Kinetic characteristics of initiated oxidation of limonene

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The kinetics of oxygen absorption in the process of limonene (4-isopropenyl-1-methylcyclohex-1-ene) oxidation was studied in chlorobenzene solution at 40—80 °C. The values of the kinetic parameters of oxidation and the activation energy (38.1 kJ mol^{-1}) have been determined. The nonlinear dependence of the rate of the oxidation of limonene on its concentration has been established. The rate constants of the chain termination reactions were estimated by chemiluminescence techniques.

Key words: limonene, oxidation, free radicals, chemiluminescence.

Limonene (4-isopropenyl-1-methylcyclohex-1-ene, LH), a natural olefin containing two unsaturated bonds, is a constituent of all turpentine and volatile oils of conifers. The wide use of limonene in perfume compositions, perfume additives and food essences, as a component in dentifrices, as a raw material in the industry of perfumes and flotation agents, as well as a solvent for varnishes, resins, and waxes explains the interest shown in its oxidation transformations and in the effect of limonene on the oxidation of other organic substances.

As has been noted in the literature,[1,2] only the cyclohexene ring is affected by the triplet ($^3O_2$) as well as by the singlet ($^1O_2$) oxygen in LH oxidation; the exocyclic isopropenyl group remains intact. Mixtures of isomeric hydroperoxides, whose compositions depend on the oxidation conditions, are the main products of LH oxidation. Quantitative kinetic studies of the reactivity of limonene and of the mechanism of its oxidation by molecular oxygen have not been carried out.

In the present work the kinetics of the dark oxidation of limonene at moderate temperatures has been studied, the kinetic parameters characterizing the oxidizability of this compound have been estimated, and the rate constants of chain termination have been determined by chemiluminescence techniques.

Experimental

D-Limonene (Koch-Light Laboratories Ltd., Colnbrook Buchs, England) was purified on a column with activated aluminum oxide. Azo-*bis*-isobutyronitrile (AIBN) and dicyclohexylperoxydicarbonate (PC) were used as initiators of oxidation. AIBN was recrystallized twice from ethanol and then dried to constant weight *in vacuo*; PC was reprecipitated from its acetone solution by a methanol/water (5 : 1) mixture. The solvent (chlorobenzene) was purified according to the standard procedure.[3] The rate of oxygen absorption was measured on a gasometric installation (volume of the unit, 4 mL) at P_{O_2} = 1 atm. The reaction vessel was equipped with a magnetic stirrer. The rate of O_2 absorption (as shown by specially performed experiments) does not depend on the stirring rate over a fairly wide interval, *i.e.*, the reaction proceeds in the kinetic region. The concentration of hydroperoxides was determined iodometrically.

The measurements of the chemiluminescence (CL) intensity were performed on a photometric installation.[4] The intensity of the CL glow was reinforced by adding an activator, Eu^{3+} chelate, europium 1,10-phenantroline-tris(thenoyltrifluoroacetonate), synthesized following the known procedure[5] and recrystallized from ethanol, in combination with naphthalene.[6] It was shown by specially performed experiments on a gasometric installation that naphthalene and the europium chelate, when introduced separately or together, cause no change in the oxidation rate of limonene.

Results and Discussion

A series of experiments on initiated oxidation of LH was carried out to obtain the kinetic characteristics of limonene. According to the theory,[1,7] the kinetic scheme of the initiated oxidation of olefins at moderate temperatures, when hydroperoxides are the main products of transformation, and chain initiation mainly occurs through radicals formed from the initiator, is :

$$\mathrm{AIBN} \longrightarrow 2f\,\mathrm{r}^{\cdot} \xrightarrow[w_i]{\mathrm{LH},\ \mathrm{O_2}} 2f\mathrm{LO_2}^{\cdot}, \qquad \mathrm{(I)}$$

$$\mathrm{LO_2}^{\cdot} + \mathrm{LH} \xrightarrow[k_p]{\mathrm{O_2}} \mathrm{LOOH} + \mathrm{LO_2}^{\cdot}, \qquad \mathrm{(II)}$$

$$\mathrm{LO_2}^{\cdot} + \mathrm{LO_2}^{\cdot} \xrightarrow[2k_t]{} \mathrm{Products}, \qquad \mathrm{(III)}$$

where the initiation rate $w_i = 2fk_0[\mathrm{AIBN}]$, $2fk_0$ is the initiation efficiency, k_p is the rate constant of chain propagation, k_t is the rate constant of chain termination.

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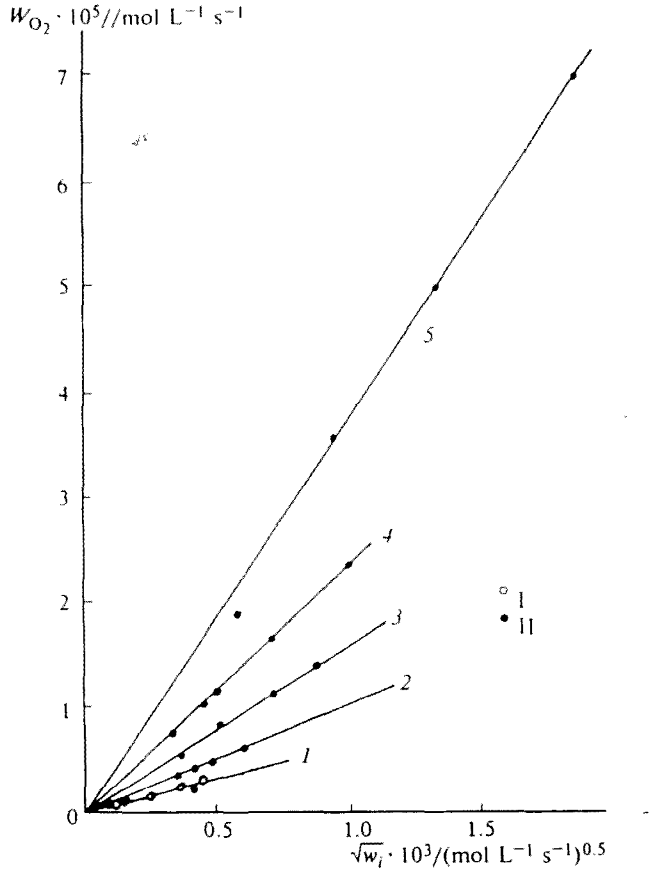

Fig. 1. The dependence of the rate of the absorption of oxygen, W_{O_2}, on $(w_i)^{0.5}$ in the oxidation of limonene at different temperatures, °C: *1*, 40; *2*, 50; *3*, 60; *4*, 70; *5*, 80. [LH] = 1.54 mol L^{-1}; initiators PC (40 °C) (I) and AIBN (II).

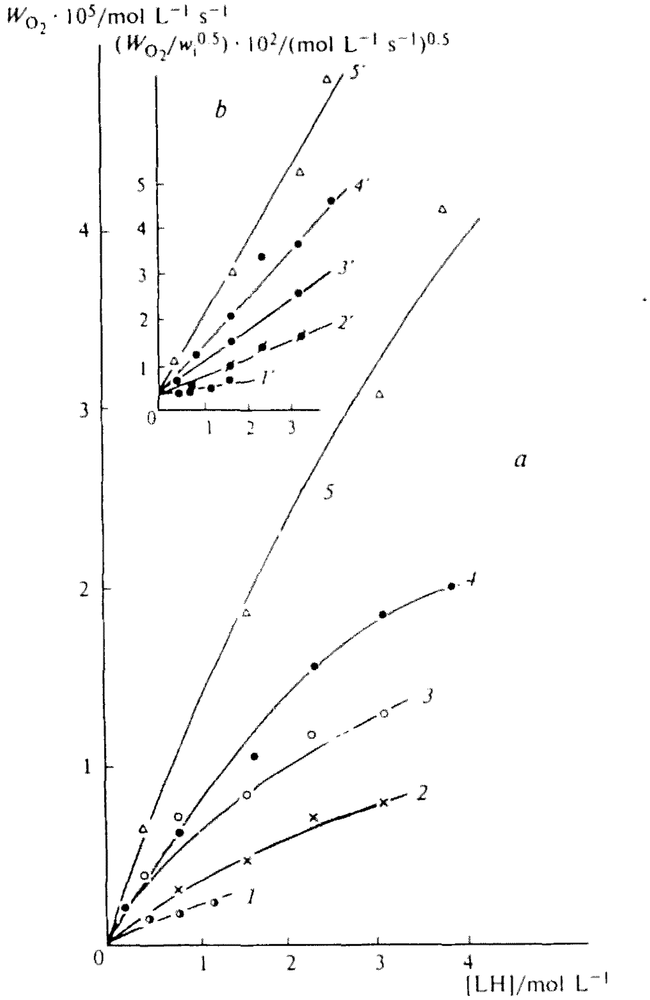

Fig. 2. The dependence of W_{O_2} (*a*) and $W_{O_2}/(w_i)^{0.5}$ (*b*) on the initial concentration of limonene, mol L^{-1} at different temperatures, °C: 40 (*1*, *1'*), 50 (*2*, *2'*), 60 (*3*, *3'*), 70 (*4*, *4'*), 80 (*5*, *5'*). Initiators: PC, $2.12 \cdot 10^{-2}$ mol L^{-1} (*1*, *1'*); AIBN, 10^{-2} mol L^{-1}: 9.0 (*2*, *2'*), 2.34 (*3*, *3'*), 0.47 (*4*, *4'*), 0.23 (*5*, *5'*).

The kinetic equation for the rate of LH oxidation, according to the scheme, is

$$W_{O_2} = W_{ROOH} = k_p/(2k_t)^{0.5}[LH]w_i^{0.5}. \qquad (1)$$

The parameter $k_p/(2k_t)^{0.5}$ traditionally characterizes the oxidizability of hydrocarbons and other organic substances.[7-9] At low degrees of transformation ($\Delta O_2 < 2 \cdot 10^{-2}$ mol L^{-1}), the rate of initiated oxidation of LH is constant, *i.e.*, the contribution of the hydroperoxides formed to chain initiation is insignificant compared with the initiator.

In all experiments the amounts of oxygen absorbed (ΔO_2) and of hydroperoxides formed (ΔROOH) nearly coincide, $(\Delta O_2)_t$ = [ROOH]$_t$, which is in agreement with the above scheme in the case of long oxidation chains.

W_{O_2} in Fig. 1 is shown to be proportional to [AIBN]$^{0.5}$, *i.e.*, to $w_i^{0.5}$, at all temperatures under study, which follows from Eq. (1). However, the W_{O_2} dependence on [LH]$_0$ deviates from linearity, and its deviation is greater at lower temperatures (Fig. 2). One of the reasons for the deviation from linearity may be the decrease in the radical yield after the decomposition of AIBN as olefin concentration increases, like that found[10] in the oxidation of the methyl esters of sun flower oil (MESO) initiated by AIBN.

We measured the rates of formation of radicals at various initial concentrations of limonene by the inhibition technique using *N*,*N'*-di-β-naphtyl-*p*-phenylenediamine (DA), whose stoichiometric inhibition coefficient is equal to 2.[11] The initiation rate w_i was determined by the accumulation of the product of the oxidation of the inhibitor, diimine (DI) (Fig. 3, *a*), as well as by the retardation periods (τ); $2fk_0$ values were calculated using the relationships

$$w_i = 2d[DI]/dt = 2[DA]_0/\tau; \quad 2fk_0 = w_i/[AIBN].$$

As can be seen from Fig. 3, *b*, where changes in $2fk_0$ are shown for increasing concentrations of limonene (curve *1*) and MESO (curve *2*, according to the data in Ref. 10), $2fk_0$ for limonene decreases, but to a lesser

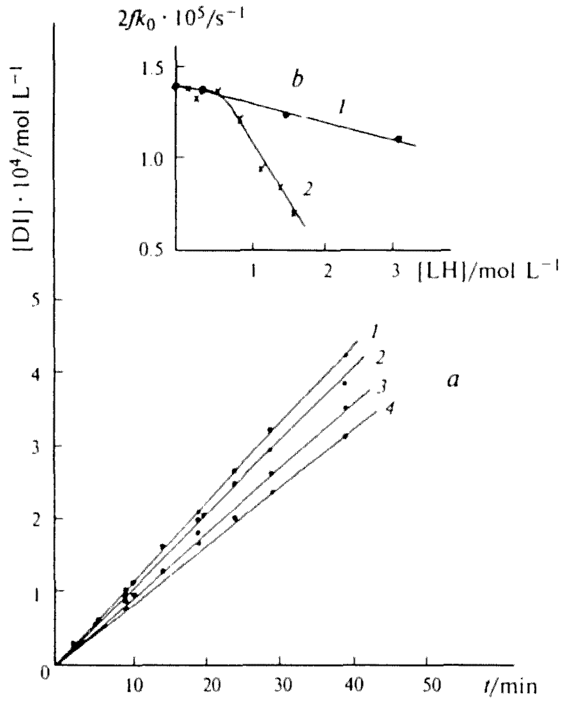

Fig. 3. *a.* Accumulation of diimine (DI) in limonene oxidation in the presence of *N,N'*-di-β-naphtyl-*p*-phenylenediamine (DA). [LH], mol L^{-1}: *1*, 0; *2*, 0.376; *3*, 1.54; *4*, 3.09. [DA] = $5 \cdot 10^{-4}$ mol L^{-1}, 60 °C, [AIBN] = $2.32 \cdot 10^{-2}$ mol L^{-1}. *b.* The dependence of the efficiency of initiation ($2fk_0$) in chlorobenzene on the substrate concentration: *1*, in limonene oxidation; *2*, data from Ref. 10. [AIBN] = $2.32 \cdot 10^{-2}$ mol L^{-1}, 60 °C.

degree than in MESO solutions, and therefore it could not provide the substantial decrease in W_{O_2} observed in the experiment.

The nonlinear dependence of W_{O_2} on $[LH]_0$ observed for MESO was explained by competition of the bimolecular reaction of chain propagation (II) with the intramolecular transformation of the lipide peroxy radical, which is followed by additional oxygen absorption:

$$LO_2^{\cdot} \longrightarrow M^{\cdot} \xrightarrow[k_m]{O_2} MO_2^{\cdot}. \qquad \text{(IV)}$$

An analogous assumption was made[12] on the basis of the kinetic regularities of the oxygen absorption in the oxidation of retinylpolyenes and β-carotene. Considering this reaction, equation for W_{O_2} takes the form

$$W_{O_2} = (2k_m + k_p[LH]_0)(w_i/2k_t)^{0.5}, \qquad (2)$$

$$\text{or } W_{O_2}/w_i^{0.5} = m + n[LH]_0. \qquad (3)$$

The dependence of W_{O_2} on MESO concentration is linearized in the coordinates of Eq. (3), which confirms the suggested mechanism of oxidation.

In the case of limonene, the dependence of W_{O_2} on $[LH]_0$ can also be linearized in the coordinates of Eq. (3). However, it is hardly probable that the intercepts on the Y-axis ($m = 2k_m/(2k_t)^{0.5}$), cut off by the straight lines corresponding to LH oxidation at various temperatures, would be nearly identical since the reactions of the isomerization and decomposition of radicals (k_m) require, as a rule, significant activation energy.

Table 1. Values of $k_p/(2k_t)^{0.5}$ and k_t for a series of olefins (60 °C, solvent, chlorobenzene)

Olefin	$k_p/(2k_t)^{0.5} \cdot 10^2$	$n \cdot 10^2$	$k_t \cdot 10^6$
	/$L^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$		/L mol^{-1} s^{-1}
	Equation (1)	Equation (2)	
Cyclohexene	0.21[7,13]	—	1.5[14] 2.88[a15]
1-Methyl-cyclohexene	0.32[13]	—	0.86[b7]
Limonene	1.04	0.7	7 ± 1[c]
β-Ionone	2.0[6]	—	2.8[6]
Methyl oleate	0.365[13]	—	0.53[a15]
Methyl linoleate	3.04[13]	—	4.4[a15]
MESO	—	2.5[10]	—

[a] At 35 °C. [b] At 40 °C. [c] At 50 °C.

It is remarkable that the values of parameter *m* for limonene and MESO at 60 °C nearly coincide: $4.6 \cdot 10^{-3}$ and $(5.0 \pm 0.8) \cdot 10^{-3}$ mol$^{0.5}$ L$^{-0.5}$ s$^{-0.5}$, respectively.[10] The values of parameter *n*, which, in accordance with Eq. (3) is virtually the oxidizability parameter $k_p/(2k_t)^{0.5}$ for limonene, is several times lower than that for MESO (Table 1).

The temperature dependences of parameter *n* and those for the ratio $k_p/(2k_t)^{0.5}$, determined from Fig. 1 at $[LH]_0$ = 1.54 mol L^{-1}, *i.e.*, assuming the validity of Eq. (1), are satisfactorily described by the Arrhenius equation (Fig. 4) with almost equal activation energies (38.1 kJ mol^{-1}):

$$n = 0.7 \cdot 10^4 \exp\{(-38100 \pm 840)/RT\} \ \mathrm{L^{0.5}\ mol^{-0.5}\ s^{-0.5}},$$

$$k_p/(2k_t)^{0.5} = 1.1 \cdot 10^4 \exp\{(-38100 \pm 840)/RT\} \ \mathrm{L^{0.5}\ mol^{-0.5}\ s^{-0.5}}.$$

Unfortunately, the kinetic data do not allow one to draw any well founded conclusions concerning the reasons for the nonlinear dependence of W_{O_2} on $[LH]_0$. A detailed analysis of the transformation products is required, which, we hope, will be done later. However, several considerations on limonene reactivity and, in particular, on the peculiarities of its oxidation mechanism as compared with other olefins (see Table 1) can be suggested.

1. Limonene is more readily oxidized than the monoolefins cyclohexene, methylcyclohexene, and methyl oleate; however, its reactivity is less than that of the dienes, β-ionone and methyl linoleate, whose double bonds are conjugated (β-ionone) or separated by a me-

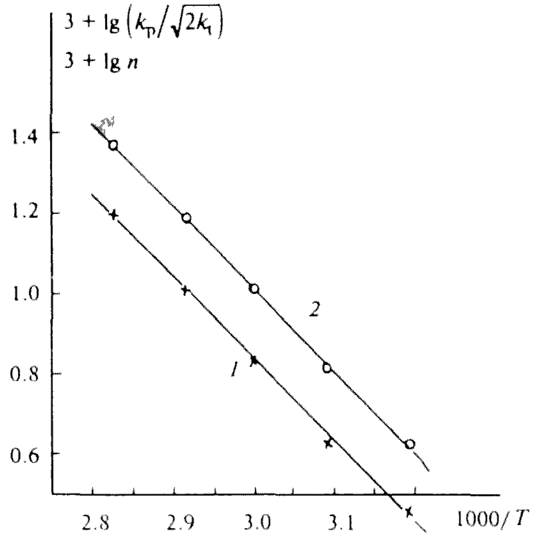

Fig. 4. Temperature dependences of parameters *n* (*1*) and $k_p/(2k_t)^{0.5}$ (*2*) in Arrhenius coordinates.

thylene group with activated C—H bonds. Limonene has isolated double bonds and according to the data reported by various authors,[1,2,16] the exocyclic double bond and the adjacent C—H are not affected in the oxidation process.

2. The main products of limonene oxidation are isomeric hydroperoxides,[17,18] which is in agreement with the results of our measurements: ΔROOH = ΔO_2. The routes of hydroperoxide formation in the process of the dark oxidation of limonene can be represented by Scheme 1.

It follows from the above scheme that in the process of free-radical oxidation limonene reacts with radicals at different centers. In this case secondary (**1**) and tertiary (**2**) peroxy radicals are formed which, as is known,[7,8] differ in their reactivity in the acts of chain propagation and, particularly, chain termination. This means that the parameter $k_p/(2k_t)^{0.5}$ in Eq. (1) is the effective parameter; it includes contributions from the rate constants of the reactions with participation of peroxy radicals **1** and **2** with pertinent statistical weights. It is likely that a substantial fraction of slowly recombining tertiary $LO_2^{\cdot}$ radicals makes the oxidizability of limonene higher than that of monoolefins. It should be noted that in the case of other olefins (except perhaps the symmetric cyclohexene) a number of isomeric hydroperoxides are also formed. As was noted in Refs. 17 and 18, the composition of the isomeric hydroperoxides formed in the oxidation of linoleic acid and its esters changes as the concentration of the substrate changes, so that the oxidizability parameter of other olefins is also effective.

The kinetic nonequivalence of $LO_2^{\cdot}$ can lead to various deviations from the conventional Eq. (1), and, at certain ratios between k_p and k_t, even to a nonlinear dependence of W_{O_2} on $[LH]_0$.

Since peroxyl radicals of different types are formed in the radical reactions of hydrocarbons with a branched carbon chain, one can expect that deviations from Eq. (1) will take place in the initiated oxidation of 1-substituted cyclohexene and other branched olefins.

A characteristic feature of CL arising during limonene oxidation is a fairly high residual glow that can not be quenched even by high concentrations of strong inhibitors; this so called molecular glow has also been observed during the oxidation of other olefins.[6,19] The amount of molecular glow (I_{mol}) increases as the concentration of limonene increases and as the temperature increases. Thus, at [LH] = 1.55 mol L^{-1} at temperatures 40, 50, and 60 °C I_{mol} is 14, 23, and 44 %, respectively. The intensity of the radical component of CL, I_{rad}, is proportional to w_i, *i.e.*, it is square-law of the quenching of $LO_2^{\cdot}$. The estimation of rate constants of chain termination in the recombination of $LO_2^{\cdot}$ and upon interaction with inhibitors was conducted using the kinetic changes in the radical component of CL at 50 °C. Typical curves of CL quenching by a strong inhibitor, 6-hydroxy-2,2,5,7,8-pentamethylchroman

Scheme 1

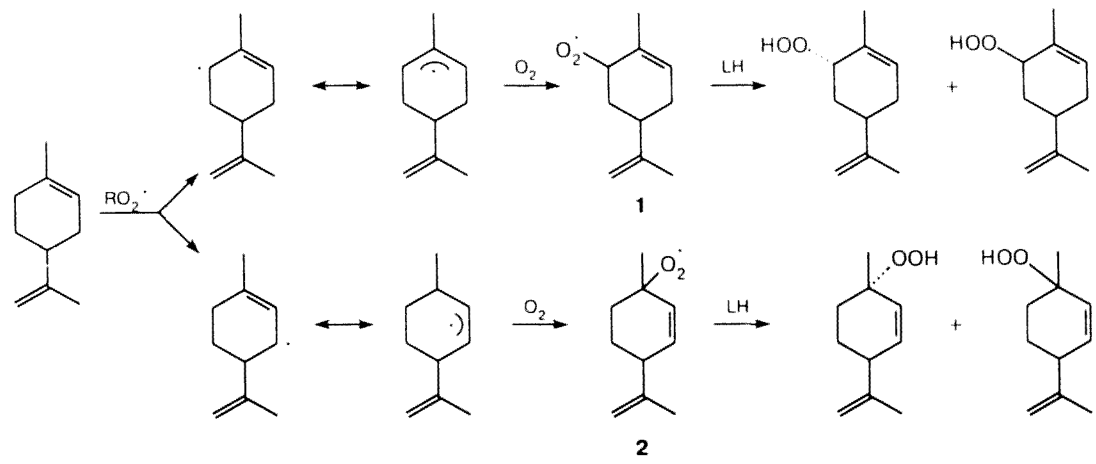

Table 2. Determination of the rate constants of the chain termination reactions in limonene oxidation, 50 °C

[LH] /mol L^{-1}	$w_i \cdot 10^8$ /mol L^{-1} s^{-1}	Chroman		Ionol		
		$k_i/(2k_t)^{0.5}$ /L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ [a]	$k_t \cdot 10^{-6}$ /L mol^{-1} s^{-1}	$k_i \cdot 10^{-4}$ /L mol^{-1} s^{-1}	$k_i/(2k_t)^{0.5}$ /L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ [b]	$k_t \cdot 10^{-6}$ /L mol^{-1} s^{-1}
1.55	2.72	860	8.20	1.97	5.70	6.02
1.55	11.40	990	6.27	2.15	6.32	5.80
1.55	2.90	896	7.60	2.80	5.70	6.10
1.55	2.10	1021	5.90	1.47	5.10	7.60
0.37	0.16	844	8.61	1.40	5.14	7.37
0.62	0.20	996	6.16	1.47	5.64	6.10
1.55	0.29	940	6.9	2.8	5.2	7.3

[a] Kinetic parameter was calculated using tan φ. [b] Kinetic parameter was calculated using $i_{\min}$.

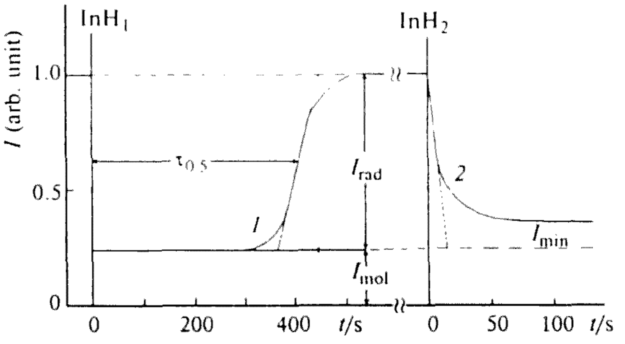

Fig. 5. CL kinetics in the process of limonene oxidation ([LH] = 1.55 mol L^{-1}) in chlorobenzene solution with successive addition of inhibitor: *1*, chroman, [InH$_1$] = $6 \cdot 10^{-7}$ mol L^{-1}; *2*, ionol, [InH$_2$] = $1.1 \cdot 10^{-6}$ mol L^{-1} (50 °C, $w_i = 2.9 \cdot 10^{-9}$ mol L^{-1} s^{-1}).

(curve *1*) and by a weaker inhibitor, ionol (2,6-di-*tert*-butyl-4-methylphenol) (curve *2*) are shown in Fig. 5. The intensity of CL in the presence of chroman characterizes I_{mol}, while $I_{rad} = I_0 - I_{mol}$. It is accepted that even if the rate constant in the reaction of an inhibitor with a peroxy radical (k_i) depends on the RO$_2$˙ structure, the effect does not exceed experimental error[20] or the solvent effect.[21] This allows one to determine the rate constants of the square-law chain termination (k_t) from the kinetic curves of CL obtained for samples with inhibitor additives using known relationships[22] for the relative intensity of CL at the minimum of the kinetic curve ($i_{\min} = I_{\min}/I_{rad}$):

$$k_i/(2k_t)^{0.5} = (1 - i_{\min})(w_i)^{0.5}/(f[\mathrm{InH}](i_{\min})^{0.5}). \qquad (4)$$

They can also be determined from the tangent of the slope of the CL curve at the point of inflection (at the end of retardation) (see Fig. 5):

$$k_i/(2k_t)^{0.5} = \mathrm{tg}\varphi/(0.237(w_i)^{0.5}). \qquad (5)$$

The results of the measurements are listed in Table 2. The average value of $k_i = 3.5 \cdot 10^6$ L mol^{-1} s^{-1} obtained from the data[20,23–25] on the oxidation of various hydrocarbons and taken as a reference constant for the strong chroman inhibitor was used in calculations of k_t. The value of k_i for the relatively less active ionol was determined using CL kinetics in the non-stationary regime[25] from the slope of the initial part of the curves (Fig. 5, *b*):

$$k_i = 1/(2\Delta T[\mathrm{InH}]_0). \qquad (6)$$

This method can be used for estimating the "absolute" values of k_i, *i.e.*, those which are not relative to $2k_t$ (or k_p). As can be seen from Table 2, the value of k_i for ionol is nearly independent of [LH] and lies in the interval of values reported in the literature for different RO$_2$˙ at 50 °C.[20,26]

The k_t data obtained for limonene are of the same order as those for several other olefins (see Table 1). It is remarkable that dilution of limonene has no essential effect on the $k_i/(2k_t)^{0.5}$ parameter and, hence, on the value of k_t. Evidently, the effective averaged rate constants of chain termination, both on inhibitors and on the acts of radical recombination, can be determined by the chemiluminescence method.

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