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Features of the initiated oxidation mechanism of *n*-heptadecane at low concentrations of oxygen

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The oxidation of *n*-heptadecane was studied at various partial pressures of oxygen in an oxygen—argon mixture from 100 to 10% and various initiation rates W_i in the range $(1—5) \cdot 10^{-6}$ mol L^{-1} s^{-1} at 413 K. The kinetic curves of oxygen uptake and hydroperoxide buildup were obtained under the indicated conditions. The observed features of *n*-heptadecane oxidation at low concentrations of oxygen may qualitatively be explained and quantitatively described if the oxidation scheme takes into account the cross termination of alkyl and peroxyl radicals $R^{\cdot} + RO_2^{\cdot} \xrightarrow{k_5} ROOR$ along with the square termination of peroxyl radicals. A method for determination of the corresponding kinetic parameter by the dependence of the initial oxidation rate on the partial oxygen pressure was proposed. A method for identification of the key reactions and determination of the kinetic parameters by the kinetics of oxygen uptake at lowered oxygen concentrations was developed. The kinetic model of the process was obtained, which quantitatively describes the kinetic curves of oxygen uptake and hydroperoxide buildup at the initial steps of initiated oxidation of *n*-heptadecane.

Key words: hydrocarbons, concentration of oxygen, chain oxidation, mechanism of process, kinetic studies, mathematical modeling.

Nearly all available information about the mechanism of hydrocarbon oxidation was obtained at maximum concentrations of dissolved oxygen, namely, during oxidation with "neat" oxygen.[1—6] However, the basic oxidation processes occur at lowered concentrations of dissolved oxygen, for example, on contact with air oxygen. These are production, storage, and exploitation of petroleum products, polymer materials, food products, and drugs, as well as oxidation processes in biological systems.

The oxidation mechanism at a low oxygen concentration of both individual hydrocarbons[1,2] and complex hydrocarbon materials (polymers,[7] fuels[8]) has a number of specific features. The experimental data on the oxidation of decene oligomer PAO-2 (see Ref. 9) and hydraulic oil RM (see Ref. 10) are presented in Fig. 1 as examples. As can be seen from Fig. 1, the both petroleum products are characterized by qualitative and quantitative differences in the processes of oxidation with oxygen and air.

Similar features can be observed for the oxidation of individual hydrocarbons. The experimental data on the initiated oxidation of *n*-heptadecane obtained on a manometric setup are shown in Fig. 2. It is seen that a decrease in the partial oxygen pressure decreases the rate of the process and qualitatively changes the kinetic curves. Most likely, the role of alkyl radicals increases in the oxidation mechanism[1,2] and, hence, the role of such reactions as the cross termination of alkyl and peroxyl radicals, induced decomposition of hydroperoxides, formation of low-molecular-weight oxidation products (gas evolution), *etc.* increases as well.

Thus, the features of the oxidation mechanism of these substances at a low oxygen concentration should be studied in detail at a quantitative level to correctly characterize and reliably predict the oxidation stability of hydrocarbons and hydrocarbon materials. The purpose of this work is the experimental study of the oxidation of *n*-heptadecane at various initiation rates and partial pressures of oxygen in the oxidizing gas, identification of the key reaction, determination of numerical values of kinetic parameters by experimental data processing, and development of the mathematical model that quantitatively describes the process under study.

Experimental

Initiated oxidation of *n*-heptadecane was studied at various pressures of oxygen in the oxidizing gas (a mixture of oxygen with argon) at 413 K. The oxygen uptake was measured on a special manometric setup.[11] The concentration of hydroperoxides was determined iodometrically using dicumyl peroxide as initiator. The typical plots of the oxygen uptake *vs* time, $[O_2](t)$, during initiated *n*-heptadecane oxidation are shown in Fig. 3.

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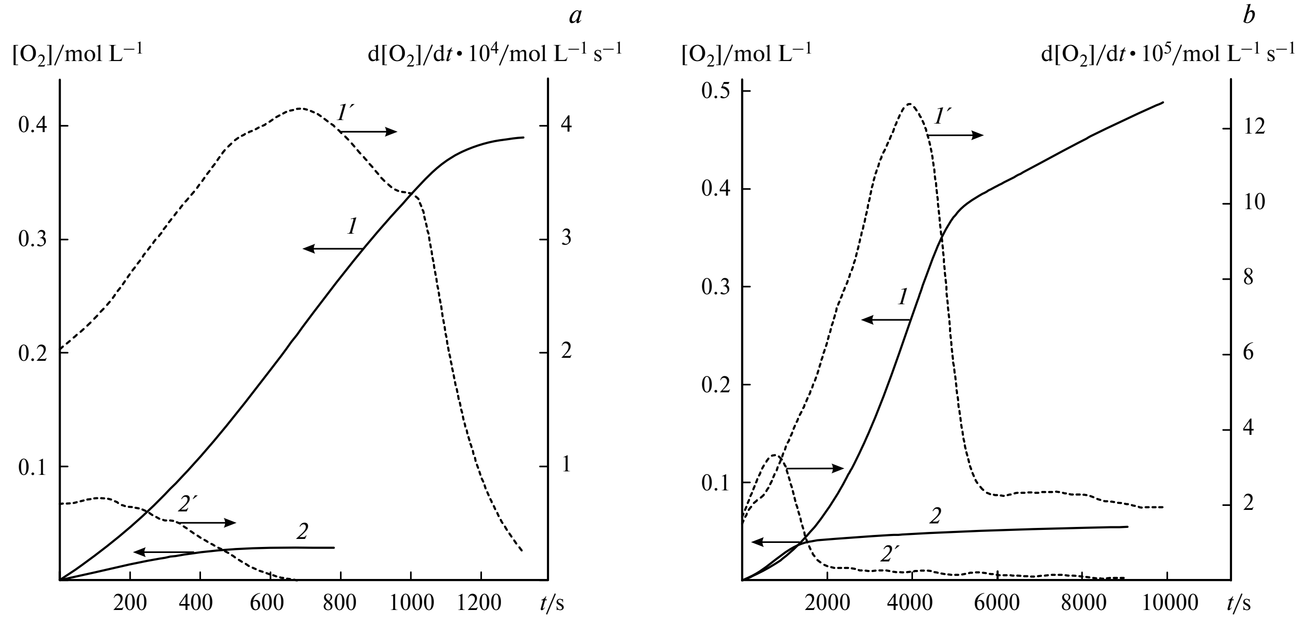

Fig. 1. Kinetic curves of oxygen uptake (*1*, *2*) and the corresponding autooxidation rate (*1*′, *2*′) at 140 °C of the fraction PAO-2 of decene oligomer (*a*) and hydraulic oil RM (*b*).

The experimental plots $[O_2](t)$ were processed on a computer and the smooth time dependences of the oxidation rate $v(t) \equiv d[O_2]/dt$ were obtained. The plots $v(t)$ calculated from the corresponding curves in Fig. 3 are presented in Fig. 4.

The amount of oxidation products (hydroperoxides ROOH) accumulated in the sample was determined using a manometric setup after each experiment. The amount of hydroperoxides accumulated in the sample during the heat treatment prior to the

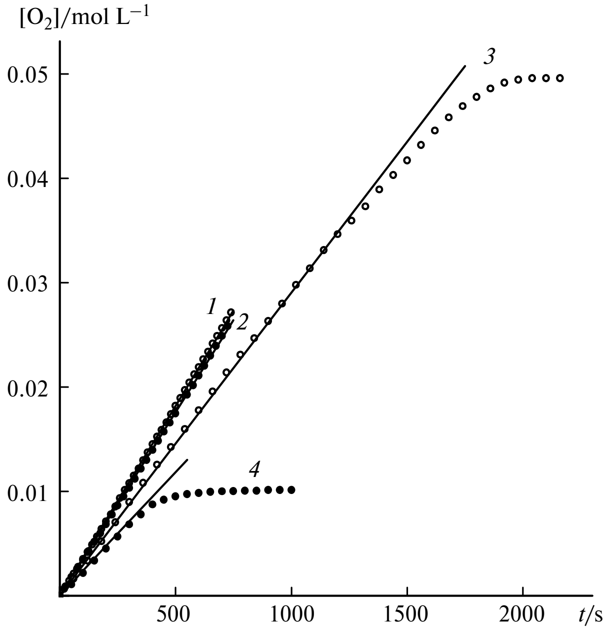

Fig. 2. Kinetic curves of oxygen uptake in the initiated oxidation of *n*-heptadecane at 140 °C. Concentration $[O_2]$ in the oxidizing gas (%): 80 (*1*), 60 (*2*), 21 (*3*), and 10 (*4*). Initiation rate $W_i = 5 \cdot 10^{-6}$ mol L^{-1} s^{-1}. Points are experiment, and lines show the calculation with allowance for the determined values of the kinetic parameters.

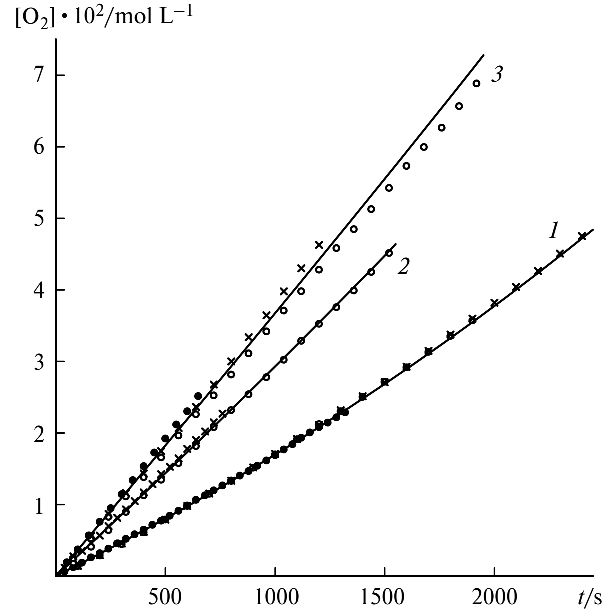

Fig. 3. Kinetic curves of oxygen uptake in the initiated oxidation of *n*-heptadecane at 140 °C. Initiation rate $W_i \cdot 10^6 = 1.06$ (*1*), 3.07 (*2*), and 5.09 mol L^{-1} s^{-1} (*3*). The concentration $[O_2]$ in the oxidizing gas is 100%. Points are experiment, and lines show the calculation with allowance for the determined values of the kinetic parameters. Here and in Fig. 4 the data of the same experiment are designated by the same symbols.

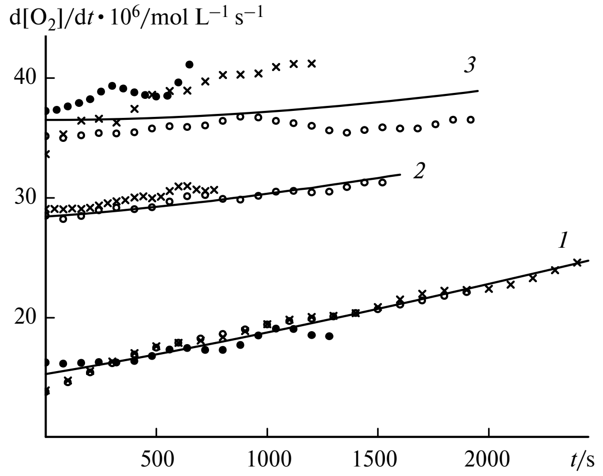

Fig. 4. Oxygen uptake *vs* duration of the initiated oxidation of *n*-heptadecane at 140 °C. The curves were obtained by the numerical differentiation of the corresponding curves in Fig. 3. Points are experiment, and lines show the calculation with allowance for the determined values of the kinetic parameters.

beginning of experimental data detection was measured in special experiments.

Three series of experiments were carried out on oxygen uptake with the manometric setup at an oxygen content in the oxidizing gas of 100, 80, 60, 21, and 10%. The initial initiation rate $W_i \cdot 10^6$ was constant in each series and equal to 1.06, 3.07, and 5.09 mol L^{-1} s^{-1}. The value of the initial oxidation rate $v(0)$ was calculated taking into account each experimental curve, and the plot of $v(0)$ *vs* partial oxygen pressure was constructed for each value of the initiation rate (Fig. 5).

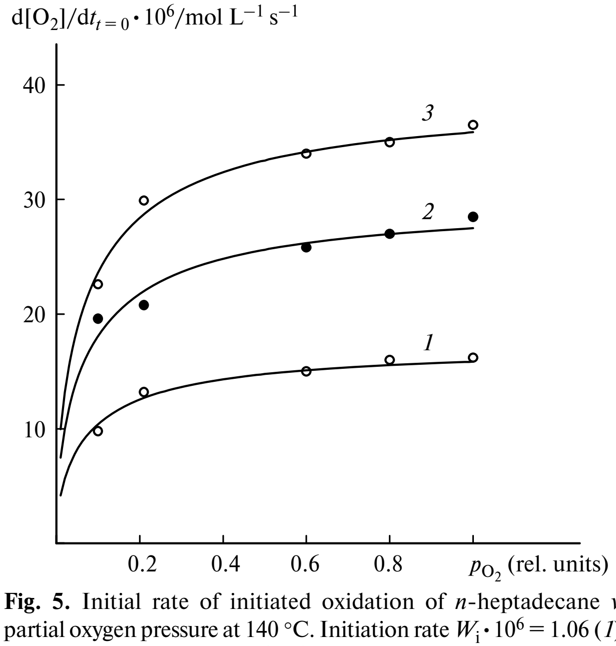

Fig. 5. Initial rate of initiated oxidation of *n*-heptadecane *vs* partial oxygen pressure at 140 °C. Initiation rate $W_i \cdot 10^6$ = 1.06 (*1*), 3.07 (*2*), and 5.09 mol L^{-1} s^{-1} (*3*). Points are experiment, and lines show the calculation with allowance for the determined values of the kinetic parameters.

Results and Discussion

The study of the kinetic regularities of the auto- and initiated oxidation of *n*-heptadecane in neat oxygen showed that the main regularities of the process, *viz*., kinetic curves of oxygen uptake and hydroperoxide buildup in the initiated oxidation and autooxidation, can quantitatively be described in terms of the classical scheme of oxidation[1]

$$\mathrm{RH} + \mathrm{O_2} \xrightarrow{k_{0.0}} \mathrm{r}^{\bullet} + \mathrm{R}^{\bullet}, \qquad (0.0)$$

$$\mathrm{RH} + \mathrm{I} \xrightarrow{k_{0.1}} 2e\mathrm{r}_i^{\bullet}, \qquad (0.1)$$

$$\mathrm{RH} + \mathrm{r}^{\bullet} \xrightarrow{k_{0.2}} \mathrm{R}^{\bullet} + \mathrm{rH}^{\bullet}, \qquad (0.2)$$

$$\mathrm{RH} + \mathrm{r}_i^{\bullet} \xrightarrow{k_{0.3}} \mathrm{R}^{\bullet} + \mathrm{r}_i\mathrm{H}^{\bullet}, \qquad (0.3)$$

$$\mathrm{O_2} + \mathrm{R}^{\bullet} \xrightarrow{k_{1.0}} \mathrm{RO_2}^{\bullet}, \qquad (1.0)$$

$$\mathrm{RH} + \mathrm{RO_2}^{\bullet} \xrightarrow{k_{2.1}} \mathrm{R}^{\bullet} + \mathrm{ROOH}, \qquad (2.1)$$

$$\mathrm{RH} + \mathrm{RO_2}^{\bullet} \xrightarrow{k_{2.2}} \mathrm{R}^{\bullet} + \mathrm{MP}, \qquad (2.2)$$

$$\mathrm{ROOH} \xrightarrow{k_{3.1}} 2\mathrm{r}^{\bullet}, \qquad (3.1)$$

$$\mathrm{ROOH} + \mathrm{ROOH} \xrightarrow{k_{3.2}} 2\mathrm{r}^{\bullet}, \qquad (3.2)$$

$$\mathrm{ROOH} \xrightarrow{k_{3.3}} \mathrm{MP}, \qquad (3.3)$$

$$\mathrm{ROOH} + \mathrm{ROOH} \xrightarrow{k_{3.4}} \mathrm{MP}, \qquad (3.4)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RO_2}^{\bullet} \xrightarrow{k_{6.0}} \mathrm{O_2} + \mathrm{MP}, \qquad (6.0)$$

where RH is the oxidized substance; I is the initiator; *e* is the escape probability of initiator radicals to the bulk; $\mathrm{r}^{\bullet}$ is a radical of any structure different from $\mathrm{r}^{\bullet}{}_i$, $\mathrm{R}^{\bullet}$, and $\mathrm{RO_2}^{\bullet}$; and MP are molecular products.

The scheme involves the following reactions:

1. Reactions (0.0)—(0.3), which model spontaneous (0.0) and initiated (0.1) chain nucleation.

2. Reactions of chain propagation (1.0)—(2.2). In this case, the situation, where not all absorbed oxygen is transformed into hydroperoxide, is modeled by reaction (2.2).

3. Reactions of degenerate branching on hydroperoxide of the first (3.1) and second (3.2) order with respect to [ROOH].

4. Reactions of hydroperoxide consumption with the formation of molecular products (3.3) and (3.4).

5. Reaction of square chain termination (6.0).

An analysis of the scheme of reactions (0.0)—(6.0) shows that in the framework of this mechanism the oxidation rate is independent of the oxygen concentration in the system. Since the experimental data obtained at low partial pressures of oxygen (see Figs 2 and 5) contradict to this fact, the initial scheme should be supplemented by the reactions involving alkyl radicals R$^\cdot$ and, first of all, by the reactions of square and cross terminations

$$\mathrm{R^\cdot + R^\cdot \xrightarrow{k_{4.0}} R{-}R}, \qquad (4.0)$$

$$\mathrm{R^\cdot + RO_2{}^\cdot \xrightarrow{k_{5.0}} ROOR}. \qquad (5.0)$$

Processes (0.0)—(6.0), (4.0), and (5.0) proceed, as a rule, in the quasi-stationary regime relative to the concentrations of radicals $\mathrm{r}_i{}^\cdot$, $\mathrm{r}^\cdot$, $\mathrm{R}^\cdot$, and $\mathrm{RO_2}^\cdot$. Taking this into account, the corresponding system of equations can be written as follows:

$$w_s = P_6v_2{}^2 + 2P_5v_1v_2/x + P_4v_1{}^2/x^2, \qquad (1)$$

$$v_1 = (1 - q)v_2 + P_6v_2{}^2 + P_5v_1v_2/x, \qquad (2)$$

$$\mathrm{d}y/\mathrm{d}t = (1 - q)v_2 - P_{s1}y - 2P_{s2}y^2, \qquad (3)$$

$$\mathrm{d}q/\mathrm{d}t = [w_s + (1 - q)v_2]/[\mathrm{RH}]_0. \qquad (4)$$

Initial conditions:

$$y(0) = [\mathrm{ROOH}]_0/P_2;\ q(0) = 0. \qquad (5)$$

Designations: $x = [\mathrm{O_2}]/[\mathrm{O_2}]_0$ is the oxygen fraction in the oxidizing gas; $[\mathrm{O_2}]$ and $[\mathrm{O_2}]_0$ are the concentrations of dissolved oxygen at a specified partial pressure of oxygen and at a 100% oxygen content in the gas, respectively.

Variables: $y = [\mathrm{ROOH}]/P_2$ is the reduced concentration of hydroperoxides; $q = ([\mathrm{RH}]_0 - [\mathrm{RH}])/[\mathrm{RH}]_0$ is the conversion of hydrocarbon; $v_1 = k_1[\mathrm{O_2}][\mathrm{R}^\cdot]$ is the rate of reaction (1.0); $v_2 = (k_{2.1} + k_{2.2})[\mathrm{RH}]_0[\mathrm{RO_2}^\cdot]$ is the value directly proportional to $[\mathrm{RO_2}^\cdot]$; $w_s = W_0 + w_i + w_3$ is the overall initiation rate; $w_i = 2ek_{0.1}[\mathrm{I}]_0\exp(-k_{0.1}t)$ is the rate of initiation due to the initiator; and $w_3 = 2P_{3.1}y + 2P_{3.2}y^2$ is the degenerate branching rate.

Parameters: $W_0 = 2k_{0.0}[\mathrm{O_2}][\mathrm{RH}]_0$ is the rate of spontaneous nucleation of radicals; $P_2 = k_{2.1}/(k_{2.1} + k_{2.2})$ is the probability of formation of [ROOH] in the act of chain growth; $P_4 = 2k_4/(k_1[\mathrm{O_2}]_0)^2$ characterizes the square termination of radicals $\mathrm{R}^\cdot$; $P_5 = k_5/(k_1[\mathrm{O_2}]_0k_2[\mathrm{RH}]_0)$ characterizes the cross termination of radicals $\mathrm{R}^\cdot$ and $\mathrm{RO_2}^\cdot$; $P_6 = 2k_6/(k_2[\mathrm{RH}]_0)^2$ characterizes the square termination of radicals $\mathrm{RO_2}^\cdot$; $P_{3.1} = k_{3.1}P_2$ and $P_{3.2} = k_{3.2}P_2{}^2$ are the parameters of degenerate branching on hydroperoxides by the first and second orders with respect to [ROOH], respectively, and $P_{s1} = k_{3.1} + k_{3.3}$ and $P_{s2} = (k_{3.2} + k_{3.4})P_2$ are the parameters of overall consumption of hydroperoxides by the first and second orders with respect to [ROOH], respectively.

The expression for the experimentally measured rate of oxygen uptake (oxidation rate) has the following form:

$$v(t) = 0.5W_0 + v_1 - 0.5P_6v_2{}^2. \qquad (6)$$

Reactions (0.1)—(3.1) and (6.0) should be included in the mechanism of initiated *n*-heptadecane oxidation for the quantitative description of the experimental data (see Figs 3—5), taking into account the character of the time dependences of the oxidation rate. Reactions (4.0) and (5.0) should also be included presumably in this mechanism, because oxidation rate $v(0)$ depends on the partial oxygen pressure (see Fig. 5). The corresponding system of equations contains five unknown parameters (P_2, $P_{3.1}$, P_4, P_5, and P_6).

The solution of this problem should be divided into two stages. At the first stage, we exclude from consideration parameter P_4 suggesting that reaction (5.0) controls the dependence of the oxidation rate on the oxygen concentration in the system. At the second stage, we evaluate the role of reaction (4.0) and parameter P_4 under the considered conditions.

The desired parameters were determined in the iteration process, *i.e.*, their values were successively refined. In each iteration, the parameters were calculated in the following sequence: P_6 and $P_{3.1}$ were calculated from the time dependences of the oxidation rate at a 100% oxygen content in the oxidizing gas and various initiation rates (see Fig. 4); P_2 was determined from a comparison of the oxygen uptake and the amount of hydroperoxides formed in experiments with various initiation rates at a 100% oxygen content in the oxidizing gas; and P_5 was calculated by the dependences of the initial oxidation rate on the partial oxygen content at various initiation rates (see Fig. 5).

At $P_4 = 0$ parameter P_5 can be determined in an explicit form as follows. The system of equations describing the dependence of the initial oxidation rate on the partial oxygen pressure takes the following form:

$$w_s = P_6v_2{}^2 + 2P_5v_1v_2/\mathrm{x}, \qquad (7)$$

$$v_1 = v_2 + P_6v_2{}^2 + P_5v_1v_2/x, \qquad (8)$$

$$v(0) = 0.5W_0 + v_1 - 0.5P_6v_2{}^2. \qquad (9)$$

Here all variables w_s, v_1, v_2, and v are considered at $t = 0$.

It should be mentioned that, under these conditions (initiated oxidation of *n*-heptadecane), parameter W_0 can be excluded from Eq. (9), since it is much lower than the initiation rate involving the initiator. However, we rejected this way for the following grounds. The method developed should be general, *i.e.*, be appropriate for investigation of various hydrocarbon substrates, including complex hydrocarbon materials and petroleum products for which the rate of spontaneous nucleation of radicals can be comparable with the initiation rate specified by the initiator.[9]

The value of W_0 should preliminarily be determined from the corresponding experimental data (by the initial region of the plots of the autooxidation rate *vs* time[12]) and, therefore, parameter P_5 will be considered unknown during its determination.

The system of Eqs (7)—(9) contains three unknowns (v_1, v_2, P_5) and can be solved as follows:

$$P_5 = 0.5x(w_s - P_6 v_2^2)/(v_1 v_2), \tag{10}$$

$$v_1 = v_2 + 0.5(P_6 v_2^2 + w_s), \tag{11}$$

$$v_2 = v(0) - 0.5(w_s + W_0). \tag{12}$$

Unknowns v_2, v_1, and P_5 are successively determined by the experimental value of the initial oxidation rate $v(0)$ from Eqs (12), (11), and (10). The results of calculation of parameter P_5 by the values of $v(0)$ presented in Fig. 5 are shown in Fig. 6.

The numerical solution of the whole problem gave the following values of kinetic parameters: $P_6 = (3.85\pm0.06)\cdot10^3$, $k_{3.1} = (3.0\pm0.1)\cdot10^{-5}$, $P_2 = 0.80\pm0.02$, and $P_5 = 363\pm17$.

Let us calculate the value of parameter a

$$a \equiv k_2[\mathrm{RH}]_0/\sqrt{2k_6} = (P_6)^{-0.5} = 1.61\cdot10^{-2}$$
$$(\mathrm{mol}^{0.5}\ \mathrm{L}^{0.5}\ \mathrm{s}^{0.5}).$$

This value agrees well with $a = 1.56\cdot10^{-2}$ found earlier.[12]

Now let us estimate the value of square termination of alkyl radicals $v_4 = P_4(v_1)^2$. Specifying $2k_6 = 2.51\cdot10^6$,[13] we find $k_2[\mathrm{RH}]_0 = 25.5$. Substituting this value into the expression for parameter P_5, we have

$$k_5/(k_1[\mathrm{O}_2]_0) = 9.2\cdot10^3. \tag{13}$$

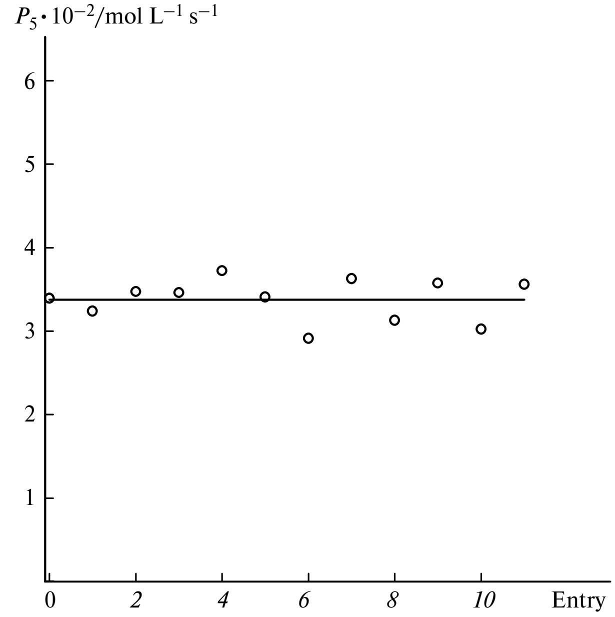

Fig. 6. Determination of parameter P_5 by the experimental data in Fig. 5.

Taking into account the published results,[14] we accept that $k_5 \geq 5\cdot10^8$. Then it follows from Eq. (13) that $k_1[\mathrm{O}_2]_0 \geq 5\cdot10^4$. If one accepts $k_4 = 3\cdot10^9$,[15] the estimated value of parameter P_4 is lower than 10. It follows from the experimental data (see Fig. 5) that the square termination rate of alkyl radicals v_1 is lower than $4\cdot10^{-5}$. Thus, $P_4(v_1)^2 < 1.6\cdot10^{-8} << w_i$, *i.e.*, the square termination of radicals R• can be neglected under the considered conditions. The same result is obtained when attempting to determine simultaneously two parameters P_4 and P_5 by the minimization of the functional

$$\Phi(P_4, P_5) = \Sigma(v_{\mathrm{exp}} - v_{\mathrm{calc}})^2,$$

which characterizes the difference between the calculated and experimental (see Fig. 5) values of the initial oxidation rate. The minimum of the functional is achieved at $P_4 = 0$ and $P_5 = 345$.

To check the solution of the problem, the determined values of parameters P_2, P_5, P_6, and $k_{3.1}$ were put into the system of Eqs (1)—(5) and the kinetic curves of the oxygen uptake and hydroperoxide buildup were calculated during the initiated oxidation of *n*-heptadecane. A comparison of the calculated and experimental curves at a 100% oxygen content and various initiation rates is presented in Figs 3 and 4. The experimental and calculated dependences of the initial oxidation rate on the partial oxygen pressure in the oxidizing gas at three values of the initiation rate are compared in Fig. 5. The kinetic curves of the oxygen uptake at the initiation rate $w_i = 5\cdot10^{-6}$ mol L^{-1} s^{-1} and various partial pressures [O$_2$] were also compared (see Fig. 2). The experimental and calculated values of concentrations of the absorbed oxygen and hydroperoxides accumulated during *n*-heptadecane oxidation to the end of experiments are listed in Table 1. The comparison of the experiment and calculation shows:

— the considered kinetic model satisfactorily describes the initial regions of the experimental curves of the oxygen uptake in the entire range studied of oxygen concentrations (10—100%) (see Figs 2 and 3);

— a systematic discrepancy of the calculation with experiment is observed at low oxygen concentrations in the system (10 and 21%) at the end of experiments, which is most likely related to the formation of low-molecular-weight products under these conditions, *i.e.*, to gas evolution (see Fig. 2, curves *3* and *4*);

— as follows from Table 1, at the 21% O$_2$ content the experimental and calculated values of the hydroxide buildup coincide within a much longer time period than the values of the oxygen uptake. This implies that, in spite of

Table 1. Comparison of the experimental (I) and calculated (II) concentrations of oxygen uptake $[O_2]$ and hydroperoxide buildup [ROOH] in the oxidation of *n*-heptadecane accumulated in the course of the experiments

Content of O_2 (%)	$W_i \cdot 10^6$ /mol L^{-1} s^{-1}	$[ROOH]_0 \cdot 10^2$ /mol L^{-1}	*t*/s	$[ROOH] \cdot 10^2$ /mol L^{-1}		$[O_2] \cdot 10^2$	
				I	II	I*	II
100	1.06	0.51	1280	2.2	2.3	2.3	2.4
	3.07	0.63	780	2.3	2.2	2.3	2.3
	5.09	0.79	650	2.4	2.2	2.4	2.4
80	1.06	0.51	1400	2.2	2.4	2.3	2.6
	3.07	0.62	780	2.2	2.2	2.2	2.2
	5.09	0.77	720	2.6	2.6	2.6	2.6
60	1.06	0.50	2000	2.5	2.6	3.0	3.5
	3.07	0.61	900	2.2	2.4	2.3	2.5
	5.09	0.74	725	2.5	2.5	2.6	2.6
21	1.06	0.48	3400	3.6	4.4	4.7	5.7
	3.07	0.58	2320	4.0	4.2	4.6	5.4
	5.09	0.71	2160	4.5	4.9	5.0	6.2
10	1.06	0.46	2000	1.4	2.2	1.2	2.4
	3.07	0.53	1480	1.2	2.4	1.3	2.7
	5.09	0.68	950	1.5	2.2	1.0	2.2

* The difference between the oxygen uptake and evolved gaseous products was experimentally measured.

the formation of low-molecular-weight products, essentially the same oxidation mechanism remains operative. However, with the further decrease in the oxygen content (10%), the discrepancy between $[ROOH]_{exp}$ and $[ROOH]_{calc}$ becomes significant, indicating that additional reactions, for instance, the induced decomposition of hydroperoxides under the action of alkyl radicals, should necessarily be taken into account.

Thus, the oxidation of *n*-heptadecane was experimentally studied at various partial oxygen pressures in the oxidizing gas and various initiation rates. It is shown that the observed features of *n*-heptadecane oxidation at low oxygen concentrations can qualitatively be explained and quantitatively described, if the cross termination of alkyl and peroxyl radicals $R^{\cdot} + RO_2^{\cdot} \rightarrow ROOR$ (k_5) is taken into account along with the square termination of peroxyl radicals. The method for determination of the corresponding kinetic parameters from the dependence of the initial oxidation rate on the partial oxygen pressure was proposed. The method was developed for the identification of the key reactions and determination of the kinetic parameters by the kinetics of the oxygen uptake at lowered oxygen concentrations. The kinetic model of the process was obtained, which quantitatively describes the kinetic curves of the oxygen uptake and hydroperoxide buildup at the initial steps of initiated *n*-heptadecane oxidation.

At the same time, the results obtained show that the understanding of features of hydrocarbon oxidation at low oxygen concentrations requires the detailed investigation of the oxidation products, including hydroperoxides, low-molecular-weight products, and others, and the comparative study of the oxidation of hydrocarbons of other classes.

References

1. N. M. Emanuel´, E. T. Denisov, Z. K. Maizus, *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* [*Chain Reactions of Hydrocarbon Oxidation in the Liquid Phase*], Nauka, Moscow, 1965, 375 pp. (in Russian).
2. V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikov, I. V. Zakharov, A. A. Vichutinskii, V. F. Tsepalov, *Khemilyuminestsentnye metody issledovaniya medlennykh khimicheskikh protsessov* [*Chemiluminescence Methods of Investigation of Slow Chemical Processes*], Nauka, Moscow, 1966, 300 pp. (in Russian).
3. A. R. Forrester, I. M. Hay, R. U. Thomson, *Organic Chemistry of Stable Free Radicals*, Academic Press, London—New York, 1968, 405 pp.
4. E. T. Denisov, N. I. Mitskevich, V. E. Agabekov, *Mekhanizm zhidkofaznogo okisleniya kislorodnykh soedinenii* [*Mechanism of Liquid-Phase Oxidation of Oxygen-Containing Compounds*], Nauka i Tekhnika, Minsk, 1975, 334 pp. (in Russian).
5. W. Pritzkov, *Wissenhaftliche Zeitschrift*, 1985, **27**, No. 6, 702.
6. V. L. Antonovskii, S. L. Khursan, *Fizicheskaya khimiya organicheskikh peroksidov* [*Physical Chemistry of Organic Peroxides*], Akademkniga, Moscow, 2003, 390 pp. (in Russian).
7. E. T. Denisov, T. G. Denisova, *Handbook of Antioxidants: Bond Dissociation Energies, Rate Constants, Activation Energies and Enthalpies of Reactions*, CRC Press, Boca Raton, 2000, 289 pp.
8. E. T. Denisov, G. I. Kovalev, *Okislenie i stabilizatsiya reaktivnykh topliv* [*Oxidation and Stabilization of Reactive Fuels*], Khimiya, Moscow, 1983, 272 pp. (in Russian).

9. T. A. Bazanov, L. V. Petrov, B. L. Psikha, S. B. Psikha, V. M. Solyanikov, V. V. Kharitonov, *Khim. Fiz.* [*Chemical Physics*], 2009, **28**, No. 7, 42 (in Russian).
10. N. A. Sheikina, L. V. Petrov, B. L. Psikha, V. V. Kharitonov, V. A. Tyshchenko, T. N. Shabalina, *Neftekhimiya*, 2005, **45**, 310 [*Petroleum Chem.* (*Engl. Transl.*), 2003, **45**, 329].
11. V. V. Kharitonov, A. I. Stanilovskii, B. N. Zhitenev, Author´s Certificate No. 582 481 USSR; *Byul. Izobr.* [*Invention Bulletin*], 1977, 44 (in Russian).
12. V. V. Kharitonov, B. L. Psikha, *Khim. Fiz.* [*Chemical Physics*], 1989, **8**, 85 (in Russian).
13. S. I. Maslennikov, A. I. Nikolaev, V. D. Komissarov, *Kinet. Katal.*, 1979, **20**, 326 [*Kinet. Catal.* (*Engl. Transl.*), 1979, **20**].
14. A. I. Nikolaev, Author´s Abstract, Ph. D. (Chem.) Thesis, Institute of Chemical Physics, Chernogolovka, 1984, 18 pp. (in Russian).
15. A. I. Nikolaev, L. R. Enikeeva, R. L. Safiullin, *Khim. Fiz.* [*Chemical Physics*], 1984, **3**, 711 (in Russian).

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