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Mechanism of Hydroquinone-Inhibited Oxidation of Acrylic Acid and Methyl Methacrylate

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Abstract—The kinetics of hydroquinone-inhibited oxidation of acrylic acid and methyl methacrylate was studied volumetrically by measuring the oxygen uptake in the presence of an initiator (azobisisobutyronitrile) at $T = 333$ K and $P_{O_2} = 1$ and 0.21 atm. The oxidation of acrylic acid inhibited by 4-methoxyphenol was studied under the same conditions for comparison. The rate constants of the reactions of the peroxyl radicals of acrylic acid ($\sim CH_2CH(COOH)O_2^\bullet$) and methyl methacrylate ($\sim CH_2CMe(COOMe)O_2^\bullet$) with hydroquinone ($HOC_6H_4OH$) ($1.20 \times 10^5$ and 7.16×10^4 l mol^{-1} s^{-1}, respectively) and of the reaction of peroxyl radicals of acrylic acid with 4-methoxyphenol (p-$CH_3OC_6H_4OH$) (3.25×10^4 l mol^{-1} s^{-1}) were measured. The stoichiometric inhibition factors f were determined. The reaction between the semiquinone radical and oxygen, $O_2 + HOC_6H_4O^\bullet$, plays an important role, decreasing the factor f and the efficiency of the inhibition effect of hydroquinone. The rate constants of this reaction were calculated from kinetic data: $k = 5.72 \times 10^2$ (in acrylic acid) and 4.60×10^2 l mol^{-1} s^{-1} (in methyl methacrylate).

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In an earlier study [1], we studied the initiated oxidation of acrylic acid (AA), proved its chain mechanism, and measured the chain propagation rate constant. The inhibition effect of phenolic inhibitors on the oxidation of AA remains unknown, although AA is the most widespread acrylic monomer [2, 3]. The purpose of this work is to clarify this issue. Hydroquinone and (for comparison) 4-methoxyphenol (MeQH), which are similar in O–H bond strength, were chosen as the inhibitors. Hydroquinone (QH_2) is especially interesting as an inhibitor, since the semiquinone radical ($HQ^\bullet$) formed by QH_2 reacts with oxygen, which has an effect on the inhibition efficiency of [4]. This reaction of the semiquinone radicals of hydroquinone and its derivatives was first discovered while investigating the inhibited oxidation of nonpolar styrene [5]. Here, we report the specific features of the reaction of peroxyl radicals with phenols in polar media (methyl methacrylate (MMA) and AA, which contain a carboxyl group).

This work is devoted to the kinetics of the oxidation of AA and MMA inhibited by QH_2 and MeQH. On the one hand, these two phenols are similar in reactivity [4], but QH_2 generates the hydroquinone radical $HQ^\bullet$, while MeQH does not. On the other hand, both monomers are polar compounds forming a hydrogen bond with phenols, but one of them is an acid and the other is an ester. Using these examples, we can elucidate the role of the carboxyl group in phenol-inhibited oxidation.

EXPERIMENTAL

Reagents

Acrylic acid (Aldrich, 99%, stabilized by 4-methoxyphenol) was purified by vacuum distillation (bp 20 ± 1°C/1.5 Torr) at a water bath temperature of 28°C. During distillation, the receiver was cooled to 5–10°C. Purified AA was stored in the dark at low temperature (~0°C). As the reactant was oxidized, subsequent distillations of AA were carried out in the same way, but the Irganox 1010 inhibitor at a concentration of 1.4×10^{-4} mol/l (0.017%) was added to the distillation flask.

Methyl methacrylate (reagent grade) stabilized by hydroquinone was purified from the inhibitor by multiple treatments with an aqueous solution of NaOH until the aqueous layer was colorless. The alkali concentration was successively decreased from 10 to 5%. An inert gas was continuously bubbled through the reactant to prevent the oxidation of hydroquinone in the alkaline medium. Next, the reactant was washed until neutral first with water, then with a 3% solution of HCl, and again with water. Thereafter, the reactant was dried using dehydrated Na_2SO_4; vacuum-distilled; twice passed through a column packed with layers of freshly calcined Al_2O_3, SiO_2, and Na_2SO_4, monitoring the purity of the reactant by thin-layer chromatography (TLC) on Silufol and Alumofol; and distilled again (bp 54.5°C/14.5 Torr).

Hydroquinone QH_2 (Aldrich, 99%) was purified by double recrystallization from distilled water and freshly distilled acetone (special purity grade), and the resulting crystals were dried in vacuo.

4-Methoxyphenol (high-purity grade) was purified by recrystallization from MeOH and PhMe and then by liquid chromatography on SiO_2. According to TLC analyses using Silufol and Alumofol, the product was an individual compound.

Azobisisobutyronitrile (AIBN, Aldrich) to be used as the initiator was purified by double recrystallization from purified methanol and benzene followed by drying in vacuo.

Kinetic Measurements

Oxidation was studied volumetrically by measuring the oxygen uptake using a manometric setup. Experiments were carried out at 333 K and oxygen pressures of 1 and 0.21 atm. A monomer, AIBN, and an inhibitor (QH_2 or MeQH) were introduced into the reactor connected to a burette. The volume of the liquid in the reactor was 4 cm^3, and the shaking frequency of the cell was 12 s^{-1}, ensuring that the reaction is kinetically controlled. The monomer concentrations at 333 K were [AA] = 14.02 and [MMA] = 8.98 mol/l. The experimental procedure was detailed earlier [1].

Primary Data Processing

The chain mechanism of oxidation of acrylic monomers inhibited by a phenolic inhibitor includes the following steps (the rate constants of the bimolecular and monomolecular reactions presented below have dimensions of l mol^{-1} s^{-1} and is s^{-1}, respectively) [1–3]:

Initiation

(i) $\mathrm{AIBN} \rightarrow 2e\mathrm{r}^\bullet + \mathrm{N_2}$ ($k_i = 1.03 \times 10^{-5}$ [6]),

(0I) $\mathrm{r}^\bullet + \mathrm{O_2} \rightarrow \mathrm{rO_2^\bullet}$ ($k_{01} = 3 \times 10^9$ [2]),

(0II) $\mathrm{rO_2^\bullet} + \mathrm{M} \rightarrow \sim\mathrm{M}^\bullet$ ($k_{02} \approx 2.84$ (AA) [1]),

(0II') $\mathrm{rO_2^\bullet} + \mathrm{M} \rightarrow \sim\mathrm{M}^\bullet$ ($k'_{02} \approx 2.96$ (MMA) [1]),

(0II") $\mathrm{HO_2^\bullet} + \mathrm{M} \rightarrow \sim\mathrm{M}^\bullet$ ($k''_{02} \approx 2.90$ (AA, MMA)).

Chain propagation

(I) $\sim\mathrm{M}^\bullet + \mathrm{O_2} \rightarrow \sim\mathrm{MO_2^\bullet}$ ($k_1 = 3 \times 10^9$ [2]),

(II) $\sim\mathrm{MO_2^\bullet} + \mathrm{M} \rightarrow \sim\mathrm{MOOM}^\bullet$ ($k_2 = 2.84$ (AA) [1]),

(II') $\sim\mathrm{MO_2^\bullet} + \mathrm{M} \rightarrow \sim\mathrm{MOOM}^\bullet$ ($k'_2 = 2.96$ (MMA) [1]).

Chain termination

(IV) $\sim\mathrm{M}^\bullet + \sim\mathrm{M}^\bullet \rightarrow \mathrm{MM}$ ($2k_4 \approx 2.6 \times 10^8$ [7]),

(V) $\sim\mathrm{MO_2^\bullet} + \sim\mathrm{M}^\bullet \rightarrow \mathrm{MOOM}$ ($k_5 \approx 10^9$ [2]),

(VI) $2 \sim\mathrm{MO_2^\bullet} \rightarrow \mathrm{O_2} + \mathrm{MOOM}$ ($2k_6 = 1.4 \times 10^7$ (AA) [2, 3]),

(VI') $2 \sim\mathrm{MO_2^\bullet} \rightarrow \mathrm{O_2} + \mathrm{MOOM}$ ($2k'_6 = 2.0 \times 10^6$ (MMA) [2, 3]),

(VII) $\sim\mathrm{MO_2^\bullet} + \mathrm{QH_2} \rightarrow \mathrm{MOOH} + \mathrm{HQ}^\bullet$ (object of investigation),

(VII') $\sim\mathrm{MO_2^\bullet} + \mathrm{MeQH} \rightarrow \mathrm{MOOH} + \mathrm{MeQ}^\bullet$ (object of investigation),

(VIII) $\sim\mathrm{MO_2^\bullet} + \mathrm{HQ}^\bullet \rightarrow \mathrm{MOOH} + \mathrm{Q}$ ($k_8 = 1.5 \times 10^9$),

(VIII') $\sim\mathrm{MO_2^\bullet} + \sim\mathrm{MeQ}^\bullet \rightarrow \mathrm{MOH} + \mathrm{MeQ{=}O}$ ($k'_8 = 1.5 \times 10^8$ [2]),

(IX) $\mathrm{HQ}^\bullet + \mathrm{HQ}^\bullet \rightarrow \mathrm{Q} + \mathrm{HQH}$ ($k_9 = 1.5 \times 10^9$ [2]),

(IX') $\sim\mathrm{MeQ}^\bullet + \sim\mathrm{MeQ}^\bullet \rightarrow$ products ($k'_9 = 1.5 \times 10^8$ [2]),

(X) $\mathrm{O_2} + \mathrm{HQ}^\bullet \rightarrow \mathrm{HO_2^\bullet} + \mathrm{Q}$ (object of investigation).

Here, M is a monomer (AA or MMA), e is the probability of radicals escaping to the bulk, $\mathrm{r}^\bullet$ is the radical $\mathrm{Me_2(CN)C}^\bullet$ formed from AIBN, MM is an oligomer of the corresponding monomer, and MOOM is the oligomeric peroxide of the corresponding monomer.

Disproportionation reactions (VIII) and (IX) are very exothermic: $\Delta H_8 = D_{\mathrm{O-H}}(\mathrm{HQ}^\bullet) - D_{\mathrm{O-H}}(\mathrm{MOOH}) = 226.3 - 376.4 = -150.1$ kJ/mol and $\Delta H_9 = D_{\mathrm{O-H}}(\mathrm{HQ}^\bullet) - D_{\mathrm{O-H}}(\mathrm{QH_2}) = 226.3 - 352.8 = -126.5$ kJ/mol [4, 6]. In isopropyl alcohol, reaction (IX) proceeds with a diffusion-controlled rate constant of $k_9 = 1.5 \times 10^9$ l mol^{-1} s^{-1} [2]. Based on the similarity of reactions (VIII) and (IX) and on their high exothermicity, we may assume that $k_9 = k_8 = 1.5 \times 10^9$ l mol^{-1} s^{-1}. Since nitrogen is evolved upon the decomposition of AIBN to radicals, the corresponding correction was applied when calculating the oxygen uptake rate:

$$v(\mathrm{O_2}) = v_{\mathrm{gas}} - v_{\mathrm{N_2}} = v_{\mathrm{gas}} - v_{\mathrm{i}}/2e, \qquad (1)$$

where $e \approx 0.55$ is the probability of a cyanisopropyl radical escaping from the solvent cage [6]. Under our experimental conditions (see below), all chains are terminated on phenol (InH = QH_2 or MeQH, reactions (VII) and (VII'), respectively) and radicals forming from phenol (reactions (VIII) and (VIII')). In this

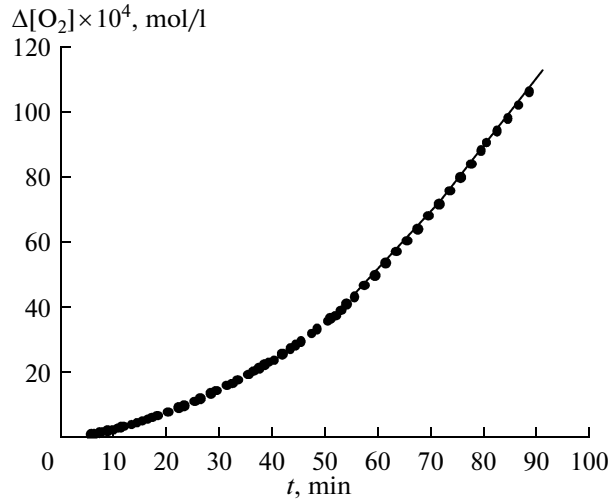


Fig. 1. Kinetics of oxygen uptake by AA in the presence of MeQH ($[MeQH]_0 = 2.19 \times 10^{-4}$ mol/l, $P_{O_2} = 1.01$ atm, $T = 333$ K, [AA] = 14.02 mol/l, $[AIBN] = 1.39 \times 10^{-2}$ mol/l, $k_i = 1.03 \times 10^{-5}$ s^{-1}).

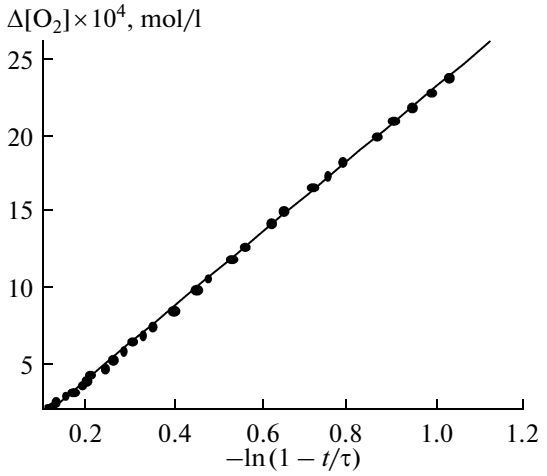


Fig. 2. O_2 uptake curve in the $\Delta[O_2]$–$(-\ln(1 - t/\tau))$ coordinates. For the experimental conditions, see caption to Fig. 1.

case, the oxygen uptake kinetics is described by the equation [2, 4]

$$\Delta[O_2] = v_i t - (k_2/k_7)[M]\ln(1 - t/\tau), \quad (2)$$

where $\tau = f[InH]_0/v_i$, is the induction period and f is the stoichiometric inhibition factor, which is calculated from experimental data ($f = v_i\tau/[InH]_0$). If oxidation yields short chains, the interaction of the peroxyl radicals with the monomer (reaction (II)) and inhibitor InH (reaction (VII)) should be taken into account. In this case, the initial oxidation rate in the presence of phenol is as follows [4]:

$$v_0 = \left\{\frac{k_2[M]}{fk_7[InH]} + 1\right\} v_i. \quad (3)$$

The oxygen uptake curves of were linearized in the coordinates of the equation $\Delta[O_2] = -(k_2/k_7)[M]\ln(1 - t/\tau)$. The slope of the straight line was used to calculate the initial oxidation rate v_0, which was used to calculate the rate constant k_7:

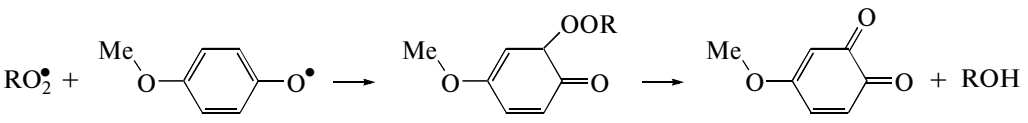
$$k_7 = \frac{k_2[M]}{f[InH]_0(v_0 - v_i)}. \quad (4)$$

The mechanism of the inhibiting effect of QH_2 turned out to be more complicated than that of MeQH and will be discussed in the next section.

RESULTS AND DISCUSSION

Oxidation of AA Inhibited by MeQH

The typical kinetics of oxygen uptake in the MeQH-inhibited oxidation of AA is shown in Fig. 1. As can be seen, oxidation occurs with acceleration caused by the consumption of the inhibitor. The kinetic curve presented in Fig. 1 is linearized well in the coordinates of the equation $\Delta[O_2] = -(k_2/k_7)[M]\ln(1 - t/\tau)$ (Fig. 2). The experimental data for the system AA–AIBN–O_2–MeQH are given in Table 1. These data show that the inhibited oxidation of AA is a chain process (chain length of $\nu = 1.6$–7.4). A change in the partial pressure of O_2 exerts no effect on the kinetic parameters of the reaction, as follows from the results of experiments at different P_{O_2} values. This finding is in agreement with the accepted reaction scheme, in which chain termination involves only peroxyl radicals. It can be assumed by analogy with the reactions of other phenols [2] that chain termination involving MeQH and MeQ$^\bullet$ takes place via reactions (VII') and (VIII'). In this case, the factor f should be 2. As can be seen from the experimental data presented in Table 1, $f > 2$ (2.26 ± 0.07). Evidently, a product exerting an inhibiting effect forms from the inhibitor. Perhaps, this is *ortho*-quinone, which results from the consecutive reactions



and terminates the chains interacting with C-centered radicals of AA. The formation of the inhibiting product is consistent with the fact that the higher the initial inhibitor concentration, the lower the AA oxidation

rate after the induction period (Fig. 3). Therefore, the value $v_f = 2$ should be used in the calculation of k_7 for the initial period of the reaction ($t \approx 0$), since at this moment the product, whose participation in oxidation chain termination results in an increase in f, is not accumulated in the system. The rate constant of the reaction of peroxyl radicals with MeQH, calculated from the experimental data (Table 1) via Eq. (4), is $k_7 = (3.25 \pm 0.48) \times 10^4$ l mol^{-1} s^{-1}.

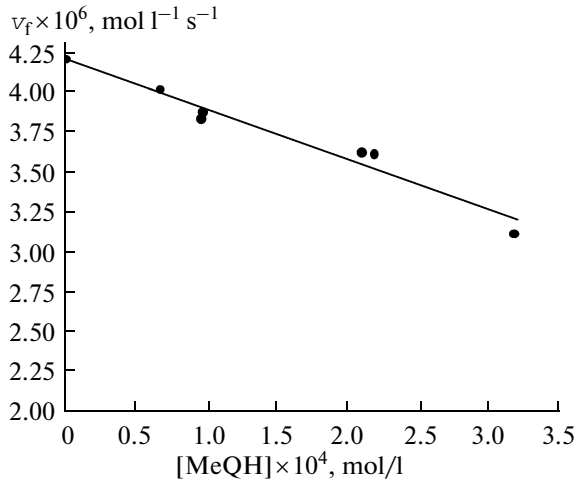


Fig. 3. Oxygen uptake rate after the complete consumption of the inhibitor versus the MeQH concentration ($T = 333$ K, $P_{O_2} = 1.01$ atm, [AIBN] = 1.39×10^{-2} mol/l, [AA] = 14.02 mol/l).

Oxidation of AA Inhibited by QH_2

The mechanism of the inhibition effect of QH_2 on AA oxidation turned out to be more complicated. The results of experiments on AA oxidation in the presence of QH_2 are listed in Table 2. The values of the factor $f = v_i\tau/[QH_2]_0$ are noteworthy. For chain termination reactions (VII)–(IX), this ratio should be 2 (see the scheme), but, in fact, it is substantially smaller in all experiments. As was shown earlier [5], this is due to the fact that the semiquinone radical HQ$^\bullet$ is involved in reactions (VIII) and (IX) and also reacts with O_2, generating the active radical $HO_2^\bullet$ [2, 3]. The larger the value of P_{O_2}, the higher the intensity of this reaction. This inference is in good agreement with the results of experiments at different partial pressures of oxygen (Table 2, entries at $P_{O_2} = 0.21$ and 1.0 atm). Since radicals are additionally generated in reaction (X), this fact should be taken into account for a correct kinetic analysis of the AA–O_2–AIBN–QH_2 system. In the inhibited oxidation of AA under quasi-steady-state conditions, the radicals are generated via the decomposition of the initiator ($v_i = k_i$[AIBN]) and via reaction (X) ($v_{10} = k_{10}[O_2]$ [HQ$^\bullet$]. Therefore, the consumption of QH_2 in reaction (VII) and the consumption of the radical HQ$^\bullet$ in reactions (VIII) and (IX) proceed at the rate $0.5(v_i + v_{10})$. In addition, because of reaction (X) taking place, the fraction of HQ$^\bullet$ radicals involved in chain termination decreases and the regeneration of QH_2 in reaction (IX) slows down. This is equivalent to the decrease of the number of QH_2 molecules involved in chain termination by $0.5v_{10}\tau$.

The rate of QH_2 consumption in this system will then be

$$v_{QH_2} = \frac{1}{2}(v_i + v_{10}) + \frac{1}{2}v_{10} = 0.5v_i + v_{10}. \quad (5)$$

In this case, the stoichiometric inhibition factor is

$$f = \frac{v_i}{v_{QH_2}} = \frac{v_i}{0.5v_i + v_{10}}, \quad (6)$$

which makes it possible to estimate the average rate of reaction (X) (Table 3):

$$v_{10} = k_i[\text{AIBN}]\left(\frac{1}{f} - \frac{1}{2}\right). \quad (7)$$

Table 1. Oxidation of AA inhibited by MeQH ([AA] = 14.02 mol/l, $P_{O_2} = 1.0$ atm, $T = 333$ K, [AIBN]) and the calculated values of the parameters v_0, f, and τ and chain length ν

$[MeQH]_0 \times 10^4$, mol/l	$v_i \times 10^7$, mol l^{-1} s^{-1}	$v_0 \times 10^7$, mol l^{-1} s^{-1}	f	τ, min	ν
0.67	1.44	12.12	2.28	17.6	7.4
0.96	1.43	9.72	2.25	25.0	5.8
0.97*	1.43	9.59	2.22	25.2	5.7
1.22	1.43	8.28	2.17	30.8	4.8
1.31*	1.42	7.92	2.08	32.0	4.6
2.10	1.43	6.72	2.37	58.0	3.7
2.19	1.43	6.61	2.37	60.0	3.8
3.18	1.43	4.20	2.31	85.6	2.0

* $P_{O_2} = 0.21$ atm.

Table 2. Oxidation of AA inhibited by QH_2 ([AA] = 14.02 mol/l, P_{O_2} = 1.0 atm, T = 333 K, [AIBN]); parameters ν_0, f, and τ; and the $2\nu_8$, $2\nu_9$, ν_{10}, and $[HQ^\bullet]_0$ values calculated using Eq. (12)

$[QH_2] \times 10^4$, mol/l	$\nu_i \times 10^7$, mol l^{-1} s^{-1}	$\nu_0 \times 10^7$, mol l^{-1} s^{-1}	f	$[HQ^\bullet]_0 \times 10^9$, mol/l	$2\nu_8 \times 10^8$, mol l^{-1} s^{-1}	$2\nu_9 \times 10^8$, mol l^{-1} s^{-1}	$\nu_{10} \times 10^8$, mol l^{-1} s^{-1}
1.54	1.43	2.84	1.48	5.02	9.25	7.56	2.51
1.56	1.41	3.20	1.48	5.02	9.01	7.55	2.48
3.03	1.38	2.01	1.32	6.01	6.52	10.83	3.55
1.58; [M] = 7.05	1.88	2.80	1.57	5.58	12.02	9.35	2.57
1.56; [M] = 10.50	1.87	3.94	1.62	5.58	11.54	9.35	2.19
1.57	1.91	5.12	1.72	5.70	1.09	9.75	1.55
1.57	1.91	5.62	1.74	5.71	10.73	9.79	1.43
1.57	0.59	1.95	1.28	3.69	3.47	4.09	1.66
1.56	1.84	5.62	1.74	5.63	10.26	9.52	1.37
1.56	0.60*	2.00	1.40	3.73	3.11	4.17	1.29
1.56	1.42*	3.66	1.63	5.12	7.95	7.86	1.61
3.09	1.41	2.43	1.60	6.06	4.86	11.0	1.76

* P_{O_2} = 0.21 atm.

The rate constant ratio k_7/k_2 was calculated from experimental data as follows. The oxygen uptake curves were linearized in the $\Delta[O_2]$–$(-\ln(1 - t/\tau))$ coordinates. The initial rate of inhibited oxidation, v_0, was calculated from the slope of the resulting straight line. The value of this rate in the AA–O_2–AIBN–QH_2 system depends on the steady-state concentration of the peroxyl radicals of AA involved in reactions (II), (VII), (VIII), and (X). According to the kinetic scheme (see above), the initial rate of oxygen uptake is determined as $v_0 = (k_2[M] + k_7[QH_2])\left[MQ_2^\bullet\right]$ and the steady-state $MQ_2^\bullet$ concentration is determined as $\left[MQ_2^\bullet\right] = (v_i + v_{10})/fk_7[QH_2]$. Therefore, the oxygen uptake rate at the initial moment of the reaction, when $f = 2$, can be written as

$$v_0 = \frac{k_2[M](v_i + v_{10})}{2k_7[QH_2]} + v_i + v_{10}. \quad (8)$$

After substituting v_{10} from Eq. (7) into Eq. (8), we have

$$v_0 = \left(\frac{1}{2} + \frac{1}{f}\right)\left(\frac{k_2[M]}{2k_7[QH_2]} + 1\right)v_i. \quad (9)$$

Equation (9) makes it possible to calculate the rate constant k_7 (k_2 = 2.84 l mol^{-1} s^{-1}, [M] = 14.02 mol/l [1]):

$$k_7 = \left(\frac{k_2[M]}{2[QH_2]}\right)\left(\frac{2fv_0}{v_i(2+f)} - 1\right)^{-1}. \quad (10)$$

The rate constant k_7 calculated from the data presented in Table 2 is $(1.20 \pm 0.28) \times 10^5$ l mol^{-1} s^{-1}.

As was mentioned above, for the AA–O_2–QH_2 system the factor f is below 2, which is due to reaction (X) taking place. The rate of this reaction can be estimated using Eq. (7). Since $v_{10} = k_{10}[O_2][HQ^\bullet]$, the concentration of semiquinone radicals in oxidized AA should be known to calculate k_{10}. On the one hand, the following equality is valid for the oxidation of AA under quasi-steady-state conditions (see the kinetic scheme):

$$2k_9\left[HQ^\bullet\right]^2 + 2k_8\left[MQ_2^\bullet\right]\left[HQ^\bullet\right] = v_i + v_{10}. \quad (11)$$

On the other hand, the concentration of peroxyl radicals at the initial moment of the reaction is $[MQ_2^\bullet] = (v_i + v_{10})/2k_7[QH_2]$. Substituting this expression into Eq. (11), we obtain the following quadratic equation with respect to $[HQ^\bullet]$:

$$2k_9\left[HQ^\bullet\right]^2 + \frac{k_8(v_i + v_{10})}{k_7[OH_2]}\left[HQ^\bullet\right] - v_i\left(\frac{2+f}{2f}\right) = 0. \quad (12)$$

The rate constants k_2 and k_7 are 2.84 [1] and 1.20×10^5 l mol^{-1} s^{-1}, respectively (see above). The values of $[HQ^\bullet]_0$ calculated using Eq. (12) and the rates v_8 and v_9 at the initial moment of inhibited oxidation are given in Table 2. As can be seen, the numerical values of v_8 and v_9 are often comparable.

Thus, we have ascertained that reaction (X) plays an important role in the inhibition effect of QH_2. In

Table 3. Oxidation of MMA inhibited by QH_2 ([MMA] = 8.98 mol/l, $P_{O_2} = 1.0$ atm, $T = 333$ K, [AIBN]) and the $[HQ^\bullet]_0$, $2v_8$, $2v_9$, and v_{10} values calculated using Eq. (12)

$[QH_2] \times 10^4$, mol/l	$v_i \times 10^7$, mol l^{-1} s^{-1}	$v_{O_2} \times 10^7$, mol l^{-1} s^{-1}	f	$[HQ^\bullet]_0 \times 10^9$, mol/l	$2v_8 \times 10^8$, mol l^{-1} s^{-1}	$2v_9 \times 10^8$, mol l^{-1} s^{-1}	$v_{10} \times 10^8$, mol l^{-1} s^{-1}
2.01	2.39	6.40	1.71	5.41	17.1	8.79	2.03
2.04	2.37	4.74	1.83	5.56	15.5	9.29	1.10
2.10*	2.27	4.92	1.69	5.43	15.9	8.86	2.08
4.02	2.32	3.09	1.71	6.95	10.7	14.5	1.97
4.77	2.24	2.54	1.79	7.16	8.34	15.4	1.31
2.07	0.70	1.89	1.75	3.76	3.26	4.24	0.50
2.07	1.57	3.76	1.77	4.93	9.43	7.28	1.02
2.03; [M] = 4.49	2.42	2.83	1.60	5.32	18.7	8.50	3.03
2.09; [M] = 6.71	2.40	3.93	1.67	5.48	17.4	9.00	2.37
2.04	2.37	4.74	1.83	5.56	15.5	9.29	1.10
2.03*	2.30	4.54	1.92	5.59	14.1	9.36	0.48
2.04*	2.40	3.06	1.98	5.72	14.3	9.80	0.12
4.11*	2.30	2.93	1.78	6.99	9.78	14.6	1.42
4.18*	2.29	3.11	1.83	7.01	9.21	14.7	1.06
4.93*	2.28	3.13	1.85	7.26	7.92	15.8	0.92

* $P_{O_2} = 0.21$ atm.

this reaction, firstly, active $HO_2^\bullet$ radicals are generated. Secondly, oxygen is consumed. Thirdly, the fraction of radicals $HQ^\bullet$ involved in the regeneration of QH_2 in reaction (IX) decreases. The data obtained in this work (Table 2) make it possible to estimate the rate constant k_{10}. Since $v_{10} = k_{10}[O_2][HQ^\bullet]$, it is necessary to know $[O_2]$ and $[HQ^\bullet]$ to calculate k_{10} from the rate of reaction (X). Under our experimental conditions, the equilibrium concentration of oxygen in the AA medium is achieved due to the vigorous agitation of the liquid in the reactor (shaking frequency of 12 s^{-1}). Assuming that the Henry coefficient γ_{O_2} for O_2 dissolution in AA is the same as that for acetic acid, i.e., $\gamma_{O_2} = 8.58 \times 10^{-3}$ mol l^{-1} atm^{-1} [1], for experiments at $P_{O_2} = 1$ atm we obtain $[O_2] = 8.6 \times 10^{-3}$ mol/l and at $P_{O_2} = 0.21$ atm $[O_2] = 1.8 \times 10^{-3}$ mol/l. The constant k_{10} calculated using the equation

$$k_{10} = \frac{v_{10}}{[O_2][HQ^\bullet]} \quad (13)$$

is $(5.72 \pm 0.63) \times 10^2$ l mol^{-1} s^{-1}.

Oxidation of MMA Inhibited by QH_2

The results of experiments on MMA oxidation with the introduction of AIBN and QH_2 are presented in Table 3. As in the case of AA oxidation, $f < 2$, which is a consequence of reaction (X) occurring to a noticeable extent. The processing of the kinetic data in the $\Delta[O_2]$–$(-\ln(1 - t/\tau))$ coordinates made it possible to calculate the initial oxygen uptake rate v_{O_2}. A comparison of v_{O_2} and v_i shows that oxidation in the presence of QH_2 proceeds via the formation of short chains. Fitting the experimental data to formula (4) ($k_2 = 2.96$ l mol^{-1} s^{-1} [1]) leads to the rate constant $k_7 = (7.16 \pm 0.18) \times 10^4$ l mol^{-1} s^{-1}. The rates of reactions (VIII)–(X) and the $[HQ^\bullet]$ values calculated using Eq. (12) are given in Table 3. It can be seen that the rates of reactions (VIII) and (IX) are comparable. Assuming that the Henry coefficient γ_{O_2} for the dissolution of O_2 in MMA is the same as that for methyl acetate, for which $\gamma_{O_2} = 1.12 \times 10^{-2}$ mol l^{-1} atm^{-1} [2], we obtain for the experiments at $P_{O_2} = 1$ atm that $[O_2] = 1.12 \times 10^{-2}$ mol/l, whereas at $P_{O_2} = 0.21$ atm, $[O_2] = 2.35 \times 10^{-3}$ mol/l. The rate constant k_{10} calculated via Eq. (13) is $(4.60 \pm 0.12) \times 10^2$ l mol^{-1} s^{-1}.

The experimental values of the rate constants of elementary reactions (VII), (VII'), and (X) for the reactions examined are $k_7(\sim MO_2^\bullet + QH_2) = 1.20 \times 10^5$ l mol^{-1} s^{-1} (AA), k_7 ($\sim MO_2^\bullet + QH_2$) $= 7.16 \times 10^4$ l mol^{-1} s^{-1} (MMA), k_7' ($\sim MO_2^\bullet + MeQH$) $= 3.25 \times 10^4$ l mol^{-1} s^{-1} (AA), $k_{10}(O_2 + HQ^\bullet) = 5.72 \times 10^2$ l mol^{-1} s^{-1} (AA), and k_{10} ($O_2 + HQ^\bullet$) $= 4.60 \times 10^2$ l mol^{-1} s^{-1} (MMA). The constants k_7 for the reactions of the peroxyl radicals of AA and MMA differ by a factor smaller than 2, while the reactivity of QH_2 per phenol group is approximately 2 times higher than the reactivity of MeQH (in the AA medium). The rate constants of reaction (X) in AA and MMA are similar. The reactivities of hydroquinone as an antioxidant in the AA and MMA media are similar, and AA as an acidic medium does not show its specificity in the reaction of peroxyl radicals with phenols, as distinct from what it does in the chain propagation reaction (see [1]). Thus, in this work we determined, for the first time, the kinetic characteristics of the reactions of peroxyl radicals of AA with such inhibitors as hydroquinone and 4-methoxyphenol. The important role of the reaction of the semiquinone radical with oxygen was demonstrated. The rate constants of this reaction in the AA and MMA media calculated from experimental data are similar.

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