Russian Chemical Bulletin, International Edition, Vol. 53, No. 10, pp. 2205—2208, October, 2004

Effect of cationic surfactants on limonene oxidation

L. M. Pisarenko, V. G. Kondratovich, and O. T. Kasaikina★

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 938 2156. E-mail: kasaikina@chph.ras.ru

Kinetic regularities of free radical formation during limonene oxidation with molecular oxygen in a chlorobenzene solution at 60 °C were studied by the inhibitor method under autooxidation conditions and with additives of surfactants (cetyltrimethylammonium chloride and bromide) using dimer 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] and α-tocopherol as acceptors of radicals. In the presence of the surfactants, the rates of radical generation and oxidation increase sharply. The catalytic activity of cetyltrimethylammonium chloride is much higher than that of the corresponding bromide.

Key words: 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione], α-tocopherol, oxidation of limonene, catalysis, formation of free radicals, cetyltrimethylammonium chloride, cetyltrimethylammonium bromide.

Limonene (4-isopropenyl-1-methyl-1-cyclohexene, LH) is a natural cycloolefin of the terpene series containing two unsaturated bonds. Limonene is found in almost all essential oils, and it is readily oxidized with molecular oxygen *via* the free chain-radical mechanism.[1—3] The oxidation products at moderate temperatures are isomeric hydroperoxides (LOOH), whose composition depends on oxidation conditions.[4] The rate of oxygen absorption (W_{O_2}) during limonene oxidation is proportional to $W_i^{0.5}$ (W_i is the chain initiation rate), indicating a square chain termination, and is described by the known[5] equation of the theory of liquid-phase oxidation of hydrocarbons (RH)

$$W_{O_2} = k_p/(2k_t)^{0.5}[\mathrm{RH}]W_i^{0.5}, \qquad (1)$$

where k_p and k_t are the apparent rate constants of chain propagation and termination, respectively.

The recent studies[6—11] showed that additives of surfactants can affect substantially the rate and mechanism of hydrocarbon oxidation. Surfactant molecules form associate-microaggregates in a nonpolar hydrocarbon medium in which polar oxidation products, *viz.*, water, alcohols, hydroperoxides, and others, are concentrated. The character of this influence depends on the nature of a surfactant and oxidized hydrocarbon.

Quaternary ammonium salts are known to accelerate the oxidation of hydrocarbons and fats[10—12] and possess a bactericidal effect.[13] The same effect is inherent in some phosphonium, sulfonium, selenium, and arsenic salts.[10] Several authors call the catalysis of oxidation with cationic surfactants as "halide catalysis" [14,15]; these surfactants are believed[16—18] to activate oxygen. The bactericidal effect is explained by binding cationic surfactants with membrane proteins.[13] We found[19,20] that the catalytic effect of cetyltrimethylammonium bromide (CTAB) on the oxidation of ethylbenzene is caused by the accelerated decomposition of ROOH in surfactant microreactors with escape of $RO_2^•$ radicals to the solvent bulk followed by the chain-radical oxidation of ethylbenzene.

We have previously[19,20] used the inhibitor method and dimer 2,2´-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione] (FF) as an acceptor of free radicals to study the kinetics of free radical formation during the oxidation of ethylbenzene with molecular oxygen initiated by an α-ethylphenyl hydroperoxide—CTAB catalytic system generating free radicals. This study showed that CTAB affects only the rate of radical initiation (W_i) under the experimental conditions.

The purpose of this work is to study the kinetic regularities of radical formation during limonene oxidation, the influence of cationic surfactants with different counterions on the rates of radical initiation, and oxidation as a whole.

Experimental

Limonene was oxidized in a chlorobenzene solution at 60 °C. *R*(+)-Limonene (Fluka) was used without additional purification. Chlorobenzene was purified by a standard method.[21] 2,2´-Azobisisobutyronitrile (AIBN) used as initiator was twice recrystallized from ethanol followed by drying *in vacuo* to a constant weight. Special experiments on AIBN-initiated oxidation showed that the kinetic parameter of oxidizability $k_p/(2k_t)^{0.5}$ for *R*(+)-limonene in chlorobenzene solution is (0.9±0.1) $\cdot 10^{-2}$ $\mathrm{L^{0.5}\,mol^{-0.5}\,s^{-0.5}}$ and virtually coincides with the previously found[2] value for *D*(–)-limonene (Koch-light Laboratories Ltd.,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2110—2113, October, 2004.

Colnbrook Buchs Engl.) in the same solvent. Cetyltrimethylammonium chloride (CTAC) and bromide CTAB (Fluka) were used without additional purification. Limonene hydroperoxide (LOOH) was obtained by the autooxidation of limonene (LH) at 60 °C in a bubble reactor in an oxygen flow to 11% conversion. The resulting oxidate was diluted with chlorobenzene and limonene in a necessary ratio.

The rate of oxygen absorption was measured on a gasometric setup at P_{O_2} = 1 atm and a volume of the reaction mixture of 4 mL. The concentration of peroxides was determined iodometrically, and the rate of radical formation was found by the inhibitor method. Dimer FF, successfully tested earlier,[19,20] and α-tocopherol (Aldrich) were used as acceptors of free radicals. The preparation of reagents, formation of a reaction mixture, and experimental and measuring conditions were similar to those published previously.[19,20]

Results and Discussion

Typical curves of oxygen absorption during limonene oxidation are presented in Fig. 1. When initiating additives are absent, LH autooxidation occurs with autoacceleration. The rate of oxygen absorption is much higher in a chlorobenzene solution than in a solution of *n*-decane at the same initial concentrations of LH and LOOH (see Fig. 1, curves *2* and *3*). When inhibitors (acceptors of free radicals) are added, the absorption of O_2 stops, and an induction period (τ) appears. After the end of the induction period, O_2 absorption begins again (see Fig. 1, curve *1*) with almost the same rate as before the induction period. The repeated introduction of the inhibitors (FF or α-tocopherol) into the reaction mixture after the end of the induction period results in the same strong inhibition. This implies that the products of transformations of both inhibitors have no effect on the rates of oxidation (W_{O_2}) and radical initiation (W_i); the latter was calculated by the formula

$$W_i = (f[\mathrm{Inh}]_0)/\tau, \quad (2)$$

where *f* is the stoichiometric coefficient of chain termination, and $[\mathrm{Inh}]_0$ is the initial concentration of an inhibitor in the reaction mixture.

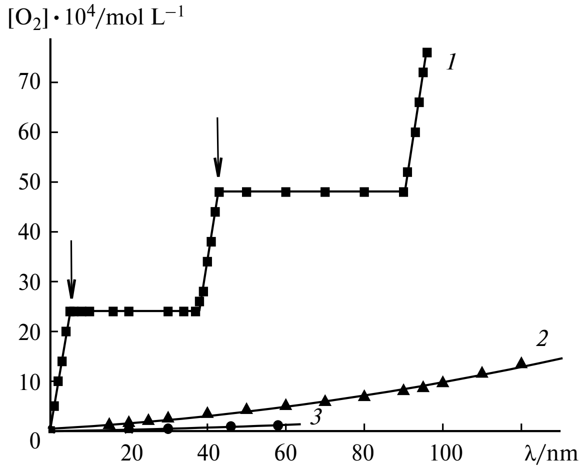

Fig. 1. Kinetic curves of O_2 absorption in limonene (LH) oxidation in solutions of chlorobenzene (*1*, *2*) and *n*-decane (*3*) at 60 °C: $[LH]_0$ = 2.8 (*1*), 1.0 mol L^{-1} (*2*, *3*); $[LOOH]_0$ = 0.28 (*1*), 0.022 mol L^{-1} (*2*, *3*). Arrows show the moments of introducing α-tocopherol ($1.2 \cdot 10^{-4}$ and $1.8 \cdot 10^{-4}$ mol L^{-1}, respectively).

A comparison of the LOOH concentrations in the beginning ($[LOOH]_0$) and end ($[LOOH]_t$) of an experiment shows that limonene is almost selectively oxidized, under these conditions, to form LOOH, and the equality takes place

$$[LOOH]_t = [LOOH]_0 + \Delta O_{2,t}, \quad (3)$$

where $\Delta O_{2,t}$ is the amount of O_2 absorbed within time *t*.

The kinetic data on the rates of oxygen absorption and radical initiation and induction periods of limonene autooxidation at different concentrations of hydrocarbon and hydroperoxide are presented in Table 1. Since almost all absorbed O_2 is consumed for LOOH formation, an increment of the LOOH concentration to the moment of introduction of an inhibitor (designated as ΔO_2) was taken into account when analyzing the plot of the initiation rate W_i *vs.* [LOOH] (see Table 1).

Based on the data in Table 1, we can conclude the following.

(1) Limonene is oxidized at 60 °C rather intensely to form long chains (ν > 30).

(2) Compounds FF and α-tocopherol are strong inhibitors of limonene oxidation and characterized by stoichiometric coefficient *f* = 2.

(3) Rate of radical formation W_i is proportional to the hydroperoxide concentration (Fig. 2, *a*)

$$W_i = k_{\mathrm{app}}[LOOH], \quad (4)$$

$k_{\mathrm{app}} = 5.6 \cdot 10^{-7}$ s^{-1}.

Table 1. Kinetic characteristics of limonene (LH) autooxidation in a chlorobenzene solution at 60 °C

[LH]	[LOOH]	[FF] · 10^4	$W_{O_2} \cdot 10^6$	$W_i \cdot 10^7$	τ /min	Chain length
mol L^{-1}			mol L^{-1} s^{-1}			
3.1	0.345	0.23	10.7	2.1	3.5	51
2.8	0.28	2.9	8.0	1.45	67	55
2.8	0.28	0.9	8.0	1.27	23	62
2.8	0.28	1.8*	8.0	1.27	47	62
2.8	0.28	1.2*	8.0	1.21	33	66
2.0	0.18	2.2	4.2	0.73	100	57
2.0	0.18	0.4	4.2	1.0	12	42
2.0	0.18	0.96	4.2	0.88	36	48
1.0	0.11	0.25	2.5	0.59	14	42
1.0	0.11	0.5	2.3	0.8	20	29
1.0	0.023	—	0.14	—	—	—

* α-Tocopherol.

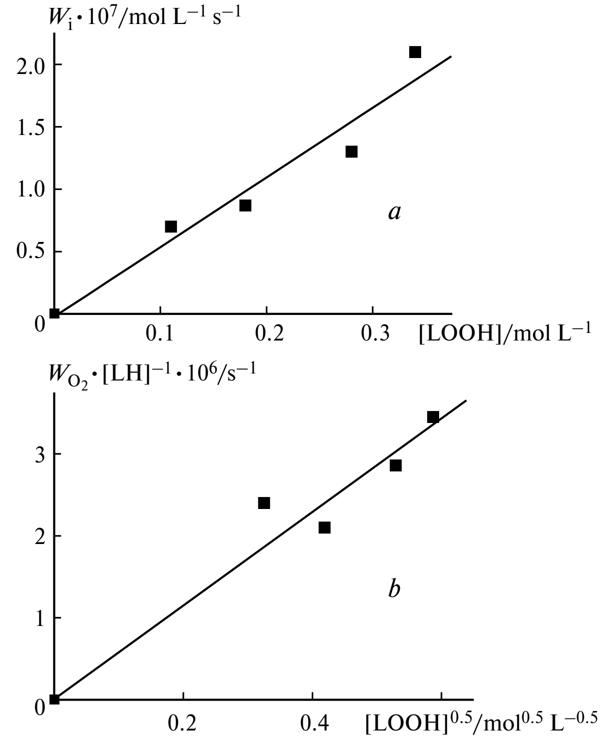

Fig. 2. Rate of chain initiation (W_i) as a function of the hydroperoxide concentration (LOOH) in the autooxidation of limonene (LH) (*a*) and the specific rate of oxygen absorption ($W_{O_2} \cdot [LH]^{-1}$) in limonene oxidation as a function of $[LOOH]^{0.5}$ (*b*) (see Table 1).

(4) Specific rate of oxygen absorption ($W_{O_2}/[LH]$) is proportional to the square root of the hydroperoxide concentration (Fig. 2, *b*). The slope ratio in Fig. 2, *b* (tanφ) is $6.2 \cdot 10^{-6}$ L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$.

(5) According to Eq. (1) under condition (4), the angular coefficient of the plot in Fig. 2, *b* is equal to $\tan\varphi = k_p(k_{app}/2k_t)^{0.5} = 6.7 \cdot 10^{-6}$ L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$, which agrees fairly well with the slope ratio found above.

Thus, in a chlorobenzene solution, the rate of limonene oxidation obeys the kinetic equation

$$W_{O_2} = k_p[LH](k_{app}[LOOH]/2k_t)^{0.5}. \qquad (5)$$

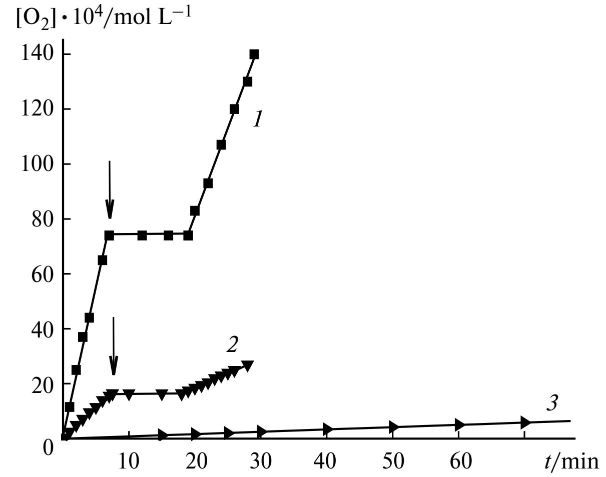

Fig. 3. Kinetic curves of O_2 absorption in the oxidation of limonene (1 mol L^{-1}) with additives of surfactants: CTAC (1 mmol L^{-1}) (*1*), CTAB (0.8 mmol L^{-1}) (*2*), and without a surfactant (*3*). $[LOOH]_0 = 2.2 \cdot 10^{-2}$ mol L^{-1}. Arrows show the moments of introducing α-tocopherol (*1*, $8.0 \cdot 10^{-4}$ mol L^{-1}) and FF (*2*, $0.5 \cdot 10^{-4}$ mol L^{-1}).

It is noteworthy that dependences (4) and (5) are fulfilled at relatively high concentrations of hydroperoxide, when its bimolecular decomposition usually predominates. The bimolecular decomposition of hydroperoxide during limonene oxidation in an *n*-decane solution has previously[3] been observed even at lower concentrations of LOOH (<0.1 mol L^{-1}). A change in the kinetic law indicates a strong influence of polarity and, perhaps, aromaticity of a solvent on the kinetic parameters and also on the mechanism of LOOH decomposition. Linear dependences of the initiation rate *vs.* hydroperoxide concentration were observed for the oxidation of ethylbenzene[22] and cumene.[5]

Additives of cationic surfactants strongly accelerate the oxidation of limonene. It follows from the data in Fig. 3 and Table 2 that the rate of oxygen absorption in the presence of CTAB and CTAC (10^{-3} mol L^{-1}) increases by 30 and 120 times, respectively. Additives of inhibitors completely suppress the absorption of oxygen,

Table 2. Influence of cationic surfactants on the rates of oxygen absorption (W_{O_2}) and radical initiation (W_i) during the oxidation of limonene (1 mol L^{-1}) containing $2.3 \cdot 10^{-2}$ mol L^{-1} hydroperoxide (solution in chlorobenzene, 60 °C)

Surfactant	C_{surf} /mmol L^{-1}	$W_{O_2} \cdot 10^6$ /mol L^{-1} s^{-1}	$[FF] \cdot 10^4$ /mol L^{-1}	τ /min	$W_i \cdot 10^7$	$W_{O_2}/W_{O_2}{}^0$
					mol L^{-1} s^{-1}	
—	—	0.14 ($W_{O_2}{}^0$)	—	—	—	1
CTAB	0.8	3.9	0.5	11	1.3	30
CTAC	1	13.5	4.2	9	16.0	100
CTAC	1	16.7	8.0*	11	24	110

* α-Tocopherol.

indicating the free radical mechanism of catalytic oxidation. Analysis of the data in Table 2 shows that the rates of catalytic oxidation and autooxidation are described by Eq. (1) with the same oxidizability parameter $k_p/(2k_t)^{0.5}$

$$W_{O_2}/([LH]W_i^{0.5}) = k_p/(2k_t)^{0.5} = (0.8\pm0.1)\cdot10^{-2}\ L^{0.5}\ mol^{-0.5}\ s^{-0.5}.$$

This means that surfactants do not virtually affect the steps of chain propagation and square termination, and their catalytic effect is due to the acceleration of hydroperoxide decomposition to free radicals.

The fact that CTAC much surpasses CTAB in catalytic activity indicates the influence of the counterion nature on the decomposition of LOOH. It contradicts the published assumptions on a special role of bromide ions in the decomposition of hydroperoxides.[14,15,23] It can be assumed that ionogenic surfactants in a hydrocarbon medium in the presence of hydroperoxides form dynamic microaggregate-microreactors in which amphiphilic hydroperoxides act as cosurfactants. Hydroperoxides contain a labile O—O bond and can undergo an accelerated decomposition, whose mechanism depends on the surfactant nature. In the case of cationic surfactants, ROOH decompose with escape of $RO_2^{\bullet}$ radicals to the solvent bulk followed by the chain-radical oxidation of a hydrocarbon substrate. A lower rate of radical formation in the case of CTAB can be related to the influence of bromine as a heavy atom facilitating the intracellular (microreactor) recombination of radicals, which decreases the apparent initiation rate.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32222) and the Foundation of the President of the Russian Federation (Program for Support of Leading Scientific Schools, Grant NSh-1221.2003.03).

References

1. K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, 1964, **9**, 507.
2. G. M. Kuznetsova, T. V. Lobanova, I. F. Rusina, and O. T. Kasaikina, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 1676 [*Russ. Chem. Bull.*, 1996, **45**, 1586 (Engl. Transl.)].
3. G. M. Kuznetsova, Z. S. Kartasheva, and O. T. Kasaikina, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 1682 [*Russ. Chem. Bull.*, 1996, **45**, 1592 (Engl. Transl.)].
4. G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *Ann. Chem.*, 1964, **674**, 93.
5. N. M. Emanuel´, E. T. Denisov, and Z. K. Maizus, *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* [*Chain Reactions of Hydrocarbon Oxidation in the Liquid Phase*], Nauka, Moscow, 1965, 375 (in Russian).
6. T. V. Sirota and O. T. Kasaikina, *Neftekhimiya*, 1994, **34**, No. 5, 467 [*Petroleum Chemistry*, 1994, **34** (Engl. Transl.)].
7. T. V. Sirota, N. M. Evteeva, and O. T. Kasaikina, *Neftekhimiya*, 1996, **36**, No. 2, 169 [*Petroleum Chemistry*, 1996, **36** (Engl. Transl.)].
8. Z. S. Kartasheva, T. V. Maksimova, E. V. Koverzanova, and O. T. Kasaikina, *Neftekhimiya*, 1997, **37**, No. 2, 153 [*Petroleum Chemistry*, 1997, **37** (Engl. Transl.)].
9. Z. S. Kartasheva, T. V. Maksimova, T. V. Sirota, E. V. Koverzanova, and O. T. Kasaikina, *Neftekhimiya*, 1997, **37**, No. 3, 249 [*Petroleum Chemistry*, 1997, **37** (Engl. Transl.)].
10. L. J. Csanyi and K. Jaky, *J. Mol. Catal. A: Chem.*, 1997, **120**, 125.
11. O. T. Kasaikina, V. D. Kortenska, Z. S. Kartasheva, G. M. Kuznetsova, T. V. Maximova, T. V. Sirota, and N. V. Yanishlieva, *Colloid Surf. A: Physicochem. Eng. Asp.*, 1999, **149**, 29.
12. V. G. Kondratovich, V. D. Kortenska, Z. S. Kartasheva, N. V. Yanishlieva, I. R. Totzeva, M. I. Boneva, and O. T. Kasaikina, in *Peroxides at the Beginning of the Third Millennium. Synthesis, Properties, Application*, Eds V. A. Antonovsky, O. T. Kasaikina, and G. E. Zaikov, Nova Science Publ., Inc., New York, 2004, 261.
13. W. B. Hugo, in *Surface-Active Agents in Microbiology*, S. C. I. Monograph 19, Soc. Chem. Ind., London, 1965, 67.
14. M. Harustik, M. Hronec, and J. Ilavki, *React. Kinet. Catal. Lett.*, 1988, **37**, 215.
15. M. Harustik, M. Hronec, and J. Ilavki, *J. Mol. Catal.*, 1988, **48**, 335.
16. K. Ohkubo and T. Yamabe, *Bull. Jpn Pet. Inst.*, 1970, **12**, 130.
17. K. Ohkubo and H. Kanaeda, *Bull. Jpn Pet. Inst.*, 1971, **13**, 177.
18. K. Ohkubo and K. Yoshinaga, *Bull. Jpn Pet. Inst.*, 1977, **19**, 73.
19. L. M. Pisarenko and O. T. Kasaikina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 419 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 449].
20. L. M. Pisarenko, Z. S. Kartasheva, T. V. Maksimova, and O. T. Kasaikina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 1419 [*Russ. Chem. Bull., Int. End.*, 2003, **52**, 1500].
21. *Organic Solvents. Physical Properties and Method of Purification*, Ed. A. Weissberger, Intersci. Publ., New York—London, 1955.
22. D. Gal and N. M. Emanuel, *Modelling of Oxidation Processes, Prototype: The Oxidation of Ethylbenzene*, Akademiai Kiado, Budapest, 1986.
23. E. T. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 1608 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, **16** (Engl. Transl.)].

Received December 30, 2003;
in revised form April 23, 2004