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Acid catalyzed multiple chain termination by quinone monoanilide in oxidizing hydrocarbons

V. I. Gol'denberg, N. A. Ermakova, and E. T. Denisov★

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

A novel ternary system that causes multiple chain termination in oxidizing hydrocarbons is suggested. The system involves *N*-phenylquinone imine, hydrogen peroxide, and citric acid. The inhibiting effect of the system is studied for the initiated oxidation of methyl oleate and ethylbenzene. The rate of the inhibiting oxidation of the hydrocarbon is proportional to the initiation rate and inversely proportional to the product of the concentrations of quinone imine, hydrogen peroxide, and the acid. The mechanism proposed involves the protonation of quinone imine, the abstraction of an H atom from quinone imine by the peroxyl radical, the reduction of the resulting radical cation by hydrogen peroxide to form the semiquinone radical, and the reaction of the latter with $RO_2^{\cdot}$.

Key words: methyl oleate, ethylbenzene, oxidation; quinone monoanilide, hydrogen peroxide, citric acid, inhibition of oxidation; acid catalysis; regeneration of inhibitor.

The multiple chain termination observed in oxidizing alcohols and aliphatic amines on inhibitors such as aromatic amines and nitroxyl radicals[1] is caused by the ability of peroxyl radicals containing hydroxyl and amino groups to drive both oxidation and reduction processes. The regeneration of these inhibitors is not typical of the oxidation of hydrocarbons, because alkyl peroxyl radicals cannot reduce other radicals. We have recently found systems that repeatedly terminate chains in oxidizing hydrocarbons and contain a nitroxyl radical, an alcohol, and an acid[2] or a nitroxyl radical, hydrogen peroxide, and an acid.[3] In both cases, the acid catalysis is of great significance. This work is devoted to the study of a novel ternary system that inhibits the oxidation of hydrocarbons and regenerates the inhibitor.

Experimental

Ethylbenzene was shaken repeatedly with H_2SO_4, washed with water, an aqueous solution of an alkali, and again with water, dried over Na_2SO_4 and then over Na metal, and distilled. The initiator, azobisisobutyronitrile (AIBN), was twice recrystallized from ethanol and then from benzene, twice recrystallized from acetone, and dried *in vacuo*. The acetonitrile (Merck) was distilled. The hydrogen peroxide (the content of H_2O_2 was 94 %) was stored in a quartz vessel in a refrigerator. Quinone monoanilide (Q) was prepared by the oxidation of 4-hydroxydiphenylamine by activated manganese dioxide in benzene (amine : MnO_2 = 1 : 4, mol/mol) with heating according to the following equation:

$$HOC_6H_4NHPh + MnO_2 \longrightarrow O{=}C_6H_4{=}NPh + MnO + H_2O.$$

Quinone monoanilide was recrystallized from benzene. Hydrogen peroxide and citric acid (HA) were added to ethylbenzene as acetonitrile solutions. The oxidizing mixture contained 85 % ethylbenzene and 15 % acetonitrile.

The oxidation was performed at 343 K on a volumetric installation. The initiation rate was calculated as $v_i = k_i[AIBN]$, $k_i = 5.48 \cdot 10^{-5}$ s^{-1} (see Ref. 3). The corrections (v_g) for the liberation of N_2 in the decomposition of AIBN and for the absorption of O_2 in the initiation act were introduced for the calculation of the rate of chain oxidation (v). In the presence of an inhibitor $v = v_g - 0.17v_i$. The efficiency of the inhibiting effect of the system was characterized by the parameter $F = v_0v^{-1} - vv_0^{-1}$, where v and v_0 are the initial rates of the oxidation of ethylbenzene in the presence and in the absence of the inhibitor, respectively.

Results and Discussion

Under the chosen conditions (T = 343 K, p_{O_2} = 10^5 Pa, [AIBN] = $2.02 \cdot 10^{-2}$ mol L^{-1}), methyl oleate is oxidized at the constant rate v = $1.42 \cdot 10^{-5}$ mol L^{-1} s^{-1} *via* a chain mechanism (chain length $\nu = v/v_i$ = 24.5 units). The addition of quinone monoanilide, hydrogen peroxide, or citric acid does not change the oxidation rate. Similarly, the addition of these compounds in binary combination exerts no effect on the rate, except that the addition of the (Q + H_2O_2) system results in a decrease in the oxidation rate (Table 1). However, the addition of all three components (Q + HA + H_2O_2) exerts a strong inhibiting effect, whose duration exceeds $\tau = [Q]_0/v_i$. In this case the inhibition coefficient $f = [Q]_0/(v_i\tau) > 18$ at $[Q]_0$ =

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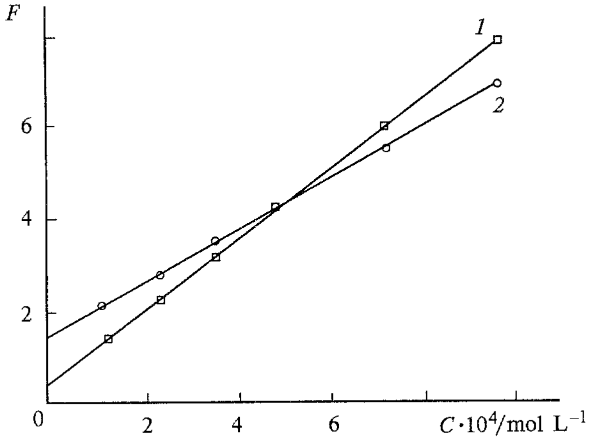

Fig. 1. Oxidation of methyl oleate in the presence of quinone imine (Q), citric acid (HA), and H_2O_2 (343 K, p_{O_2} = 100 kPa, $[H_2O_2]_0$ = 0.125 mol L^{-1}, and $v_i = 5.81 \cdot 10^{-7}$ mol $L^{-1}s^{-1}$): *1*, the dependence of *F* on [Q] at $[HA]_0 = 5 \cdot 10^{-4}$ mol L^{-1}; *2*, the dependence of *F* on [HA] at $[Q]_0 = 5 \cdot 10^{-4}$ mol L^{-1}.

$5 \cdot 10^{-4}$ mol L^{-1}, and $v_i = 5.21 \cdot 10^{-7}$ mol L^{-1} s^{-1}, *i.e.*, there is multiple chain termination. The inhibition increases as the concentration of each of the components of the (Q + HA + H_2O_2) system increases, and the efficiency of the inhibiting effect expressed by parameter *F* increases linearly as the concentrations of both quinone imine and the acid increase (Fig. 1). The increase in *F* as $[H_2O_2]$ increases is nonlinear (Fig. 2). This testifies that the interaction of quinone imine, hydrogen peroxide, and the acid results in the formation of products that actively react with the peroxyl radicals driving the oxidation. If the sum of the concentrations ($[Q]_0 + [HA]_0$) is unchanged and only their ratio is varied, depending on the composition of the system, the value of *F* passes through a maximum (see Fig. 2), which is reached when the ratio of the components is 1 : 1.

Similar results were obtained for the oxidation of ethylbenzene. Quinone imine and hydrogen peroxide added individually exert an extremely small inhibiting effect (Table 2). The (Q + HA), (Q + H_2O_2), and (H_2O_2 + HA) systems also weakly inhibit the oxidation. Only the combined addition of the three components to oxidizing ethylbenzene exerts strong and prolonged inhibition (see Table 2). The parameter *F* increases linearly as the concentration of each of the components increases (Fig. 3). The rate of the inhibiting oxidation $v \sim v_i$ (see Fig. 3), *i.e.*, the inhibitor causes linear chain termination. For binary systems $F \approx 1$, therefore, the inhibiting effect of the ternary system can be characterized as $(F - 1)v_i^{1/2}$ (see Experimental). As seen from Table 2, the ratio of this value to the product of the concentrations of the three components is almost constant and is equal to $(1.35\pm0.37) \cdot 10^6$ $mol^{-5/2}$ $L^{5/2}$ $s^{-1/2}$.

Table 1. Inhibiting oxidation of methyl oleate (343 K, p_{O_2} = 10^5 Pa, $v_i = 5.8 \cdot 10^{-7}$ mol L^{-1} s^{-1})

$[Q]_0 \cdot 10^4$ /mol L^{-1}	$[H_2O_2]_0 \cdot 10^2$ /mol L^{-1}	$[HA]_0 \cdot 10^4$ /mol L^{-1}	$v \cdot 10^6$ /mol L^{-1} s^{-1}	*F*
0.0	0	0	14.18	0
5.0	0	0	14.18	0
5.0	0.125	0	14.18	0
0.0	25.0	5.0	14.18	0
5.0	0.0	5.0	14.18	0
5.0	12.5	0	9.51	0.82
1.25	12.5	5.0	7.13	1.49
2.50	12.5	5.0	5.25	2.33
3.75	12.5	5.0	3.93	3.33
5.0	12.5	5.0	3.16	4.27
7.5	12.5	5.0	2.28	5.07
10.0	12.5	5.0	1.76	7.93
5.0	12.5	1.25	5.56	2.16
5.0	12.5	2.50	4.47	2.85
5.0	12.5	3.75	3.70	3.57
5.0	12.5	5.00	3.16	4.27
5.0	12.5	7.50	2.48	5.53
5.0	12.5	10.00	2.02	6.88
5.0	0.125	5.0	11.70	0.39
5.0	2.50	5.0	7.03	1.52
5.0	3.125	5.0	6.41	1.76
5.0	6.25	5.0	4.86	2.58
5.0	18.75	5.0	2.48	5.53
5.0	25.00	5.0	2.13	6.50

Note. The oxidizing mixture contains 85 vol. % methyl oleate and 15 vol. % MeCN.

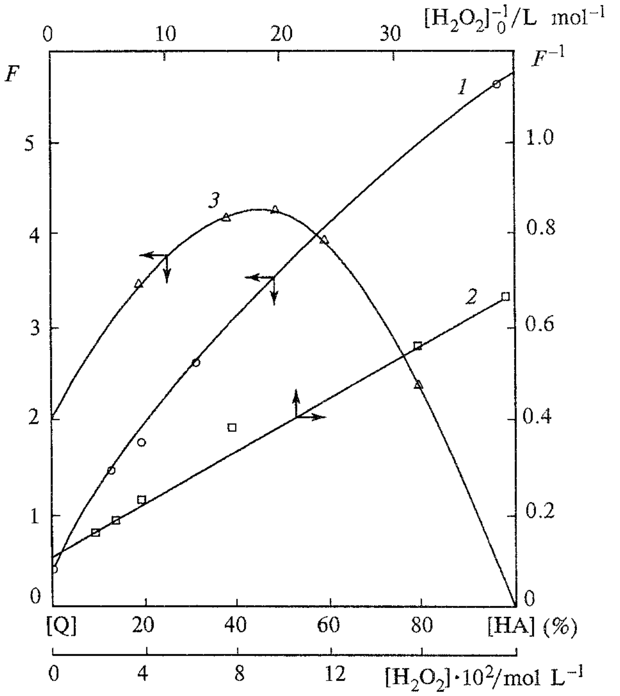

Fig. 2. Oxidation of methyl oleate in the presence of Q, HA, and H_2O_2 (see Fig. 1 for the conditions): *1*, the dependence of *F* on $[H_2O_2]$ at $[Q]_0 = [HA]_0 = 5 \cdot 10^{-4}$ mol L^{-1}; *2*, the dependence of F^{-1} on $[H_2O_2]_0^{-1}$; *3*, the dependence of *F* on the ratio of [Q] : [HA] at ($[Q]_0$ + $[HA]_0$) = 10^{-3} mol L^{-1} and $[H_2O_2]_0$ = 0.125 mol L^{-1}.

Table 2. Inhibiting oxidation of ethylbenzene (343 K, p_{O_2} = 10^5 Pa, v_0 = $4.92 \cdot 10^{-6}$ mol L^{-1} s^{-1})

$[Q]_0 \cdot 10^4$ /mol L^{-1}	$[H_2O_2]_0 \cdot 10^3$ /mol L^{-1}	$[HA]_0 \cdot 10^4$ /mol L^{-1}	$v_i \cdot 10^7$ /mol L^{-1} s^{-1}	$v \cdot 10^6$ /mol L^{-1} s^{-1}	F	$\frac{(F-1) \cdot v_i^{1/2} \cdot 10^{-6}}{[Q][HA][H_2O_2]}$
5.0	0.0	0.0	5.21	3.01	1.02	—
0.0	0.0	5.0	5.21	3.93	0.45	—
0.0	1.25	0.0	5.21	3.27	0.84	—
5.0	0.0	5.0	5.21	2.86	1.14	—
0.0	1.25	5.0	5.21	3.78	0.53	—
5.0	1.25	0.0	5.21	3.01	1.02	—
5.0	1.25	5.0	5.21	2.39	1.57	1.32
5.0	0.5	5.0	5.21	2.81	1.18	—
5.0	5.0	5.0	5.21	1.34	3.38	1.37
5.0	12.5	5.0	5.21	0.69	7.03	1.39
5.0	5.0	5.0	10.42	2.64	2.64	1.34
5.0	5.0	5.0	7.81	1.99	2.97	1.39
5.0	5.0	5.0	3.91	0.97	3.57	1.29

Note. The oxidizing mixture contains 85 vol. % ethylbenzene and 15 vol. % MeCN.

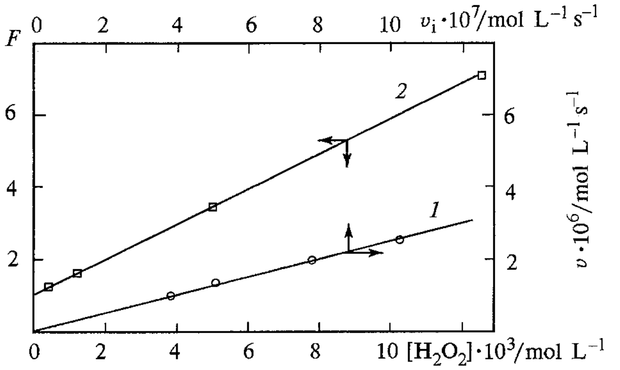

Fig. 3. Oxidation of ethylbenzene (343 K, p_{O_2} = 100 kPa, $[Q]_0$ = $5 \cdot 10^{-4}$ mol L^{-1}, $[HA]_0$ = $5 \cdot 10^{-4}$ mol L^{-1}): *1*, the dependence of v on v_i at $[H_2O_2]_0$ = $5 \cdot 10^{-3}$ mol L^{-1}; *2*, the dependence of F on $[H_2O_2]$.

Inhibition mechanism. As shown above, only the simultaneous addition of the three components (quinone imine, hydrogen peroxide, and the acid) to an oxidizing hydrocarbon causes prolonged inhibition. The period of the inhibition is considerably greater than $\tau = [Q]_0/v_i$ or $[HA]_0/v_i$, *i.e.*, the chain termination reaction in the initiated oxidation occurs several times, at least for each added amount of quinone monoanilide. Since $v \sim v_i$ in the presence of the inhibiting system (see Fig. 3) and $F \sim v_i^{-1/2}$ (see Table 2), the chains are terminated through the reaction of the inhibitor with free radicals, most likely, peroxyl radicals, because alkyl radicals react very rapidly with oxygen under these conditions. The slight inhibition caused by the addition of quinone monoanilide to ethylbenzene (see Table 2) is probably caused by the addition of $R^{\cdot}$ radicals to quinone imine. Hydrogen peroxide also exerts a weak inhibiting effect on the oxidation of ethylbenzene (see Table 2), which seems to be caused by the exchange reaction

$$RO_2^{\cdot} + H_2O_2 \longrightarrow ROOH + HO_2^{\cdot}$$

and the subsequent rapid interaction

$$RO_2^{\cdot} + HO_2^{\cdot} \longrightarrow ROOH + O_2 \, .$$

We suggest the following mechanism for the inhibiting effect of the ternary system. The acid protonates quinone imine, which in the form of an ion pair is attacked by the peroxyl radical (Eqs. (1) and (2)).

$$Q + HA \xrightleftharpoons{K_1} QH^+,A^- \qquad (1)$$

$$RO_2^{\cdot} + QH^+,A^- \xrightarrow{k_2} ROOH + Q^+,A^{\cdot -} \qquad (2)$$

The radical cation is reduced by hydrogen peroxide to the semiquinone radical and in this form it is rapidly attacked by the peroxyl radical (Eqs. (3) and (4)).

$$Q^+,A^{\cdot -} + H_2O_2 \xrightarrow{k_3} {}^{\cdot}QH + HA + O_2 \qquad (3)$$

$${}^{\cdot}QH + RO_2^{\cdot} \xrightarrow{k_4} Q + ROOH \qquad (4)$$

This results in cyclic termination of the chain with the regeneration of the initial quinone imine. This scheme must be completed by the reduction of the radical cation in the absence of H_2O_2. The latter must be accompanied by the generation of the radical propagating the oxidation chain, because the (Q + HA) binary system does not have a greater ability to terminate chains than quinone imine itself. An oxidizing substrate containing a double bond (methyl oleate) or a benzene ring (ethylbenzene) can act as the reducing agent.

$$Q^+,A^{\cdot -} + RH \xrightarrow{k_5} R^{\cdot} + HA + Q \qquad (5)$$

For the rate of chain termination (v_t) in the oxidizing system (by Eqs. (2) and (4)) *via* the reaction

$$RO^{\bullet}_2 + RO^{\bullet}_2 \xrightarrow{k_6} R'{=}O + ROH + O_2 \qquad (6)$$

we obtain the following expression:

$$v_t = 2k_6[RO^{\bullet}_2]^2 + k_2K_1[Q]\,[HA]\,[RO^{\bullet}_2] + k_4[{}^{\bullet}QH][RO^{\bullet}_2].$$

It is likely that reaction (4) is limited by the preceding reduction of the radical cation by hydrogen peroxide. For a quasi-stationary concentration of the radical cation, the rate of chain termination is equal to

$$v_t = 2k_6[RO^{\bullet}_2]^2 + 2k_3[Q^+A^-]\,[H_2O_2] = 2k_6[RO^{\bullet}_2]^2 + \\ + \frac{2K_1k_2k_3[Q][H_2O_2][HA][RO^{\bullet}_2]}{k_3[H_2O_2] + k_5[RH]}.$$

After substituting $[RO_2{}^{\bullet}] = v_i/k_p[RH]$ and $k_p[RH] = v_0(2k_6/v_i)^{1/2}$ into the expression for F (see above), we obtain

$$F = \frac{2K_1k_2k_3[Q][H_2O_2][HA]}{(k_3[H_2O_2] + k_5[RH])\,(2k_6v_i)^{1/2}}. \qquad (7)$$

This dependence agrees with the experimental data. $F \sim [Q]$ and $F \sim [HA]$ for the oxidation of both methyl oleate and ethylbenzene (see Fig. 1). At low concentrations of H_2O_2 the value F increases linearly as $[H_2O_2]$ increases (the oxidation of ethylbenzene, see Fig. 3); if the concentration of hydrogen peroxide is sufficiently high, the dependence of F on $[H_2O_2]$ becomes nonlinear (see Fig. 2).

The experiments on the inhibition of the oxidation of methyl oleate by the ternary system with a constant total concentration ($[Q] + [HA] = \text{const}$) agree well with Eq. (7) (see Fig. 2). In this case, $[Q]_0$ and $[HA]_0$ can be expressed by their summarized concentration (C_0) and, after designating $[Q] = xC_0$ and $[HA] = (1 - x)C_0$ the expression for parameter F can be transformed to the following form:

$$F = A(1 - x)x,$$

where $A = 2K_1k_2k_3[H_2O_2]_0C_0(2k_6v_i)^{-1/2} \cdot (k_3[H_2O_2] + k_5[RH])^{-1}$. As can be easily seen, the maximum value of F is achieved at $x = 0.5$ or $[Q]_0 = [HA]_0$. Thus, the suggested scheme of the inhibiting effect of the ternary system ($Q + H_2O_2 + HA$) is in accordance with all of the kinetic regularities and explains the multiple (with respect to quinone imine) chain termination in oxidizing hydrocarbons. The mechanism considered is similar to the mechanism of the inhibiting system (nitroxyl radical + hydrogen peroxide + acid).[3] Both examples attest to the possibility that inhibitors in oxidizing hydrocarbons can be regenerated using multicomponent inhibiting systems.

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