu_{C=C} - \nu_{C-C} - \nu_{C-O}) \\ &= \Delta H - 3.6\ \text{kJ/mol},\end{aligned} \qquad (3)$$

and the classical potential barrier is related to the activation energy E by the equation

$$\begin{aligned}E_e &= E + 0.5hN_A(\nu_{C=C} - \nu_{C-C}) - 0.5RT \\ &= E + 1.7\ \text{kJ/mol} - 0.5\ RT.\end{aligned} \qquad (4)$$

The E_e value was calculated through the enthalpy of the reaction using the equation

$$\sqrt{E_e} = B\left\{\alpha\sqrt{1 + \frac{\Delta H_e}{Bbr_e}} - \gamma\right\}, \qquad (5)$$

where $B = br_e/(\alpha^2 - \gamma^2)$. For the reactions of peroxyl radicals with monomers, the above parameters have the following values [3]: $\alpha = 1.737$, $\gamma = 0.202$; br_e is calculated from experimental data as the average for a series of reactions of one class, and this calculation is performed using the formula

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \gamma\sqrt{E_e}. \qquad (6)$$

Table 2. Oxidation rate of AA (w_{O_2}) and the chain length (ν) at different concentrations of the initiator (AIBN) and AA ($T = 333$ K, $P_{O_2} = 1.0 \times 10^5$ Pa, chlorobenzene solvent)

$w_{O_2} \times 10^6$, mol l^{-1} s^{-1}	[AA], mol/l	[AIBN] $\times 10^2$, mol/l	$w_i \times 10^7$, mol l^{-1} s^{-1}	ν	$k_2/(2k_6)^{1/2} \times 10^4$, $(\text{l mol}^{-1}\text{ s}^{-1})^{1/2}$
2.04	14.02	0.366	0.38	53.7	7.52
3.86	14.02	1.35	1.39	27.8	7.49
3.99	14.02	1.46	1.50	26.6	7.46
6.64	14.02	3.87	3.99	16.6	7.68
1.02	3.52	1.49	1.53	6.67	7.86
1.98	7.00	1.46	1.50	13.2	7.53
2.28	7.05	1.83	1.88	12.1	7.71
3.38	10.5	1.82	1.87	18.1	7.61
3.99	14.02	1.46	1.50	26.6	7.46
3.86	14.02	1.35	1.39	27.8	7.49

Average: $k_2/(2k_6)^{1/2} = (7.58 \pm 0.12) \times 10^{-4}$

The initial data (ΔH and E) for a series of additions of secondary alkyl peroxide radicals to various olefins and the br_e values calculated via Eq. (4) are listed in Table 1. The latter are similar and, hence, characterize one class of reactions. The average value is $br_e = 17.25 \pm 0.39$ (kJ/mol)$^{1/2}$.

RESULTS AND DISCUSSION

Kinetic Scheme of Monomer Oxidation

The monomers are oxidized as the chain copolymerization of the monomer with O_2 to form oligomeric polyperoxide MOOM. The kinetic scheme of oxidation includes the following elementary steps [1, 2]:

Initiation (here e is the probability of radical escape to the bulk):
(i) $\quad I \longrightarrow 2er^{\bullet} + N_2,\quad k_i = 1.03 \times 10^{-5}$, s^{-1} [7, 8],
(01) $\quad r^{\bullet} + O_2 \longrightarrow rO_2^{\bullet},\quad k_{01} \approx 2 \times 10^9$, l mol^{-1} s^{-1} [8, 9],
(02) $\quad rO_2^{\bullet} + M \longrightarrow M^{\bullet}$,
Chain propagation:
(1) $\quad M^{\bullet} + O_2 \longrightarrow MO_2^{\bullet},\quad k_1 \approx 2 \times 10^9$, l mol^{-1} s^{-1} [8, 9],
(2) $\quad MO_2^{\bullet} + M \longrightarrow MOOM^{\bullet}$,
Chain termination:
(4) $\quad MO_2^{\bullet} + M^{\bullet} \longrightarrow MOOM,\quad k_4 \approx 10^9$, l mol^{-1} s^{-1} [1],
(5) $\quad M^{\bullet} + M^{\bullet} \longrightarrow MM,\quad k_5 \approx 2.6 \times 10^8$, l mol^{-1} s^{-1} [10],
(6) $\quad 2\,MO_2^{\bullet} \longrightarrow O_2 + \text{molecules},\quad 2k_6 = 1.4 \times 10^7$, l mol^{-1} s^{-1}
for $MO_2^{\bullet}$ AA,
$2k_6 = 2.0 \times 10^6$, l mol^{-1} s^{-1}
for $MO_2^{\bullet}$ MMA [1, 11].

For fairly high P_{O_2} and $[O_2]$ ($[O_2] > 10^{-5}$ mol/l), the concentration of peroxyl radicals $MO_2^{\bullet}$ in the oxidized monomer far exceeds the concentration of carbon-centered $M^{\bullet}$ radicals, whose participation in the chain termination reactions can be neglected. In this case, $w_6 \gg w_4 + w_5$ and, accordingly, in the quasi-steady-state regime, at an almost invariable initiator concentration under the experimental conditions, $[\text{AIBN}] \cong [\text{AIBN}]_0$ and, according to the above scheme of reactions, the chain oxidation rate is

$$w_{O_2} = k_2(2k_6)^{-1/2}\,[\text{monomer}]\,w_i^{1/2}, \qquad (7)$$

where $w_i = k_i[\text{AIBN}]$ is the initiation rate.

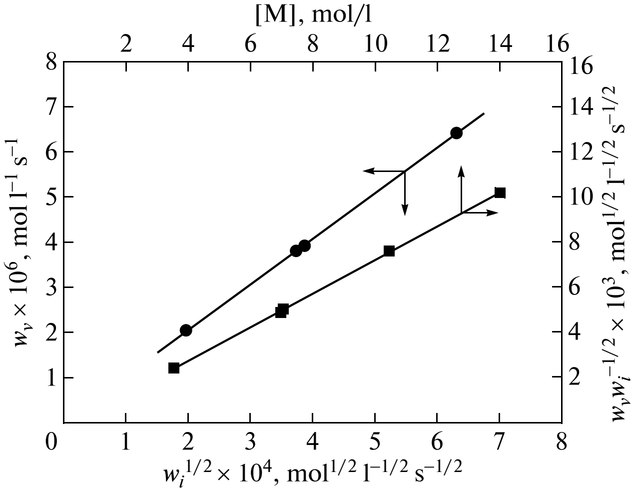


Fig. 1. Oxidation rate of AA as a function of the monomer concentration [M] and initiation rate w_i (AIBN initiator, $k_i = 1.03 \times 10^{-5}$ s^{-1}, [CH$_2$=CHCOOH] = 14.02 mol/l, $P_{O_2} = 1.0 \times 10^5$ Pa, $T = 333$ K, chlorobenzene solvent).

Kinetics of AA Oxidation

The rate constants of initiation (k_i) and decomposition (k_d) of the AIBN initiator ($k_i = 2ek_d$) in AA are the following: $k_i = 1.03 \times 10^{-5}$ s^{-1} and $k_d = 9.4 \times 10^{-6}$ s^{-1} ($k_i = 2ek_d$) [7, 8]. The rates of AA oxidation were measured at different initiator and monomer concentrations. As can be seen from Table 2, which lists the initial data and kinetic characteristics, AA is oxidized via the chain mechanism and the chain length ν varies from 12 to 54 units, depending on the experimental conditions. The dependences of the chain oxidation rate on [AA] and w_i are shown in Fig. 1.

Clearly, the oxidation rate is directly proportional to the AA concentration, indicating that reaction (2) is the rate-determining step of chain propagation. At the same time, as was demonstrated by experiments on AA oxidation with oxygen and air, the oxidation rate is independent of the oxygen partial pressure. This suggests that step (1) is very fast and is not rate-determining for the process. The chain oxidation rate is proportional to $w_i^{1/2}$, indicating quadratic-law chain termination involving peroxyl radicals. All this agrees well with the above kinetic scheme of monomer oxidation. The following facts were taken into account when calculating the parameter $k_2/(2k_6)^{1/2}$, which characterizes the chain oxidation of AA: nitrogen evolution from AIBN, oxygen uptake by initiator radicals, and oxygen evolution due to the disproportionation of peroxyl radicals. The overall rate of this gas evolution is $-(k_d/k_i)\, w_i + w_i - 0.5w_i = -0.41\, w_i$. The parameter $k_2/(2k_6)^{1/2}$ was calculated via the equation

$$k_2/(2k_6)^{1/2} = (w_{O_2} + 0.41\, w_i)/([AA] \times w_i^{1/2}). \quad (8)$$

The results of the calculation of this parameter are given in Table 2, and its average value is $k_2/(2k_6)^{1/2} = (7.58 \pm 0.12) \times 10^{-4}$ (l mol^{-1} s^{-1})$^{1/2}$ ($T = 333$ K). Thus, the rate of AA oxidation for long chains is described by the following equation ($T = 333$ K):

$$w_{O_2} = 7.58 \times 10^{-4}\, [AA] w_i^{1/2}. \quad (9)$$

The average rate constant of the disproportionation of the peroxy radicals of methyl and butyl acrylates is $2k_6 = (1.4 \pm 0.3) \times 10^7$ l mol^{-1} s^{-1} [11]. Assuming that the $2k_6$ value for the $MO_2^{\bullet}$ radicals of AA is the same as is presented above, we obtain the following estimate for the rate constant of chain propagation in oxidized AA: $k_2 = 2.84$ l mol^{-1} s^{-1}. The average value of the preexponential factor for the addition of peroxy radicals to the monomers is $A = 10^9$ l mol^{-1} s^{-1} [3]. Correspondingly, the Arrhenius activation energy for the reaction $RO_2^{\bullet}$ + AA is $E = RT\ln(A/k_2) = 54.5$ kJ/mol.

Theoretical Calculation of the Activation Energy of the Reaction $RO_2^{\bullet}$ *+ AA*

The enthalpy of reaction should be known for calculating the activation energy. The enthalpy of the radical addition reactions

$$RO_2^{\bullet} + CH_2{=}CHCOOH \longrightarrow ROOCH_2C^{\bullet}HCOOH$$

was calculated using the sequence of the thermochemical processes

$$CH_3CH_2COOH \longrightarrow C^{\bullet}H_2C^{\bullet}HCOOH + 2\,H^{\bullet},$$

$$RO_2^{\bullet} + C^{\bullet}H_2C^{\bullet}HCOOH \longrightarrow ROOCH_2C^{\bullet}HCOOH,$$

$$RO_2^{\bullet} + CH_2{=}CHCOOH \longrightarrow ROOCH_2C^{\bullet}HCOOH,$$

as the difference

$$\Delta H = \Delta H(ROOCH_2C^{\bullet}HCOOH) - \Delta H(CH_2{=}CHCOOH) - \Delta H(RO_2^{\bullet}). \quad (10)$$

The following ΔH_f^0 values borrowed from [12] were used in the calculations: $\Delta H_f^0(CH_3CH_2COOH) = -447.7$ kJ/mol, and $\Delta H_f^0(CH_2{=}CHCOOH) = -322.4$ kJ/mol. The dissociation energies were taken from [8]: D(ROO–R) = 289.7 kJ/mol, D(H–CH$_2$CH$_2$COOH) = 422.0 kJ/mol, and D(CH$_3$CH–HCOOH) = 398.9 kJ/mol. The thus-calculated enthalpy of the reaction $RO_2^{\bullet} + CH_2{=}CHCOOH \longrightarrow ROOCH_2C^{\bullet}HCOOH$ is $\Delta H = -30.1$ kJ/mol. The classical enthalpy of this reaction is $\Delta H_e = -33.9$ kJ/mol (Eq. (3)). Substituting the corresponding parameters and ΔH_e into Eq. (5), we obtain $E_{e2} = 49.3$ kJ/mol and $E_2 = 48.8$ kJ/mol (Eq. (4), $T = 333$ K). This value differs substantially from the experimental value of $E_2 = 54.5$ kJ/mol. The difference is due to the fact that the calculation was performed for the nonpolar (hydrocarbon) solvent ignoring the polar interaction in the transition state. Therefore, this difference reflects the important contribution from the polar interaction and solvation of the transition state to the activation of the given reaction. This contribution is $\Delta E_\mu = 54.5 - 48.8 = 5.7$ kJ/mol.

Estimation of the Chain Initiation Rate in the Reaction of AA with Oxygen

The generation of free radicals in monomers in the presence of dissolved oxygen occurs via the bimolecular reaction of oxygen addition to the double bond of the monomer (see [1, 2])

$$O_2 + CH_2{=}CHCOOH \longrightarrow {}^{\bullet}OOCH_2C^{\bullet}HCOOH.$$

The resulting biradical reacts rapidly with another oxygen molecule, and this is the beginning of the chain oxidation of the monomer:

$$O_2 + {}^{\bullet}OOCH_2C^{\bullet}HCOOH$$
$$\longrightarrow {}^{\bullet}OOCH_2CH(OO^{\bullet})COOH,$$
$${}^{\bullet}OOCH_2CH(OO^{\bullet})COOH + CH_2{=}CHCOOH$$
$$\longrightarrow {}^{\bullet}OOCH_2CH(OOCH_2C^{\bullet}HCOOH)COOH.$$

This reaction is very endothermic ($\Delta H \sim 100$ kJ/mol [1]) and proceeds very slowly. By special experiments, we succeeded to measure very low oxidation rates of AA in the absence of the initiator. The oxygen uptake curves in the AA autooxidation regime are linear for a long time, which is due to the slow accumulation of MOOM polyperoxide at the very low rate of radical generation in acrylic acid and the stability of polyperoxide to decomposition at the experimental temperature. The average rate of AA autooxidation is

$$w_{O_2} = (6.30 \pm 1.45) \times 10^{-8}\ \text{mol l}^{-1}\ \text{s}^{-1}$$
$$(P_{O_2} = 1.0 \times 10^5\ \text{Pa},\quad T = 333\ \text{K}). \tag{11}$$

As follows from the above experimental data (Fig. 1), in the regime of the initiated chain oxidation of acrylic acid, $w_{O_2} \sim w_i^{1/2}$ and $w_{O_2}/w_i^{1/2} \sim$ [AA] (Eq. (7)). Based on these results, we obtain that the rate of AA autooxidation obeys the equation

$$w_{O_2} = k_2(2k_6)^{-1/2}\,[\text{AA}]w_{i0}^{1/2}, \tag{12}$$

where w_{i0} is the rate of radical generation in AA autooxidation.

Taking into account that $k_2/(2k_6)^{1/2} = 7.58 \times 10^{-4}$ (l mol^{-1} s^{-1})$^{1/2}$ and [AA] = 14.02 mol/l, we calculated the average chain initiation rate in the AA + O_2 system using the chain oxidation rate:

$$w_{0i} = k_{oi}[\text{AA}][O_2]$$
$$= (3.51 \pm 0.85) \times 10^{-11}\ \text{mol l}^{-1}\ \text{s}^{-1}. \tag{13}$$

Chain initiation occurs via the bimolecular reaction, whose rate is proportional to [AA] = 14.02 mol/l and the concentration of dissolved oxygen. The Henry coefficient (γ_{O_2}, mol l^{-1} atm^{-1}) for the dissolution of oxygen in AA was accepted to be equal to the same parameter measured for acetic acid ($\gamma_{O_2} = 8.11 \times 10^{-3}$ mol l^{-1} atm^{-1} at 293 K [1]. Also using the experimental temperature dependence of the O_2 solubility in acetone were used, we obtained $\gamma_{O_2} = 1.31 \times 10^{-2} \times \exp(-141/T) = 8.58 \times 10^{-3}$ mol l^{-1} atm^{-1} at 333 K. This value coincides well with the average solubility of O_2 in vinyl monomers: $(8.5 \pm 1.5) \times 10^{-3}$ mol l^{-1} atm^{-1} [13]. Using Eq. (13), we find $k_{i0} = 2.92 \times 10^{-10}$ l mol^{-1} s^{-1} ($T = 333$ K). Accepting that the preexponential factor A for the reaction of oxygen with AA is two times higher than that of the addition of the peroxyl radical to the monomer, we determine the Arrhenius activation energy for this reaction: $E = RT\ln(A/k) = 120.1$ kJ/mol. The general expression for the rate constant of chain initiation in the reaction of AA with oxygen takes the form

$$k_{i0} = 2.0 \times 10^9 \exp(-120.1/RT)\ \text{l mol}^{-1}\ \text{s}^{-1}. \tag{14}$$

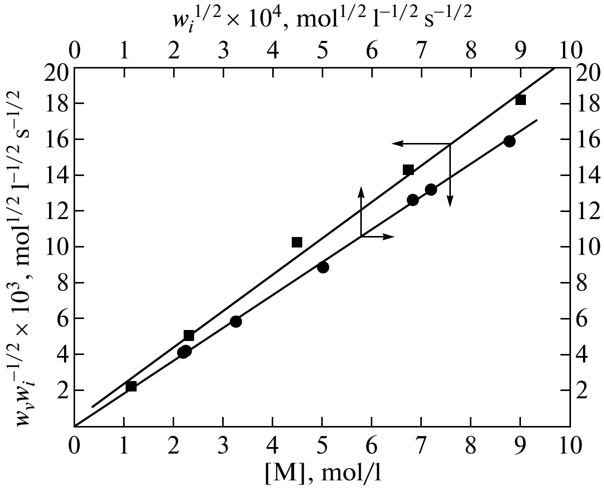


Fig. 2. Oxidation rate of MMA as a function of the monomer concentration [M] (chlorobenzene solvent) and initiation rate w_i (AIBN initiator). $P_{O_2} = 1.0 \times 10^5$ Pa, $T = 333$ K, $k_i = 1.03 \times 10^{-5}$ s^{-1}, [MMA] = 8.98 mol/l.

Kinetics of Initiated MMA Oxidation

MMA is known to be oxidized via the chain mechanism as the chain MMA copolymerization with the formation of an oligomeric polyperoxide [1, 2]. The kinetic scheme of MMA oxidation includes the same elementary steps as the scheme of AA oxidation (see above). At fairly high P_{O_2} and $[O_2]$ in MMA ($[O_2] > 10^{-5}$ mol/l) $w_6 \gg w_4 + w_5$, so the rate of MMA chain oxidation obeys Eq. (7). The rate constants of initiation (k_i) and decomposition (k_d) of the AIBN initiator in MMA are as follows: $k_i = 1.03 \times 10^{-5}$ s^{-1} and $k_d = 9.4 \times 10^{-6}$ s^{-1} ($k_i = 2ek_d$) [7, 8]. The oxidation rate was measured at varied initiator and monomer concentrations (chlorobenzene as the solvent). The experimen-

Table 3. Oxidation rate of MMA (w_{O_2}), the chain length ν, and the parameter $k_2/(2k_6)^{1/2}$ at different concentrations of the initiator (AIBN) and MMA ($T = 333$ K, $P_{O_2} = 1.0 \times 10^5$ Pa, chlorobenzene solvent)

$w_{O_2} \times 10^6$, mol l^{-1} s^{-1}	[MMA], mol/l	[AIBN] × 10^2, mol/l	$w_i \times 10^7$, mol l^{-1} s^{-1}	ν	$k_2/(2k_6)^{1/2} \times 10^3$, (l mol^{-1} s^{-1})$^{1/2}$
4.11	8.98	0.46	0.47	87.4	2.11
4.17	8.98	0.48	0.49	85.1	2.10
5.83	8.98	1.01	1.04	56.1	2.02
8.84	8.98	2.45	2.52	35.1	1.96
12.59	8.98	4.53	4.67	27.0	2.05
13.21	8.98	5.03	5.18	25.5	2.04
15.84	8.98	7.43	7.65	20.7	2.02
0.69	1.13	0.93	0.96	7.2	2.08
1.57	2.28	0.95	0.98	16.0	2.26
3.17	4.49	0.93	0.96	33.0	2.28
4.62	6.75	1.02	1.05	44.0	2.11
5.83	8.98	1.01	1.04	56.1	2.02

Average: $k_2/(2k_6)^{1/2} = (2.09 \pm 0.09) \times 10^{-3}$

tal results are presented in Table 3 and Fig. 2. We can see that the concentration dependences are in good agreement with the kinetic scheme and Eq. (7), specifically, $w_{O_2} \sim w_i^{1/2}$ and $w_{O_2} \sim$ [MMA] (see Fig. 2). The chain length ranges from 7 to 87 units, depending on the experimental conditions. The average value of the parameter $k_2/(2k_6)^{1/2}$ is $(2.09 \pm 0.09) \times 10^{-3}$ (l mol^{-1} s^{-1})$^{1/2}$, whereas in pure MMA $k_2/(2k_6)^{1/2} = (2.04 \pm 0.05) \times 10^{-3}$ (l mol^{-1} s^{-1})$^{1/2}$ (333 K). The ratios of the rate constants and experimental errors were calculated by least squares. The $k_2/(2k_6)^{1/2}$ value available from the literature is 2.14×10^{-3} (l mol^{-1} s^{-1})$^{1/2}$ (333 K) [14]. The rate constant of recombination of MMA peroxy radicals is $2k_6 = 2.0 \times 10^6$ l mol^{-1} s^{-1} (333 K) [11]. Hence, using the parameter $k_2/(2k_6)^{1/2} = 2.09 \times 10^{-3}$ (l mol^{-1} s^{-1})$^{1/2}$, we calculated the rate constant of chain propagation in oxidized MMA: $k_2 = 2.96$ l mol^{-1} s^{-1}. The average value of the preexponential factor for the addition of peroxy radicals to the monomers is $A = 10^9$ l mol^{-1} s^{-1} [3]. Accordingly, the Arrhenius activation energy for the reaction $RO_2^{\bullet}$ + MMA is $E_2 = RT\ln(A/k_2) = 54.4$ kJ/mol.

Theoretical Calculation of the Activation Energy of the Reaction between $RO_2^{\bullet}$ *and MMA*

According to [6], the enthalpy of this reaction is −24.7 kJ/mol and the classical enthalpy is $\Delta H_e = -28.3$ kJ/mol. Substituting ΔH_e and the corresponding parameters into Eq. (5), we obtain $E_{e2} = 54.0$ kJ/mol and $E_2 = 53.5$ kJ/mol (Eq. (4), $T = 333$ K). This value is close to the experimental value of $E_2 = 54.4$ kJ/mol. The difference is due to the fact that the calculations were performed for the nonpolar (hydrocarbon) solvent ignoring the polar interaction in the transition state. Therefore, this difference reflects the contribution from the polar interaction and solvation of the transition state to the activation of this reaction. This contribution is small: $\Delta E_\mu = 54.4 - 53.5 = 0.9$ kJ/mol.

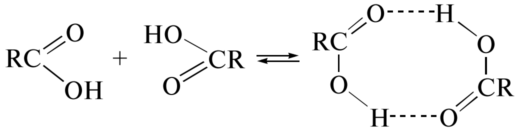
Comparison of the Reactivities of Acrylic Monomers

Let us compare the enthalpies and activation energies of the reactions of peroxy radicals with acrylic acid and other acrylic monomers. The necessary data are given in Table 4. It follows from the column of ΔH values that the enthalpy of the $RO_2^{\bullet}$ + AA reaction is the lowest. It might seem that, according to the Polanyi–Semenov rule [15], this reaction should have the highest activation energy and the largest rate constant. In fact, this is not so. As can be seen from the data in Table 4, a wide variety of $RO_2^{\bullet}$ + acrylate reactions with $\Delta H > \Delta H$ ($RO_2^{\bullet}$ + AA) occur more rapidly and with a lower activation energy. Why? The answer to this question can be found in the column of the ΔE_μ values (Table 4). It follows from the ΔE_μ values that, firstly, a noticeable contribution to the activation energy is made by the polar interaction and solvation

Table 4. Comparison of ΔH, E_2, and ΔE_μ data for the reactions of $RO_2^\bullet$ with acrylic monomers

Monomer	$RO_2^\bullet$	$-\Delta H$, kJ/mol	E_2, kJ/mol	k_2 (333 K), $l\ mol^{-1}\ s^{-1}$	ΔE_μ, kJ/mol	Literature
$CH_2{=}CHCOOH$	$\sim CH_2CH(OO^\bullet)COOH$	30.1	54.5	2.77	5.7	This work
$CH_2{=}CHCOOMe$	*sec*-$RO_2^\bullet$	22.5	52.3	6.26	−4.8	[11]
$CH_2{=}CHCOOMe$	*tert*-$RO_2^\bullet$	15.8	57.9	0.83	−3.2	[11]
$CH_2{=}CHCOOMe$	$\sim CH_2CH(COOMe)O_2^\bullet$	22.5	54.2	3.15	−2.9	[2]
$CH_2{=}CHCOOMe$	$\sim CH_2CH(OAe)O_2^\bullet$	22.5	54.2	3.15	−2.9	[2]
$CH_2{=}CMeCOOMe$	$HO_2^\bullet$	24.7	46.0	60.9	−9.9	[12]
$CH_2{=}CMeCOOMe$	*sec*-$RO_2^\bullet$	24.7	50.5	12.0	−5.3	[12, 13]
$CH_2{=}CMeCOOMe$	*tert*-$RO_2^\bullet$	18.0	55.5	1.97	−4.3	[12, 13, 14]
$CH_2{=}CMeCOOMe$	$\sim CH_2CH(COOMe)O_2^\bullet$	24.7	54.4	2.96	0.9	This work
$CH_2{=}CMeCOOMe$	$\sim CH_2CMe(COOMe)O_2^\bullet$	24.7	54.3	3.03	0.8	[2]
$CH_2{=}CMeCOOMe$	$\sim CH_2CH(COOMe)O_2^\bullet$	24.7	52.4	6.03	−3.4	[2]
$CH_2{=}CMeCOOMe$	$\sim CH_2CH(OAc)O_2^\bullet$	24.7	49.2	19.2	−6.6	[2]
$CH_2{=}CMeCOOMe$	$\sim CH_2CH(CN)O_2^\bullet$	24.7	47.4	36.7	−8.4	[2]

of the transition state and, secondly, AA is the only acrylate for which $\Delta E_\mu > 0$. For the $RO_2^\bullet$ + MMA reaction, $\Delta E_\mu = 0.9$ kJ/mol. However, since the error of ΔE_μ estimation is 2 kJ/mol, it can be assumed that, for this reaction, $\Delta E_\mu \approx 0$. It is practically for AA only that the polar interaction raises the potential barrier of the reaction. Thus, the $RO_2^\bullet$ + AA reaction is the exception from the entire series of reactions of peroxy radicals with acrylic monomers. This is most likely due to the presence of a carboxyl group in AA. Carboxylic acids form stable association species through hydrogen bonding:



This is likely responsible for the specific features of AA reactivity that were revealed by combining experimental and theoretical studies of this reaction.

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