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Mathematical Modeling of Action Mechanisms of Some Aromatic Amine Class Inhibitors for Polymers

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The kinetic rules of inhibited oxidation of *n*-hexadecane have been investigated in presence of aromatic amine inhibitors. The studies were carried out in autooxidative conditions at different rates of oxidation initiation. The study included a wide range of inhibitor concentrations and hydroperoxides at different partial pressures of oxygen. A mathematical model of the investigated process has been worked out that describes the main rules of the process and quantitatively predicts the experimental data.

KEY WORDS Antioxidants, aromatic amine inhibitors, peroxides

INTRODUCTION

Some Problems of Quantitative Characteristics and Selection of Highly Effective Antioxidants

Working time, exploitation conditions, quality of articles from hydrocarbon materials are generally defined by correct selection of optimal antioxidant. A lot of effort and means were spent for the solution of this problem. However, a theory of creation of antioxidants with defined activity is still absent. There are no methods of scientifically proven selection of antioxidants for the stabilization of organic substances in industry, processing, storing, and exploitation. Even antioxidant being selected correctly, the choice is to a considerable extent of chance character. High probability is left that there is another regulator somewhere that appears to be effective under these conditions.^{1–4}

It is not a chance situation, moreover, it is law-governed. Its causes are hidden in the complexity of the mechanism of chain oxidation process and the stabilization of organic substances. In an oxidizing system, tens of different, interdependable

reactions proceed simultaneously. Efficiency of an antioxidant is defined by the result of simultaneous proceeding of many reactions in which InH molecule, In[·] radical and other products of transformation participate. It is clear that for estimation of antioxidant effect the detailed quantitative information is necessary both about the mechanism of oxidation of material and the reactions with InH and In[·] participation in concrete oxidative conditions. All this should be taken into account such that even small changes of the conditions of oxidation (temperature, concentration of ingredients, special additions and admixtures) should lead to a noticeable change of oxidation mechanism—both the structure of reactions and their absolute and relative intensities.

The conclusion, important for correctly solving the problem, follows that the mechanism of oxidation of any substance is always concrete, i.e. correct only for those very conditions. Similarly, one antioxidant should have different efficiencies for both different substances and the same substance under different conditions of oxidation. Universal antioxidants do not exist. The best, most effective antioxidant for this concrete substance in definite conditions of oxidation is unique to a considerable degree. In this connection the principle difficulty of empiric selection of antioxidations becomes clear: it is impossible to try everything under all conditions. Therefore, the choice made is a result of chance to a considerable degree.

Our task is not to analyze in detail the existing methods of estimation of antioxidant quality. However, estimation, classification, and conclusions of the most general character are necessary. To the list of positive properties of the traditional methods of antioxidant-activity examinations, one should attribute their quickness and cheapness. These advantages distinguish the traditional examination methods from the tests conducted under conditions of exploitation. However, all these numerous and different methods have a general principal shortcoming—they do not fix information about mechanisms of reactions proceeding during the test. Values of just a couple of parameters are being determined from the results, for example, induction period (τ), which have too general a character. Such methods of estimation allow arrangement of all the tested antioxidants in a row according to the "activity" (for example, according to τ increase). It allows for selecting the best of them for concrete test conditions. However, even small changes in conditions (temperature, concentration of antioxidant) would lead to unpredictable changes in the built row "according to activity," and all the tests should be performed from the very beginning. This is one of the main reasons that the tremendous amount of experimental material had not led to creation of a theory of directed synthesis and selection of antioxidants. Until now there were no trustworthy criteria of a priori estimation and prognosis of their efficiency. Nevertheless, the necessity of prognosis does exist because conditions of laboratory tests always differ from real conditions of exploitation. Meanwhile, standard tests should not be transformed into scientific research of the mechanisms of inhibited oxidation. It would demand highly qualified personnel and complicated equipment, thereby sacrificing quickness and increasing the cost of the test sharply. This situation seriously decelerates technical progress.

The analysis performed leads to the following conclusion: a new complex of test methods is badly needed that would receive all the necessary information on the

mechanisms of antioxidant action efficiently. As a result of such tests, the mechanisms of antioxidant action in concrete conditions should be identified. All the reactions influencing its efficiency should be characterized reliably on a quantitative level. The volume and accuracy of received data should guarantee the possibility of prognosis: how the efficiency of antioxidant should change according to changes of conditions of its use.

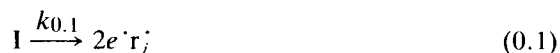
To solve this problem, we have developed new equipment, methodology, and methods of investigation. According to our methodologists the mathematical model of considered process is the result of investigation. It contains concise information about the mechanism of oxidation of a concrete medium and the mechanism of action of an inhibitor under concrete conditions, in the form of totality of kinetic parameters, which characterize quantitatively all the key reactions of the process under investigation. Representing versatile characteristics of the process, the mathematical model performs deep investigations of its properties and specificities by calculations, including prognosticating behavior of the system under changes of oxidation conditions.

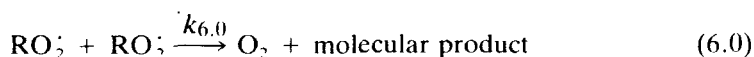
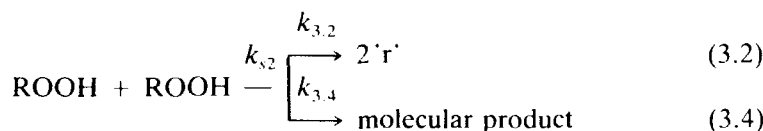
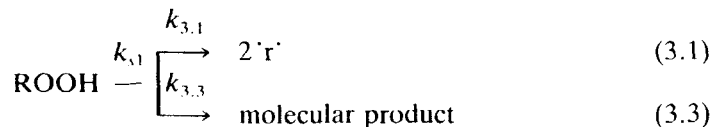
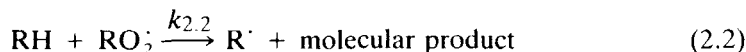
Thus, mathematical modeling represents an important instrument of investigation, and its development is a necessary stage in the study of processes of inhibited oxidation. The task of the present work lies in investigation of the acting mechanisms of four inhibitors with approximately similar structure of aromatic amine class on the level of mathematical models: Naugard 1–4, Naugard R, Naugalube 640, Naugalube 680. The investigation was performed in oxidizing *n*-hexadecane at 140°C.

STATEMENT OF THE PROBLEM

The study of inhibited oxidation is usually performed in two stages. At the first stage the investigation of the mechanism of oxidation of hydrocarbon medium is being carried out, and at the second one—the investigation of inhibitor acting mechanism in this medium. Let us consider these two stages in consecutive order.

Common scheme of hydrocarbon oxidation at non-deep stages is the basis of investigation on the first stage:





Here RH—oxidizable medium, I—initiator, $r \cdot$ —radical of any structure, different from $r_i \cdot$, $\text{R} \cdot$, $\text{RO}_2 \cdot$. The scheme includes: 1) reactions of chain formation (0.0)–(0.3), a spontaneous one (0.0) and on initiator (0.1); 2) reactions of chain propagation (2.1)–(2.2). In this case it has been taken into account, that not all the consumed oxygen could be transformed to hydroperoxide (2.2); 3) reactions of degenerative branching on hydroperoxides by first and second orders (3.1), (3.2), and of additional expense of ROOH by first and second orders (3.3), (3.4) either; and 4) reactions of quadratic chain termination (6.0).

This process proceeds in a quazistationar regime by concentrations of radicals $r_i \cdot$, $r \cdot$, $\text{R} \cdot$, $\text{RO}_2 \cdot$ and is fully characterized by nine kinetic parameters, which can be presented as following:

1) $k_{0.1}$, e —constant of initiator decomposition and probability of its radicals going out into volume.

2) $W_o = 2 \cdot k_{0.0} [\text{RH}]_o$ —the rate of radical formation without calculation of ROOH decomposition.

3) $P_2 = k_{2.1}/k_{2.1} + k_{2.2}$ —part of reactions of chain propagation, proceeding with ROOH formation.

4) $P_6 = 2 \cdot k_6 / (k[\text{RH}])^2$ —parameter of quadratic termination of $\text{RO}_2 \cdot$ radicals.

5) $P_{3.1} = k_{3.1} \cdot P_2$ —parameter of degenerative branching by 1st order by ROOH.

6) $P_{3.2}$ —parameter of degenerative branching by 2nd order by ROOH.

7) $k_{3.1}$ —constant of total expense of hydroperoxide by 1st order.

8) $P_{3.2} = k_{3.2} \cdot P_2$ —parameter of total expense of hydroperoxide by 2nd order.

Initiator constants $k_{0.1}$ and e should be determined preliminarily from an independent experiment and are considered known in further investigation.

System of equations, corresponding to oxidation scheme (0.0)–(6.0) can be presented as following:

$$v = v_1 - 0,5 \cdot P_6 v_2^2 + 0,5 \cdot w_o \quad (1)$$

$$v_1 = (1 - q) \cdot v_2 + P_6 v_2^2 \quad (2)$$

$$w_s = P_6 v_2^2 \quad (3)$$

$$\dot{y}_p = (1 - q) \cdot v_2 - k_{s1} y_p - 2 \cdot P_{s2} y_p^2; \quad y_p(0) = y_p^o \quad (4)$$

$$\dot{q} = (0,5 \cdot w_o + v_1) / [\text{RH}]_o; \quad q(0) = 0 \quad (5)$$

Here the following notations have been introduced:

$$v = k_{0,0}[\text{RH}][\text{O}_2] + k_2[\text{RH}][\text{RO}_2] - k_6[\text{RO}_2]^2 \quad (6)$$

$$v_1 = k_1[\text{O}_2][\text{R}\cdot] \quad (7)$$

$$v_2 = k_2[\text{RH}]_o[\text{RO}_2] \quad (8)$$

$$y_p = [\text{ROOH}] / P_2 \quad (9)$$

$$q = ([\text{RH}]_o - [\text{RH}]) / [\text{RH}]_o \quad (10)$$

$$w_s = w_o + w_i + w_y \quad (11)$$

$$w_i = 2 \cdot e \cdot k_{0,1}[\text{I}] \quad (12)$$

$$w_y = 2 \cdot P_{3,1} y_p + 2 \cdot P_{3,2} y_p^2 \quad (13)$$

The introduced variables have simple physical sense: v —rate of oxygen consumption; v_1 —reaction rate (1.0); v_2 —total initial rate of reactions (2.1) and (2.2); y_p —reduced concentration of hydroperoxides; q —depth of transformation of oxidizing substance; w_s —total rate of initiation; w_i —initiation rate, conditioned by initiator; w_y —rate of degenerative branching.

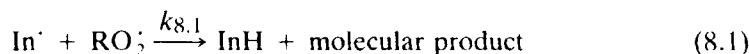
System (1)–(5) does not contain equations concerning concentration of solved oxygen $[\text{O}_2]$, because it is being held constant during the experiment: $[\text{O}_2] = \text{constant}$.

During investigation of oxidation of a concrete substance in concrete conditions, it is necessary, first of all, to determine if the supposed scheme is in accordance with the process under investigation. And if so, which reactions from the scheme play essential roles, and which do not, i.e. to perform identification of the mech-

anism. Second of all, numerical values of parameters, which really define the oxidation process, should be determined.

We have worked out methods of identification of oxidation mechanisms and determination of kinetic parameters by kinetics of oxygen consumption.⁵ The methods have proven useful during investigation of hydrocarbon materials of different structures, including individual hydrocarbons *n*-heptadecane⁶ and *n*-pentadecane.⁷

The next stage of the investigation is identification of the mechanisms of inhibitor action and determination of its quantitative characteristics. As the mechanism of breaking is unknown beforehand, we will consider as initial approximation, the following scheme of transformations, which have been advantageous during the investigation of inhibitors of steric hampered phenol and aromatic amine nature:



The scheme includes:

1) Reactions (7.0), (7.1), (7.2) of inhibitor molecules InH with radicals RO_2 , R^\cdot , r_i^\cdot . These reactions define the intensity of retardant influence of inhibitor.

2) Reactions (8.0), (8.1) of inhibitor radical In^\cdot with peroxyradical RO_2 . The presence of reaction (8.1) with regeneration of the initial inhibitor molecule in acts of chain termination increases the duration of retardance.

3) Reactions (-7.0), (9.0), (10.0) of In^\cdot radical, weakening retardant influence of inhibitor.

Process (7.0)–(10.0) proceeds in quazistationar regime by concentration of In^\cdot radical and is characterized quantitatively by the following kinetic parameters:

$$\begin{aligned}
 P_{7.0} &= \frac{k_7}{k_2[\text{RH}]_o} & P_{7.1} &= \frac{k_{7.1}}{k_1[\text{O}_2]} & P_{7.2} &= \frac{k_{7.2}}{k_{0.3}[\text{RH}]_o} \\
 P_8 &= \frac{k_{8.0}}{k_{8.0} + k_{8.1}} & P_{-7} &= k_{-7} \cdot C & P_9 &= 2 \cdot k_9 \cdot C^2 \\
 P_{10} &= k_{10} \cdot [\text{RH}]_o \cdot C & & & \text{Notation: } C &= \frac{k_2[\text{RH}]_o}{k_{8.0} + k_{8.1}}.
 \end{aligned}$$

The system of equations, describing the whole process of inhibited oxidation (0.0)–(10.0), looks like:

$$v = v_1 - 0,5 \cdot P_6 v_2^2 + 0,5 \cdot w_o \quad (14)$$

$$v_1 = (1 - q) \cdot v_2 + P_6 v_2^2 + P_{7.0} v_2 z - P_{-7} xy + v_2 x \quad (15)$$

$$w_s = P_6 v_2^2 + 2 \cdot v_2 x + P_9 x^2 \quad (16)$$

$$\begin{aligned}
 P_{7.0} v_2 z + P_{7.1} v_1 z + P_{7.2} w_i z / (1 - q + P_{7.2} z) \\
 = P_{-7} xy + v_2 x + P_9 x^2 + P_{10} (1 - q) x \quad (17)
 \end{aligned}$$

$$\dot{y} = P_2 (1 - q) \cdot v_2 - k_{s1} y - 2 \cdot k_{s2} y^2 + P_{7.0} v_2 x - P_{-7} xy \quad (18)$$

$$\dot{z} = -(P_8 v_2 x + P_9 x^2) \quad (19)$$

$$\dot{q} = (0,5 \cdot w_o + v_1) / [\text{RH}]_o \quad (20)$$

$$y(0) = y_o; \quad z(0) = z_o; \quad q(0) = 0 \quad (21)$$

Along with notations (6)–(13) the following ones have been introduced:

$$x = [\text{In.}] \cdot (k_{8.0} + k_{8.1}) / k_2 [\text{RH}]_o \quad (22)$$

$$z = [\text{InH}] \quad (23)$$

Instead of reduced concentration of hydroperoxides, y_p has been introduced:

$$y = [\text{ROOH}] \quad (24)$$

The expression for w_y changes correspondingly:

$$w_y = 2 \cdot k_{3.1} y + 2 \cdot k_{3.2} y^2 \quad (25)$$

During investigation of acting mechanisms of a concrete inhibitor, it should be cleared up which of supposed reactions (7.0)–(10.0) play the essential role, i.e. to identify mechanism of breaking and to determine corresponding kinetic parameters.

We have worked out the methods of identification of inhibitor acting mechanism

and determination of kinetic parameters by the kinetics of oxygen consumption.⁸ With the help of these methods, a number of inhibitors from the class of steric-hampered phenols⁹ and aromatic amines¹⁰ were investigated successfully. However, at further investigations the necessity can appear to supplement the initial scheme of reactions by new stages, in particular, by reactions with participation of products of initial inhibitor transformation.

EXPERIMENTAL

n-Hexadecane (HD) was used, which was subjected to following purification. HD was shaken consecutively with alkaline potassium permanganate, sulphuric acid, oleum, and washed after each operation from corresponding reagents with distilled water. HD, purified in this way, was dried above sodium sulphate, and then above calcium hydride and was being distilled in inert gas current (argon) in vacuum. After purification, HD contained not more than 10^{-4} mole/l of hydroperoxides and 10^{-5} mole/l of double bonds.

Cumyl peroxide recrystallized twice from ethanol was used as an initiator.

Other reagents and solvents were used either without additional purification or were purified in usual ways.

Investigation was performed at 140°C. Quantity of oxygen absorbed during oxidation and quantity of hydroperoxides stored in the system during heating by the initial moment of registration of experimental data and concentration of hydroperoxides at the end of the experiment either have been measured experimentally.

Kinetic curves of oxygen absorption during HD oxidation were received with the help of a special manometric device.¹¹ After each experiment, preliminary treatment of experimental data was being performed—differentiation and smoothing of kinetic curves. As a result, in each experiment the dependence of oxidation rate on time $v(t)$ was calculated, and then used for identification of process mechanisms and determination of kinetic parameters.

To obtain a mathematical model of *n*-hexadecane oxidation, a single experiment on auto-oxidation of the initial sample with the minimal content of hydroperoxides (Figures 1 and 2) and a series of experiments on initiated oxidation with different rates of initiation W_i (Figures 3 and 4) have been performed. A series of experiments on auto-oxidation of preliminary oxidized samples with different content of hydroperoxides was also performed (Figures 5 and 6).

To investigate the breaking mechanisms of inhibitors, four series of experiments were performed. Kinetics of oxygen absorption was measured depending on the following initial conditions:

1) The initial concentration of inhibitor $[\text{InH}]_0$ at a definite rate of initiation, $W_i = 1 \cdot 10^{-6}$ mole/l·sec (Figures 7 and 8, 11–16)—for Naugard 1-4 inhibitor, experiments with $W_i = 2,5 \cdot 10^{-7}$ mole/l·sec were also performed (Figures 9 and 10).

2) The rate of initiation W_i at a definite, rather large concentration of inhibitor $[\text{InH}]_0$ (Figures 17–20)—for Naugalube 640 and Naugalube 680, $[\text{InH}]_0 = 5 \cdot 10^{-2}$ mole/l was taken, and for Naugard 1-4 and Naugard R it was $[\text{InH}]_0 = 5 \cdot 10^{-3}$ mole/l, because at larger concentrations of these inhibitors oxidation rate is close to zero and is hard to measure.

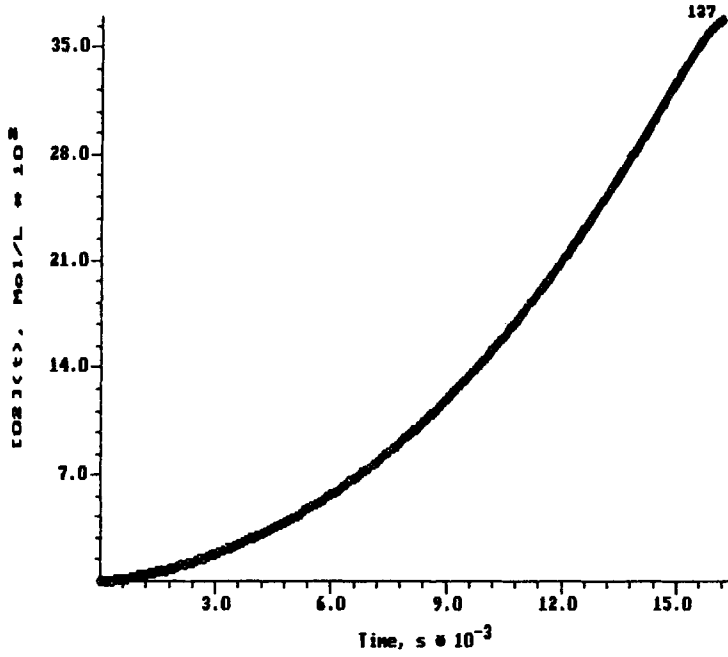


FIGURE 1 Hexadecane $T = 140$ auto-oxidation $ROOH_0 = 0$.

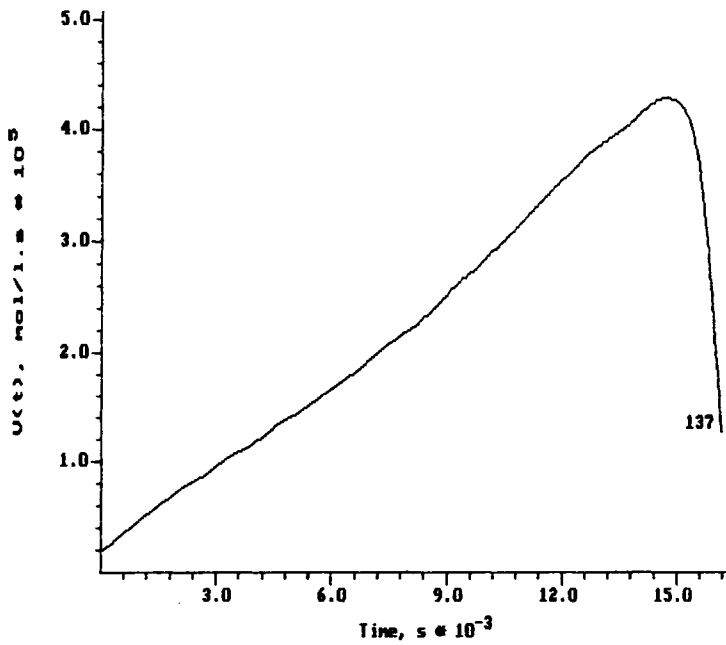
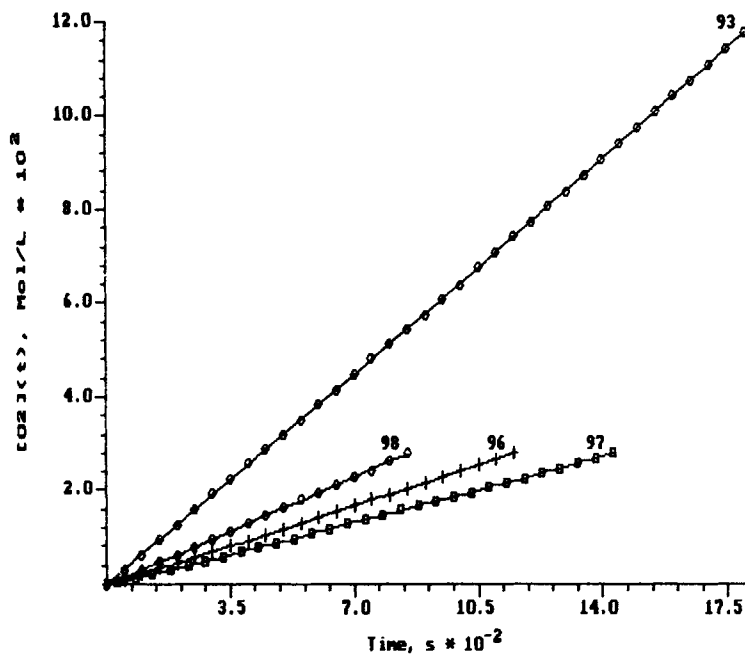
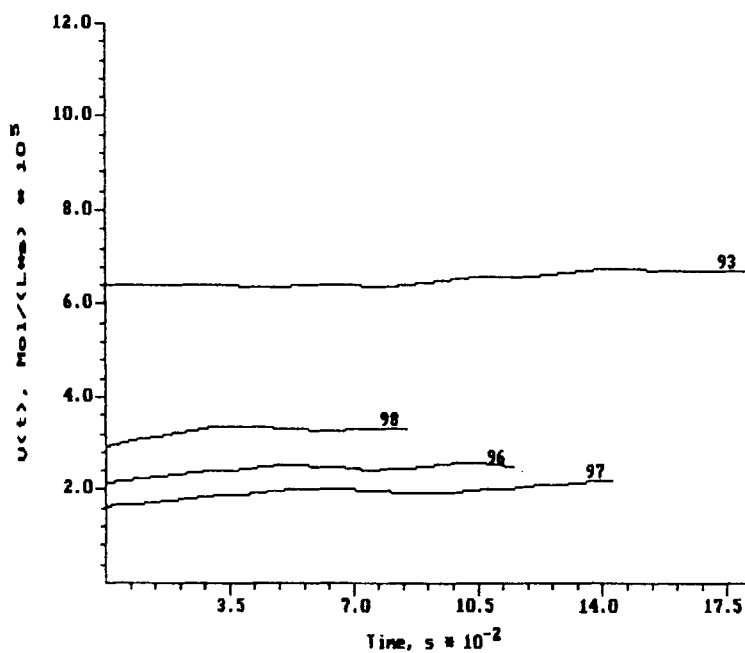


FIGURE 2 Hexadecane $T = 140$ auto-oxidation $ROOH_0 = 0$ $v(t) = d[O_2]/dt$.

FIGURE 3 Hexadecane $T = 140$ $W_i = (1, 2, 4, 16.7)e-6$.FIGURE 4 Hexadecane $T = 140$ $W_i = (1, 2, 4, 16.7)e-6$ $v(t) = d[O_2]/dt$.

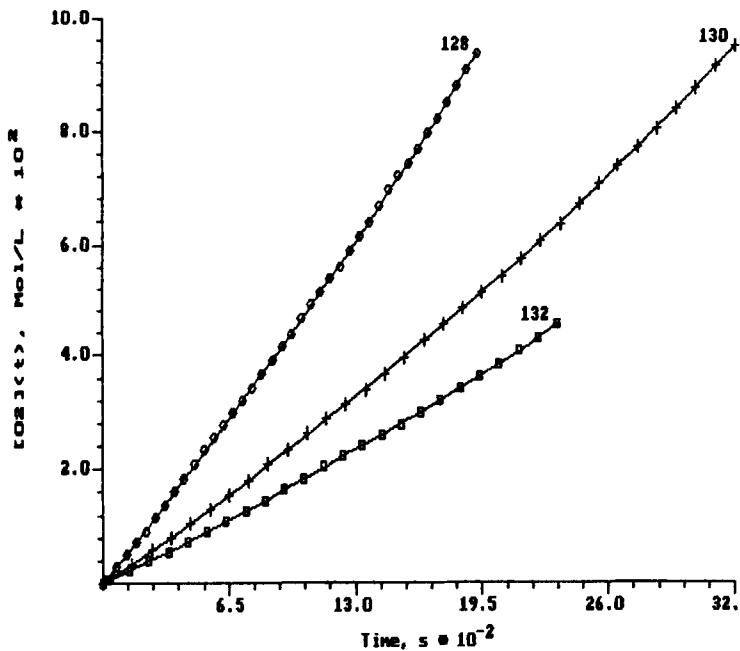


FIGURE 5 Hexadecane $T = 140$ auto-oxidation $\text{ROOH}_0 = (4, 8, 21)e-2$.

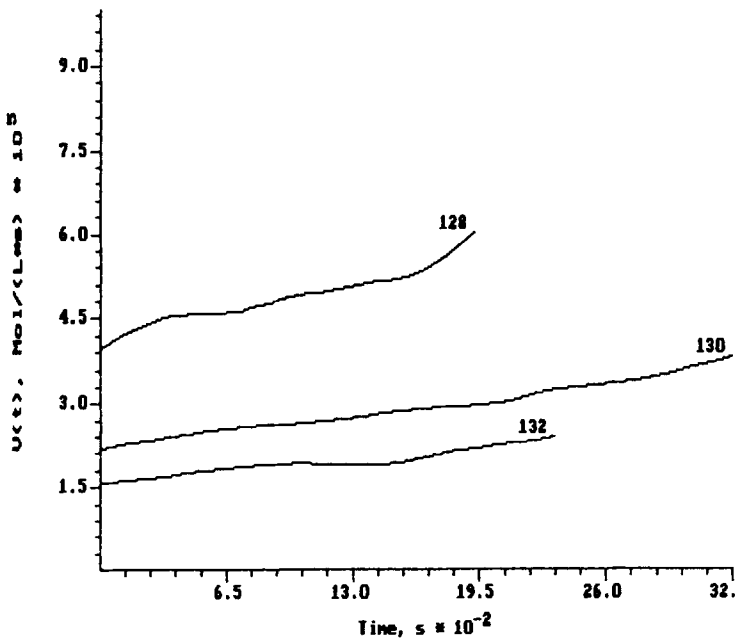


FIGURE 6 Hexadecane $T = 140$ (auto-oxidation $\text{ROOH}_0 = (4, 8, 21)e-2$) $v(t) = d[\text{O}_2]/dt$.

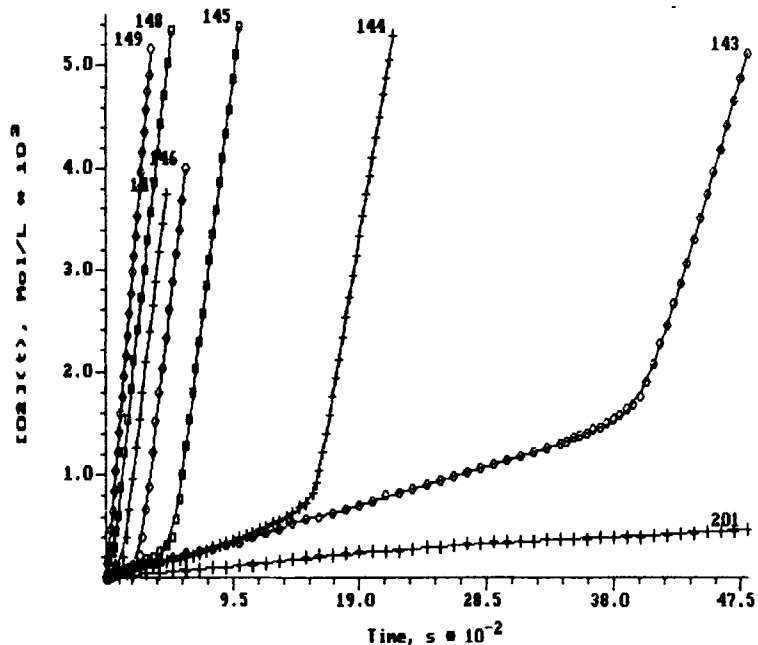


FIGURE 7 Naug-1-4 hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = (0, 0.25-50)e-4$.

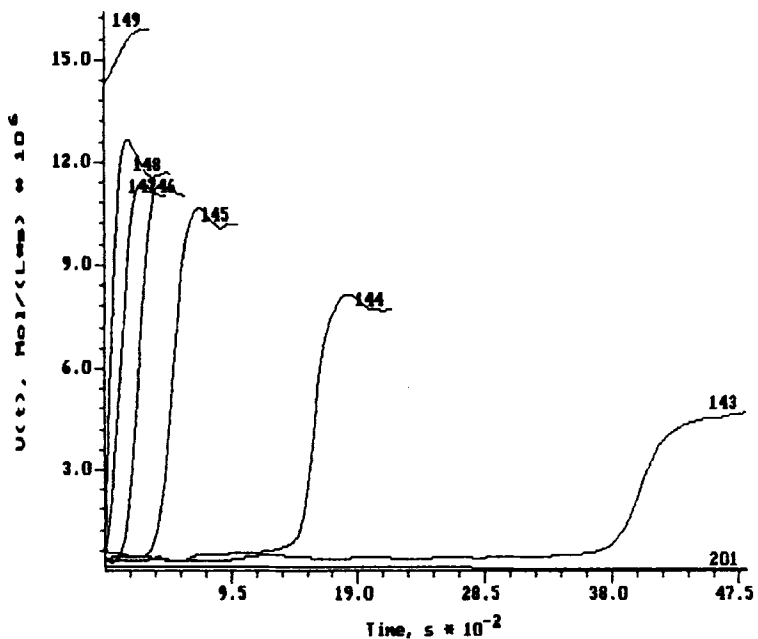


FIGURE 8 Naug-1-4 hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = (0, 0.25-50)e-4$.

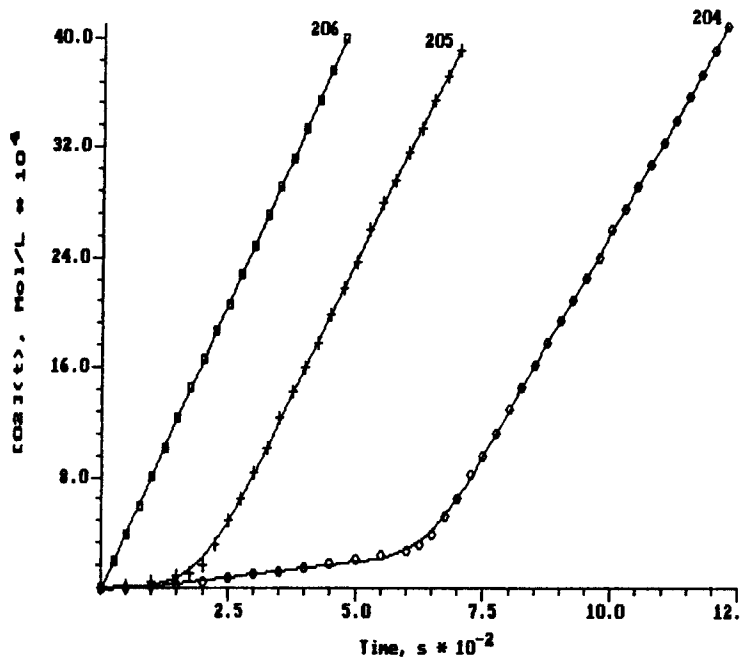


FIGURE 9 Naug₁₋₄ hexadecane $T = 140$ $W_i = 0.25e-6$ $\ln H = (0, 2.5, 5)e-5$.

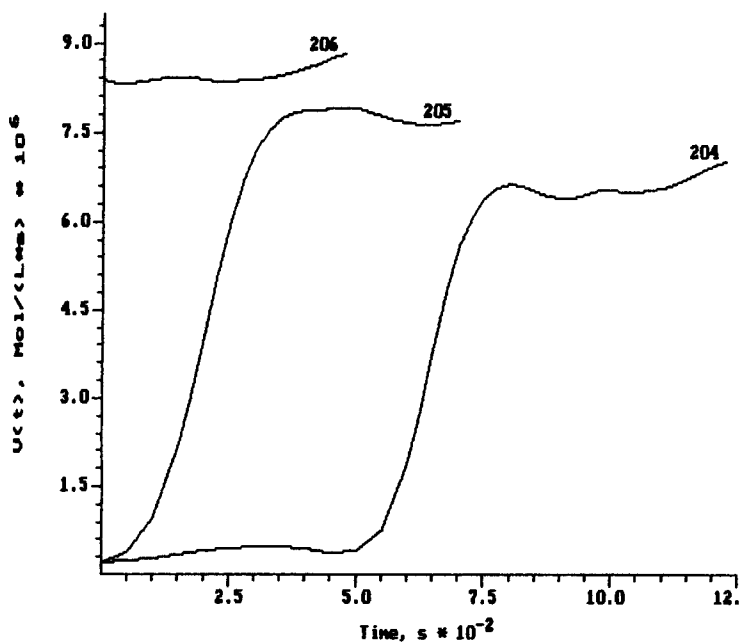


FIGURE 10 Naug₁₋₄ hexadecane $T = 140$ $W_i = 0.25e-6$ $\ln H = (0, 2.5, 5)e-5$ $v(t) = d[O_2]/dt$.

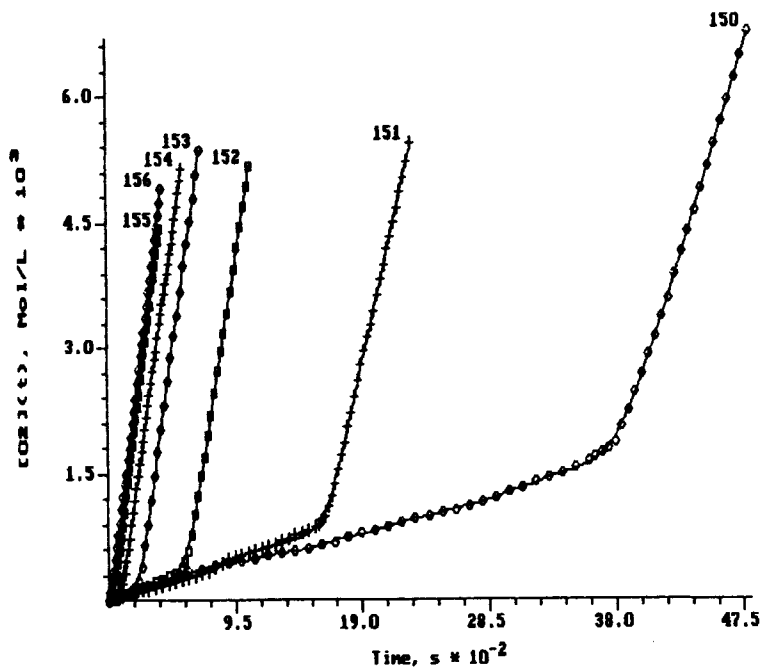


FIGURE 11 Naug_R hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = (0.1-50)e-4$.

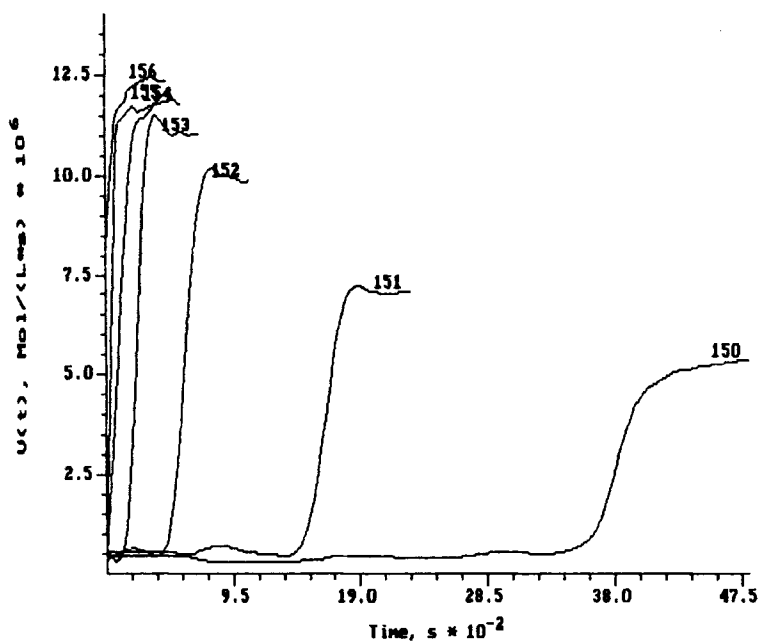


FIGURE 12 Naug_R hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = (0.1-50)e-4$ $v(t) = d[O_2]/dt$.

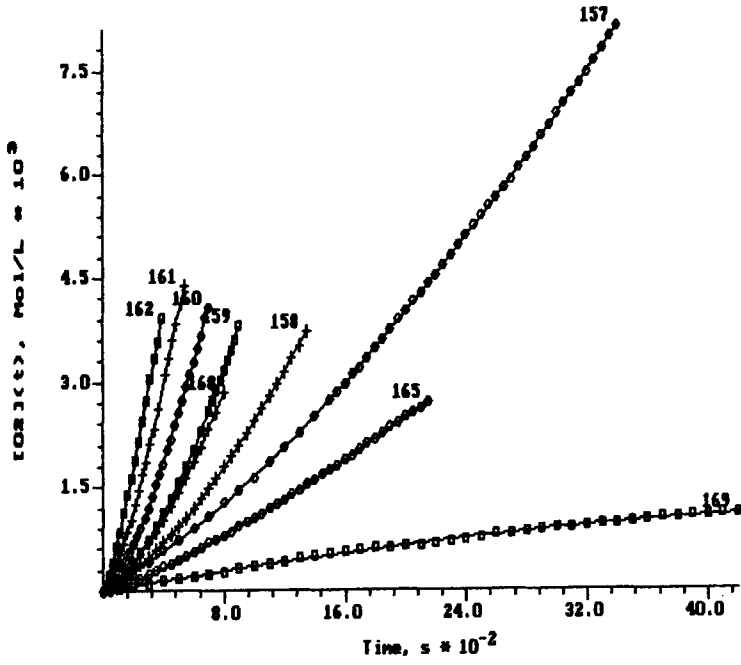


FIGURE 13 Naug_640 hexadecane $T = 140$ $W_i = 1e-6$ $\ln H = (0.2-500)e-4$.

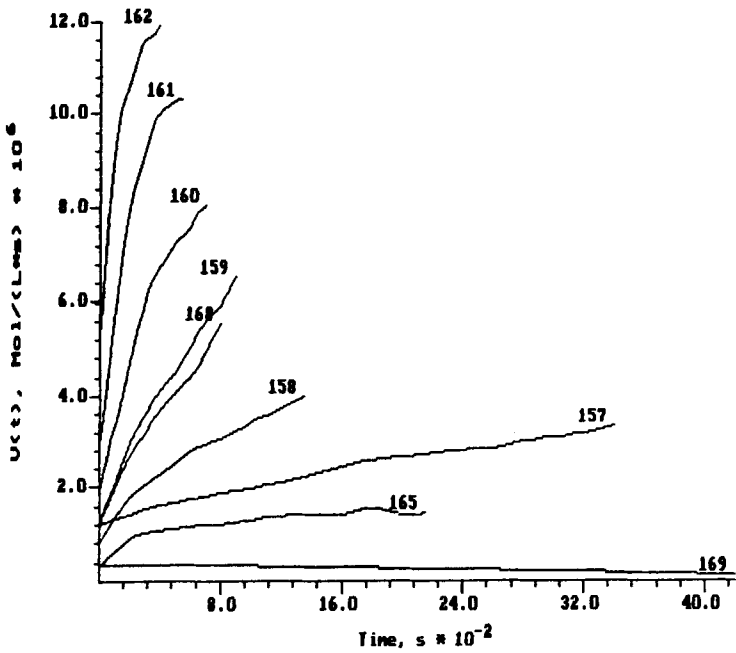


FIGURE 14 Naug_640 hexadecane $T = 140$ $W_i = 1e-6$ $\ln H = (0.2-500)e-4$ $v(t) = d[O_2]/dt$.

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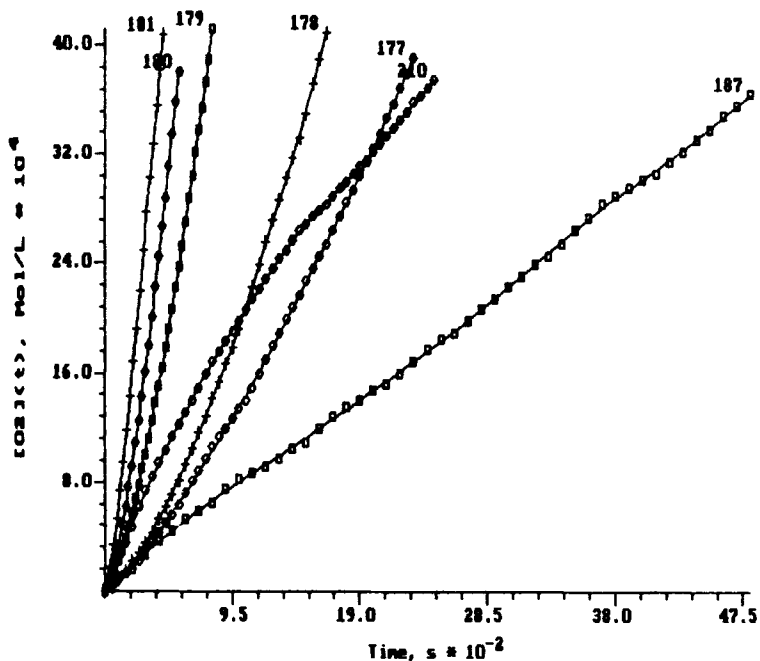


FIGURE 15 Naug_680 hexadecane $T = 140$ $W_1 = 1e-6 \ln H = (0.4-500)e-4$.

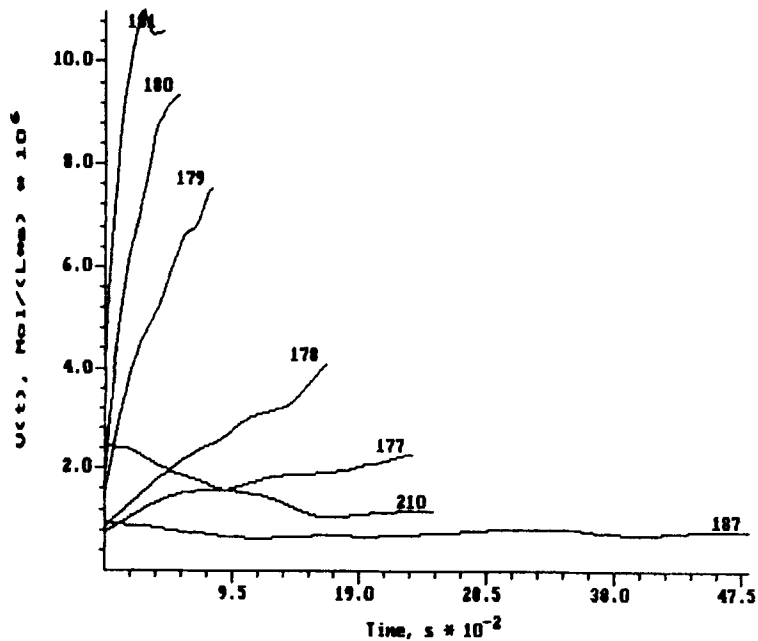


FIGURE 16 Naug_680 hexadecane $T = 140$ $W_1 = 1e-6 \ln H = (0.4-500)e-4$ $v(t) = d[O_2]/dt$.

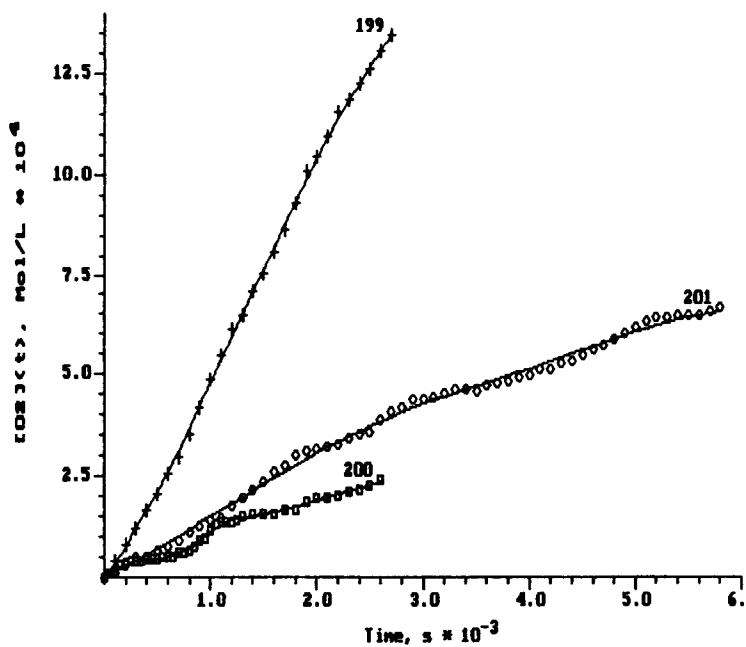


FIGURE 17 Naug_1-4 hexadecane $T = 140$ InH $= 5e-3$ $W_i = (0.5, 1, 3)e-6$.

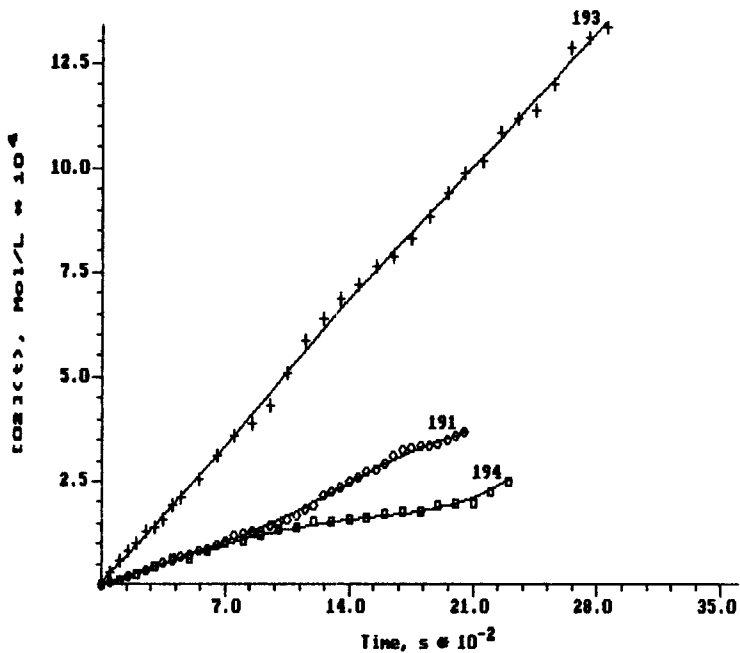


FIGURE 18 Naug_R hexadecane $T = 140$ InH $= 5e-3$ $W_i = (0.5, 1, 3)e-6$.

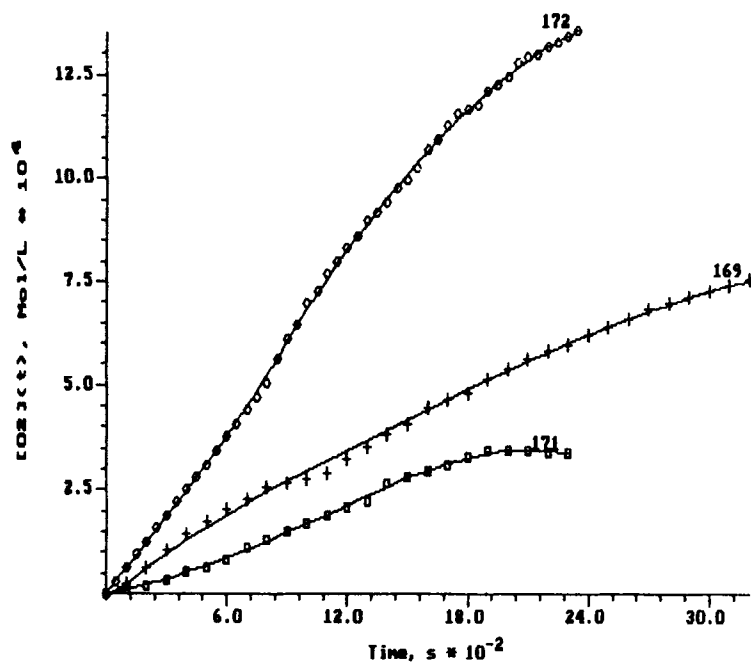


FIGURE 19 Naug_640 hexadecane $T = 140$ InH = $5e-3$ W, = (0.5, 1, 3)e-6.

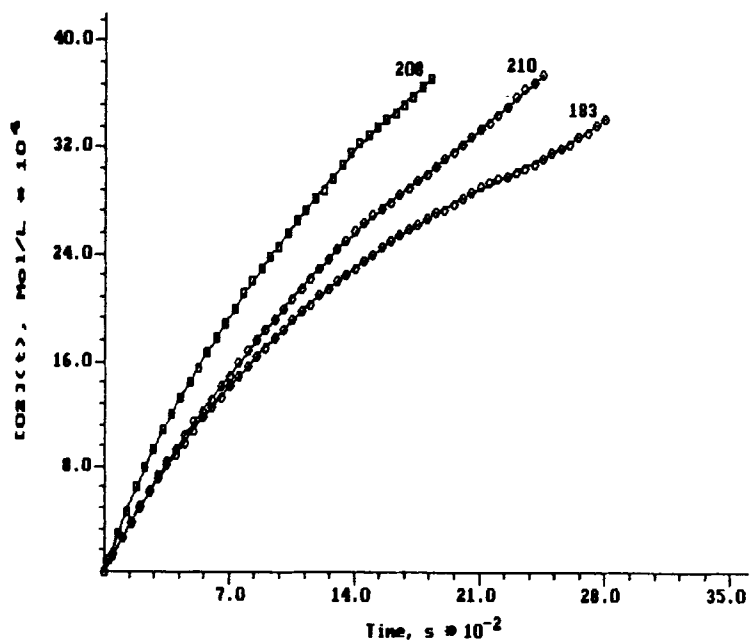


FIGURE 20 Naug_680 hexadecane $T = 140$ InH = $5e-2$ W, = (0.5, 1, 3)e-6.

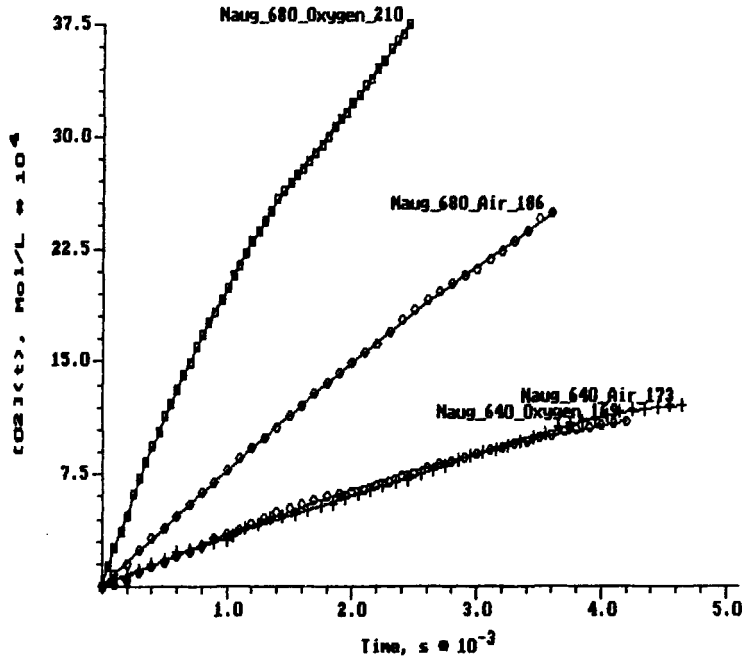


FIGURE 21 Naug_640 & Naug_680 oxygen & air $W_i = 1e-6$ InH = $5e-2$.

3) Partial oxygen pressure at a large $[\text{InH}]_o$. One control experiment in air was made for each inhibitor. Among four investigated inhibitors, only for the Naugalube 680 did the decrease of partial pressure of oxygen lead to decrease of oxidation rate. Figure 21 shows the data for Naugalube 640 and Naugalube 680 for comparison.

Concentration of hydroperoxides $[\text{ROOH}]_o$ in specially oxidized samples of *n*-hexadecane at definite $[\text{InH}]_o$ (Figures 22–29).

ANALYSIS AND TREATMENT OF EXPERIMENTAL DATA

Mathematical Model of Oxidation of *n*-Hexadecane at 140°C.

For the identification of oxidation mechanisms of *n*-hexadecane and determination of kinetic parameters, the following experimental data have been used:

- 1) The dependence of oxidation rate on time $v(t)$ in the experiment of auto-oxidation of the initial sample of *n*-hexadecane (experiment 137).
- 2) Dependences $v(t)$ in experiments of initiated oxidation of *n*-hexadecane at $w_i = (1, 2, 4) \cdot 10^{-6}$ mole/l/sec (experiments 96, 97, 98).
- 3) Values of concentrations of hydroperoxides accumulated by experiments 96, 97, 98.

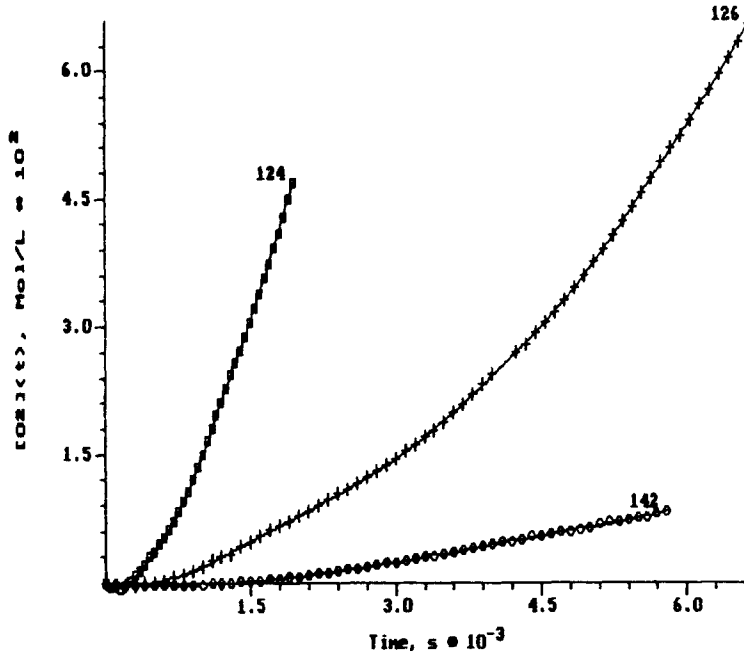


FIGURE 22 Naug-1-4 hexadecane $T = 140$ $\ln H = 8e-4$ $ROOH = (45, 103, 218)e-3$.

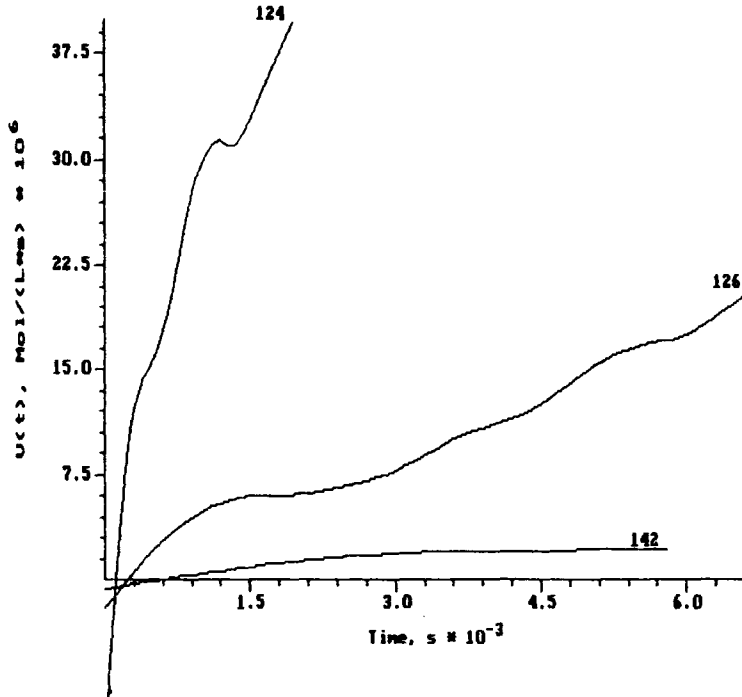


FIGURE 23 Naug-1-4 hexadecane $\ln H = 8e-4$ $ROOH = (45, 103, 218)e-3$ $v(t) = d[O_2]/dt$.

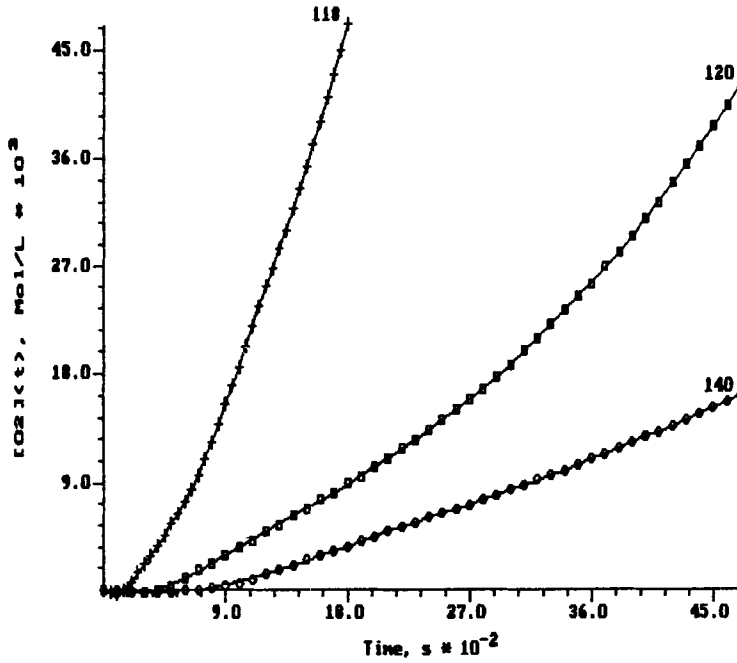


FIGURE 24 Naug_R hexadecane $T = 140$ InH = $5e-4$ ROOH = (60, 100, 203)e-3.

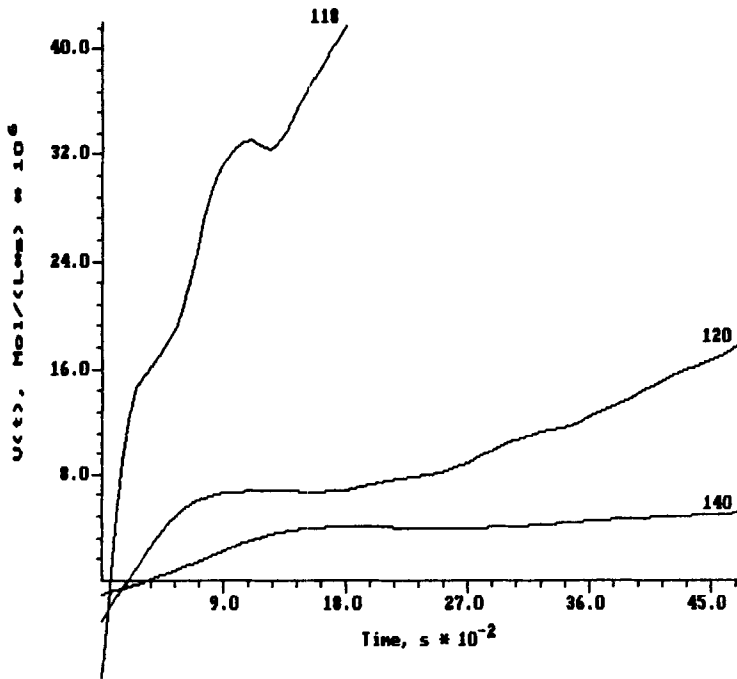


FIGURE 25 Naug_R hexadecane InH = $5e-4$ ROOH = (60, 100, 203)e-3 $v(t) = d[O_2]/dt$.

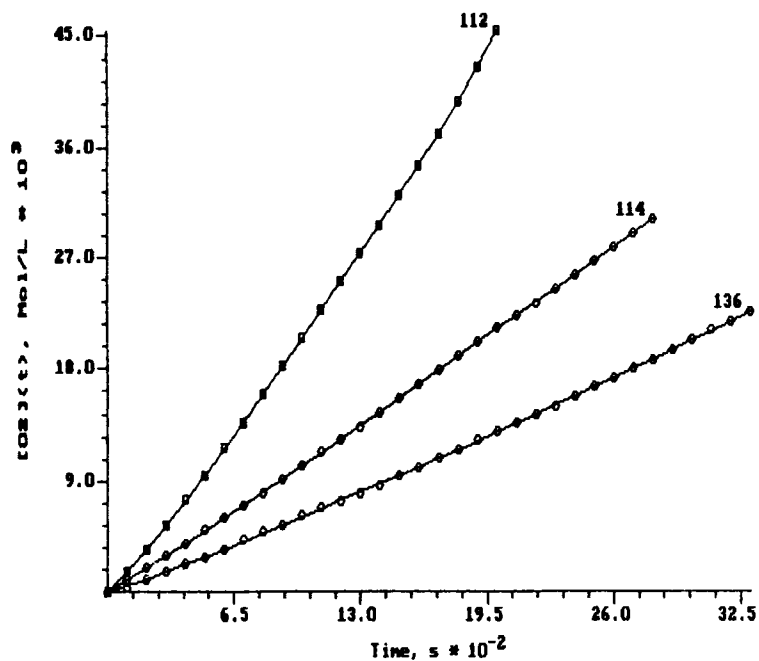


FIGURE 26 Naug_640 hexadecane $T = 140$ InH = $5e-4$ ROOH = $(50, 96, 198)e-3$.

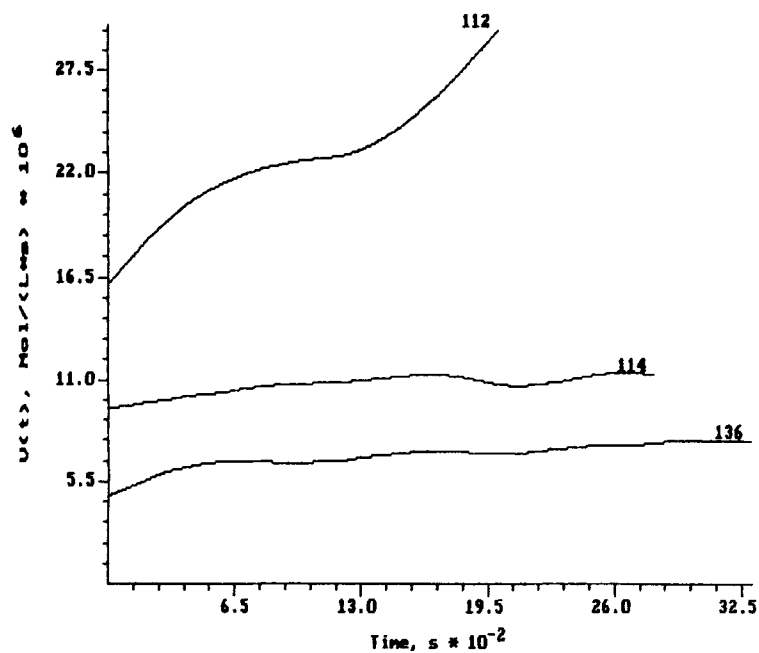


FIGURE 27 Naug_640 hexadecane InH = $5e-4$ ROOH = $(50, 96, 198)e-3$ $v(t) = d[O_2]/dt$.

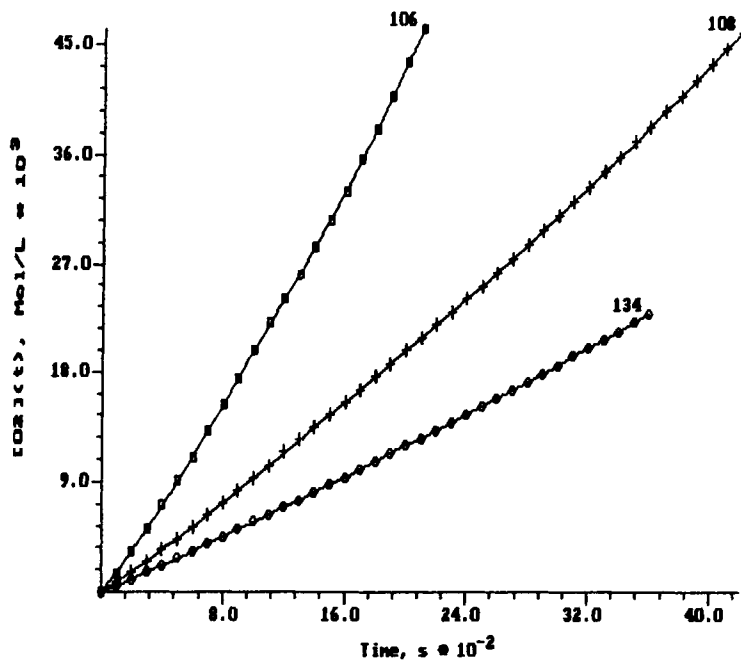


FIGURE 28 Naug_680 hexadecane $T = 140$ InH = $5e-4$ ROOH = $(50, 101, 209)e-3$.

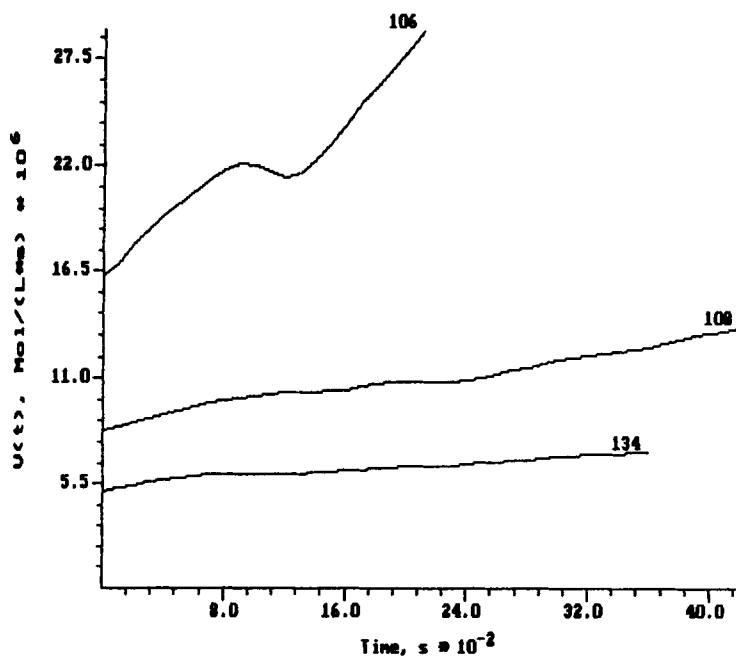


FIGURE 29 Naug_680 hexadecane InH = $5e-4$ ROOH = $(50, 101, 209)e-3$ $v(t) = d[O_2]/dt$.

The following values of parameters have been found as a result of treatment of these data:

$$P_0 = (4.21 \pm 0.08) \cdot 10^3$$

$$W_0 = (1.72 \pm 0.10) \cdot 10^{-8}$$

$$P_{3.1} = (9.64 \pm 0.12) \cdot 10^{-6}$$

$$P_{3.2} = (1.82 \pm 0.02) \cdot 10^{-5}$$

$$k_{s1} = (2.56 \pm 0.17) \cdot 10^{-5}$$

$$P_2 = 0.82 \pm 0.02$$

It is seen that nearly all the reactions of the proposed scheme (0.0)–(6.0) play an essential role. The reaction (3.4) is the only exception: it does not manifest itself with the depth of oxidation reached in experiment.

To control the results, the obtained values of the parameters were put into the equation system (1)–(5), and the kinetic curves of the oxygen absorption were calculated. Figures 30–33 show the comparison of all the experimental data on oxidation with calculations. Down to a definite depth of oxidation, the calculations

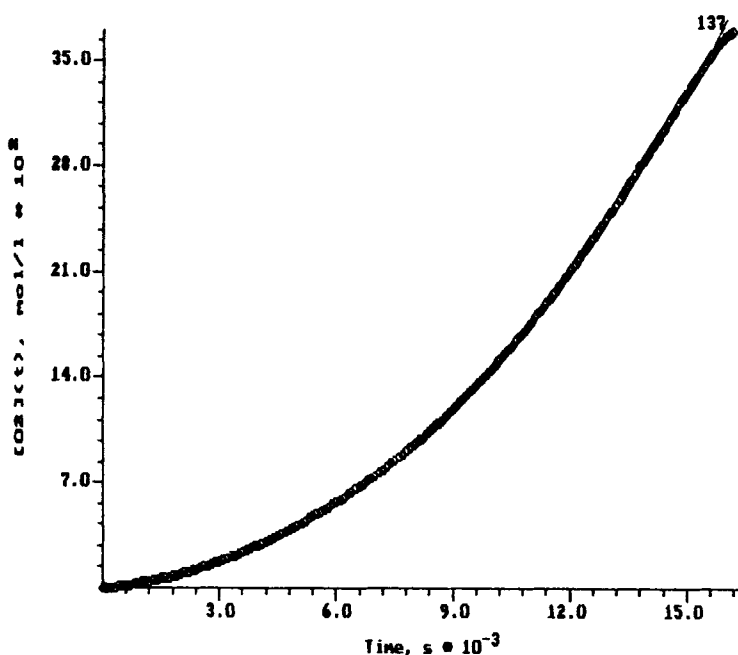


FIGURE 30 Hexadecane $T = 140$ auto-oxidation $\text{ROOH}_0 = 0$ experiment & calculation.

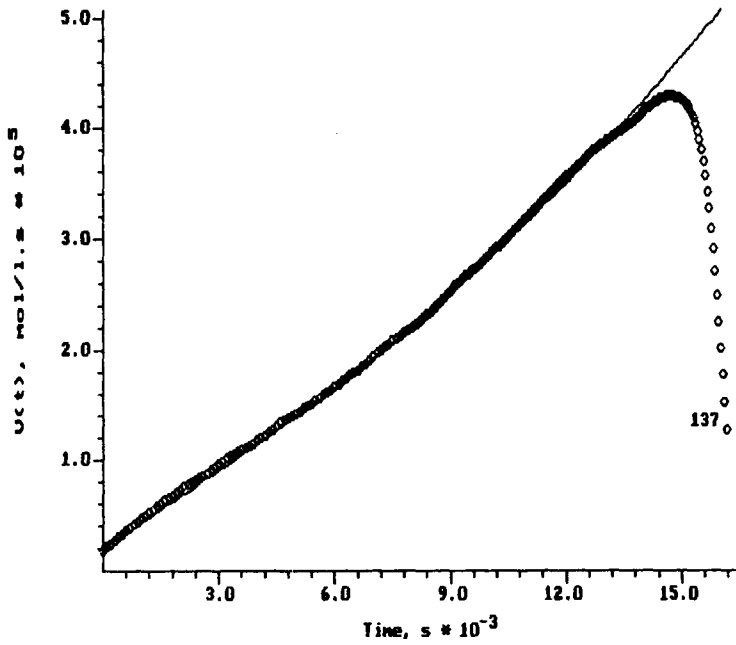


FIGURE 31 Hexadecane $T = 140$ auto-oxidation $ROOH_0 = 0$ experiment & calculation.

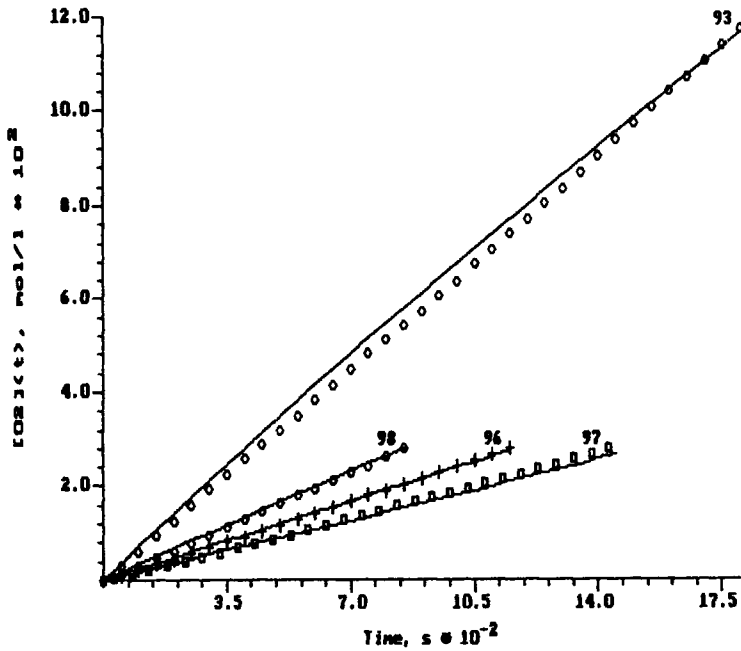


FIGURE 32 Hexadecane $T = 140$ $W_i = (1, 2, 4, 16.7)e-6$ experiment & calculation.

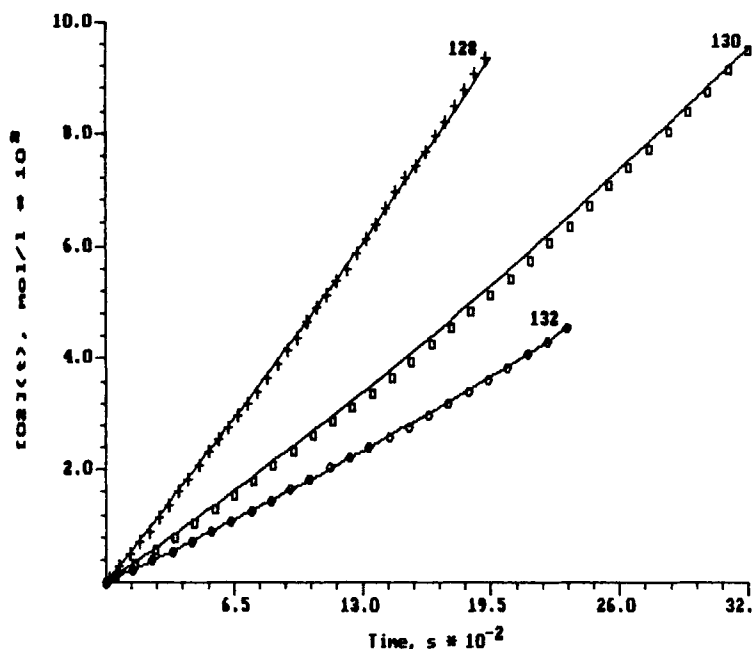


FIGURE 33 Hexadecane $T = 140$ ROOH = $(4.8, 20)e^{-2}$ experiment & calculation.

correctly describe both the main experimental data, used in the treatment, and the independent experiment (experiments 93, 128, 130, 132), until the scheme (0.0)–(6.0) corresponds to mechanism of the process. It allows to conclude that the mechanism of hexadecane oxidation at 140°C has been identified correctly and the kinetic parameters have been found with sufficient accuracy.

Preliminary Identification of Action Mechanism of Inhibitors

Preliminary identification means clarifying the role of reactions (7.1), (7.2), (10.0) in breaking mechanisms of inhibitors under investigation. It is easy to show that the reaction (7.1) being present, the oxidation rate $v(t)$ is larger, the higher the concentration of solved oxygen $[\text{O}_2]$. A series of experiments in air showed that for inhibitors Naugard 1–4, Naugard, R and Naugalube 640, reaction (7.1) is absent. For Naugalube 680, the decrease of partial pressure of oxygen leads to the decrease of oxidation rate (Figure 21). In the framework of the supposed scheme (7.0)–(10.0), it is simply explained by the presence of the reaction (7.1). However, it seems strange that the change of structure of the inhibitor molecule from Naugalube 640 to Naugalube 680 has led to the appearance of the reaction (7.1). Analogous behavior of experiment 210 ($[\text{InH}]_0 = 1 \cdot 10^{-2}$ mole/l), depending on the initial concentration of the inhibitor (Figure 15), induces alert either. That is why the final conclusion about the flowing of reaction (7.1) for Naugalube 680 is put aside until the detailed investigation of this inhibitor is undertaken.

Identification of reactions (7.2), (10.0) are being performed according to the results of a series of experiments with different initiation rates w_i (Figures 17–20).

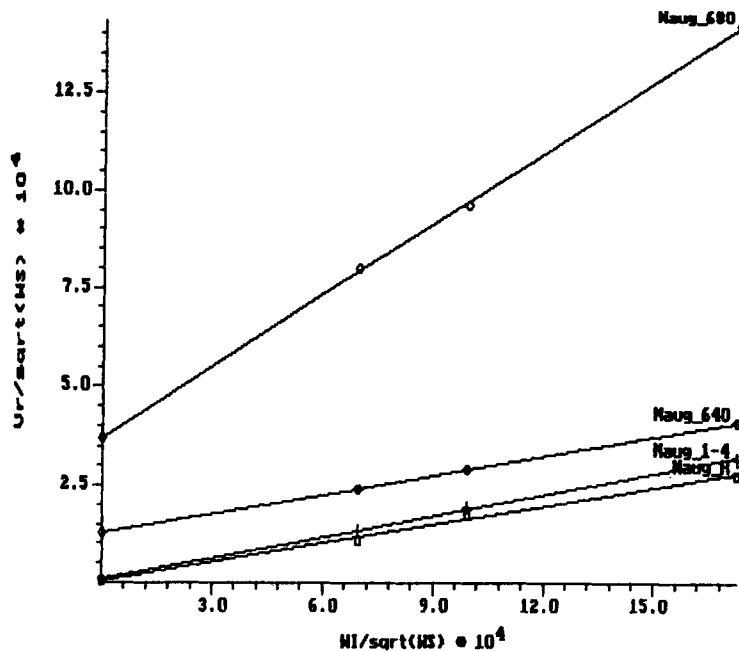


FIGURE 34 The identification of the inhibitors mechanisms.

At the same rather larger concentration of the inhibitor, the dependence of $v(0)/\sqrt{w_s}$ on $w_i/\sqrt{w_s}$ represents a straight line with angle coefficient equal to $1/(1 + P_{7.2}[\text{InH}]_0)$, and a segment $P_{10}/\sqrt{P_9}$ cut off on the y-axis. Figure 34 shows the corresponding dependences for four investigated inhibitors. For all the inhibitors, the presence of reaction (7.2) is characteristic because the tangent of the dip angle of straight lines is smaller than the unit. There is no hesitation in flowing of reaction (10.0) for Naugalube 640 and Naugalube 680. The parameter $P_{10}/\sqrt{P_9}$ for the other two inhibitors is sufficiently smaller and even close to zero. It points to a small role of the reaction (10.0) in acting the mechanism of Naugard 1-4 and Naugard R.

Quantitative treatment of the dependence considered gives the following initial approximations for parameters:

P_j/InH	Naugard 1-4	Naugard R	Naugalube 640	Naugalube 680
$P_{7.2}$	$9 \cdot 10^2$	$1.1 \cdot 10^3$	$1 \cdot 10^2$	$0.14 \cdot 10^2$
$P_{10}/\sqrt{P_9}$	$9 \cdot 10^{-6}$	$8 \cdot 10^{-6}$	$1.3 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$

Investigation of Action Mechanism of Naugard 1-4 and Naugard R Inhibitors

Qualitative behavior of experimental data allows to divide investigated inhibitors into two groups: (Naugard 1-4—Naugard R) and (Naugalube 640—Naugalube

680). Moreover, observed kinetic laws of the first two inhibitors are not only alike qualitatively, but also close quantitatively. It gives the hope that they have similar acting mechanisms without the values of kinetic parameters differing considerably. Let us consider the first of these two inhibitors: Naugard 1-4.

At first, our methods⁶ let us estimate parameters $P_{7,0}$, P_8 , P_9 by the initial parts of $v(t)$ dependences in experiments with small concentrations of inhibitor $[\text{InH}]_0 = 2 \cdot 10^{-5} - 2 \cdot 10^{-4}$ mole/l. Taking into account the results from item 4.2, we will receive the first approximation for parameters: $P_{7,0} = 2 \cdot 10^4$, $P_8 = 1$, $P_9 \approx 1 \cdot 10^{-6}$, $P_{10} \approx 1 \cdot 10^{-8}$.

Substituting these value to the system (14)-(21), we will calculate the change of oxidation rate $v(t)$ in each experiment and compare received data with the experiment (Figure 35). Evident deviation of the calculation from the experiment shows that the number of parameters calculated is not enough for description of the experimental data while the time and the inhibitor concentration change in wide ranges.

We will underline the most characteristic differences in behavior of the experiment and the calculation:

- 1) While the inhibitor concentration $[\text{InH}]_0$ is increasing, the induction period in experiment increases to greater extent than in calculation.
- 2) Initial oxidation rates become smaller than w_i in the experiment already at concentration $[\text{InH}]_0 \geq 2 \cdot 10^{-4}$ mole/l. This fact is unexplainable in the framework of the supposed mechanism.
- 3) Final oxidation rates, being established after leaving the induction period in

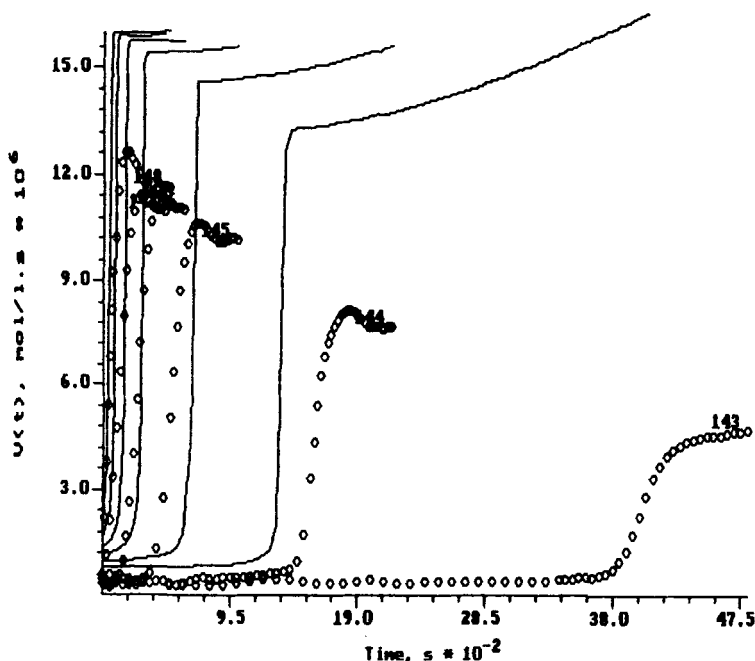


FIGURE 35 Naug_1-4 $W_i = 1e-6$ $K_w = K_p = K_i = 0$ $v(t) = d[\text{O}_2]/dt$.

experiment, are sufficiently smaller than the calculated ones. Calculated final rate is on the whole defined by the inhibitor concentration and parameters $k_{0.1} \cdot e$.

4) A stronger dependence of the final oxidation rate on the inhibitor concentration is observed in the experiment than in calculation. The decrease of final rate along with the increase of $[\text{InH}]_o$ in the ranges of initial mechanism is explained by the initiator expense during the experiment.

It is easy to see that it is impossible to explain the whole totality of specificities mentioned in the framework of traditional conceptions on the acting mechanism of inhibitors and the products of their transformation. To solve this problem, we have put forward a hypothesis about the effect of molecules of Naugard 1–4 on initiating properties of dikumylperoxide. A formal mechanism of such influence is the following. In presence of Naugard 1–4, molecules, the initiator exists equilibrium in two states with equilibrium constant, proportional to the quantity of inhibitor $[\text{InH}]_o$:



Initiator I_2 decomposes to radicals with constants k_{i2} and e_2 , which are, generally speaking, different from $k_{0.1}$ and e . As a result a real rate of initiator depends on time and $[\text{InH}]_o$ as following:

$$w_i(t) = w_i^0 \cdot \exp \left(-k_{0.1} \frac{1 + K_p [\text{InH}]_o}{1 + K_w [\text{InH}]_o} \cdot t \right) \quad (26)$$

Notations introduced here are the following:

$$w_i^0 = 2 \cdot k_{0.1} e \cdot [I]_o \cdot \frac{1 + K_i [\text{InH}]_o}{1 + K_w [\text{InH}]_o} \quad (27)$$

$$K_w = k_w^+ / k_{\bar{w}} \quad (28)$$

$$K_p = K_w \cdot k_{i2} / k_{0.1} \quad (29)$$

$$K_i = K_w \cdot (k_{i2} e_2) / (k_{0.1} e) \quad (30)$$

It follows from (27)–(30) that at $[\text{InH}]_o = 0$, initiation is performed by initial initiator with $k_{0.1}$ and e parameters; when $[\text{InH}]_o$ is increasing, the parameters of initiation change; and in approaching the limit at $[\text{InH}]_o \rightarrow \infty$, the parameters become equal to k_{i2} , e .

The rate of initiation dependence on inhibitor concentration is quantitatively characterized by three parameters: k_w , K_p , K_i . The description of experimental data can be improved considerably (Figure 36) if proper values of these parameters have been selected. For this the ratios $k_{i2}/k_{0.1}$ and e_2/e are defined simply. For K_w ,

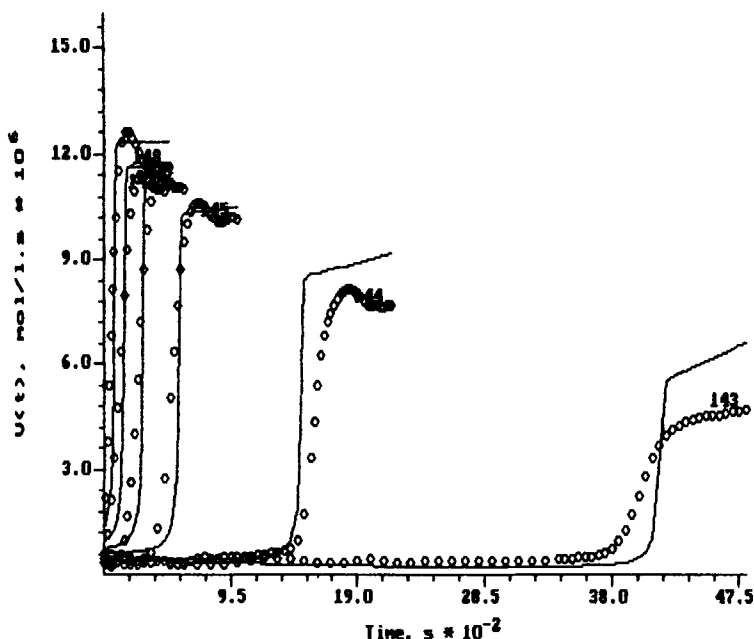


FIGURE 36 Naug-1-4 $W_i = 1e-6$ $K_n = 1.55e5$ $K_p = 2.2e5$ $K_i = 0.77e5$ $v(t) = d[O_2]/dt$.

the following estimation is received: $K_W > 5 \cdot 10^4$. The calculation, shown in Figure 36, was performed at following values of parameters:

$$K_W = 1,55 \cdot 10^5, \quad K_p = 2,1 \cdot 10^5, \quad K_i = 0,77 \cdot 10^5.$$

We have considered a formal quantitative aspect of hypothesis for inhibitor effect on initiator properties. Physical nature of this phenomenon will be discussed in the next chapter. For now, let's consider the last series of experimental data for Naugard 1-4, auto-oxidation of preliminarily oxidized samples (Figures 22 and 23).

The following features of these experimental data should be noted:

1) Qualitative behavior $v(t)$ dependences of oxidized samples during auto-oxidation is principally different from that during initiated oxidation.

2) In every experiment, at its initial period, the oxidation process is followed by gas isolation ($v < 0$), where the intensity is higher, the larger the content of hydroperoxide in the sample.

These features leave no hope that the present experiment can be described with the help of parameters found from initiated oxidation. Indeed, Figure 37 shows the comparison of $v(t)$ dependences with calculated ones. The attention should be paid to a very fast inhibitor expense. It can be supposed that in reality the main part of the inhibitor is already being spent during heating (≈ 200 sec), prior to the registration of experimental data. And all the observed breaking is performed by a product of its transformation, which is formed during interaction with hydroperoxide, for example, according to the reaction:

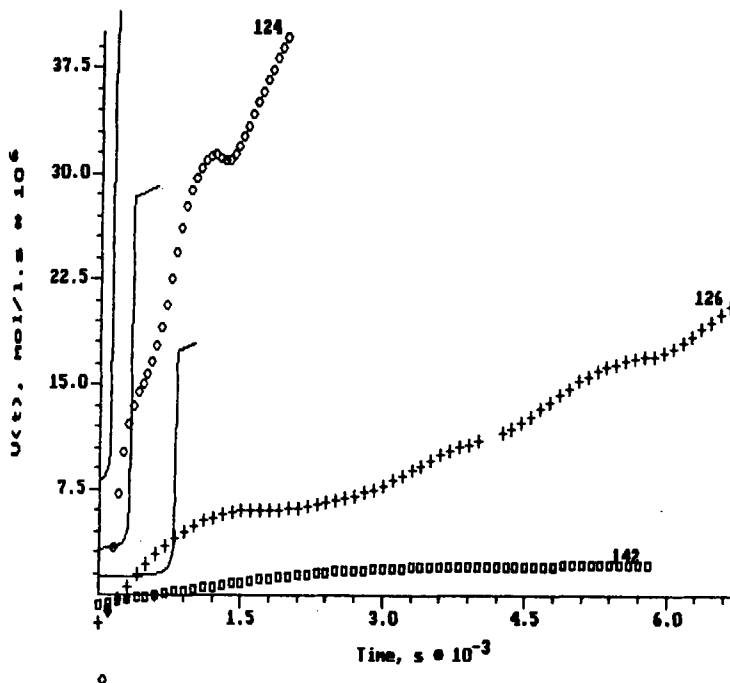
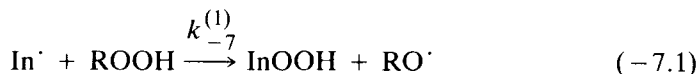


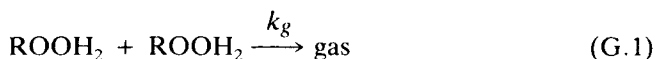
FIGURE 37 Naug-1-4 auto-oxidation $ROOH = (45, 103, 218)e-3$ $InH = 8e-4$ no product.



The data existed are not enough for detailed characterization of the mechanism of the product action. Moreover, its concentration by the moment of registration of the data is unknown. That is why one should be limited by a necessary minimum of parameters $P_7^{(1)}$, $P_8^{(1)}$, which characterize intensity and duration of breaking action of the product, respectively.

Let us consider now another feature of the experiment—gas isolation. The observed dependence of initial rate of the process on $[ROOH]_0$, witnesses to a strong dependence of gas isolation rate v_g on the concentration of hydroperoxides (detailed investigation has shown that $v_g \approx [ROOH]^2$).

Gas isolation occurs only at a certain initial period, so its source has to be expended during that time. Several hypotheses on the physical nature of this phenomenon can be considered. We took the supposition that gas isolation follows the decomposition of certain hydroperoxides having a specific structure. Decomposition of this small part of the hydroperoxides, in presence of Naugard 1-4, is followed by gas isolation:



Thus, parameters $P_7^{(1)}$, $P_8^{(1)}$, k_g need to be determined from the experimental data of the considered series, and the unknown concentrations of $[InOOH]_0$,

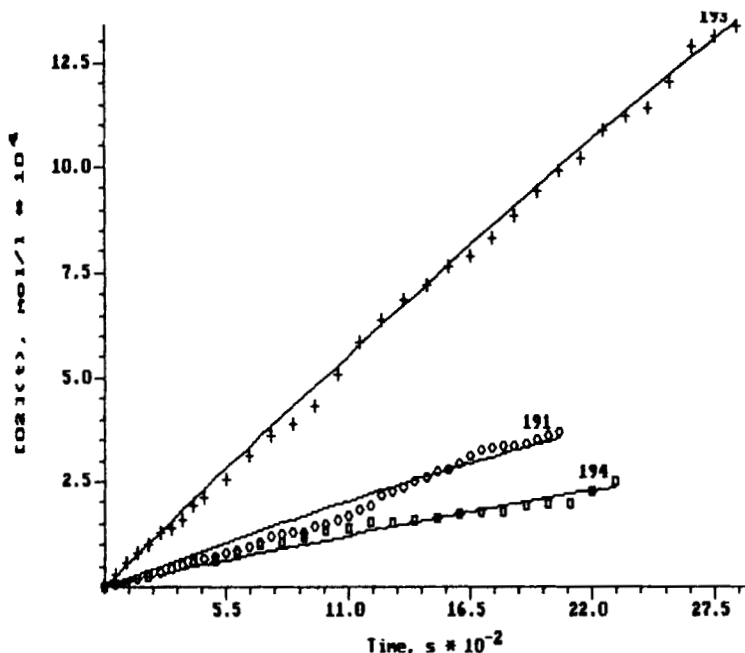


FIGURE 38 Naugard R $\text{InH} = 5e-3 W_i = (0.5, 1, 3)e-6$ experiment & calculation.

$[\text{ROOH}_2]_0$, either. This problem can be solved simply, and the parameters received as a result of its solution allow description of the corresponding experimental data satisfactorily. The initial parts of dependences of $[\text{O}_2](t)$ for calculation and experiment are being compared on a large scale in Figure 38.

At a concluding stage of the investigation, a final optimization of parameters in all the experimental data have been performed. Final values of P_i are shown in Table I, and comparison of the corresponding calculated and experimental data is made in Figures 39–44.

Let us pass to the investigation of the second inhibitor from a considered group—Naugard R. As mentioned above, the kinetic laws of inhibited oxidation for Naugard 1–4 and Naugard R are close both qualitatively and quantitatively. It appears natural to try to characterize Naugard R action in terms of the model worked out for Naugard 1–4. It is possible to determine values of all the kinetic parameters of the model from the existing experimental data. P_i values have been determined and are shown in Table I, and the comparison of calculation with experiment is shown in Figures 45–51.

Investigation of Action Mechanism of Inhibitors Naugalube 640 and Naugalube 680

Let us now pass to the investigation of another group of inhibitors, Naugalube 640 and Naugalube 680. The main qualitative difference between inhibitors from the first and the second groups lies in the behavior of $v(t)$ dependences in series of experiments with different initial concentrations $[\text{InH}]_0$ (Figures 13–16). According

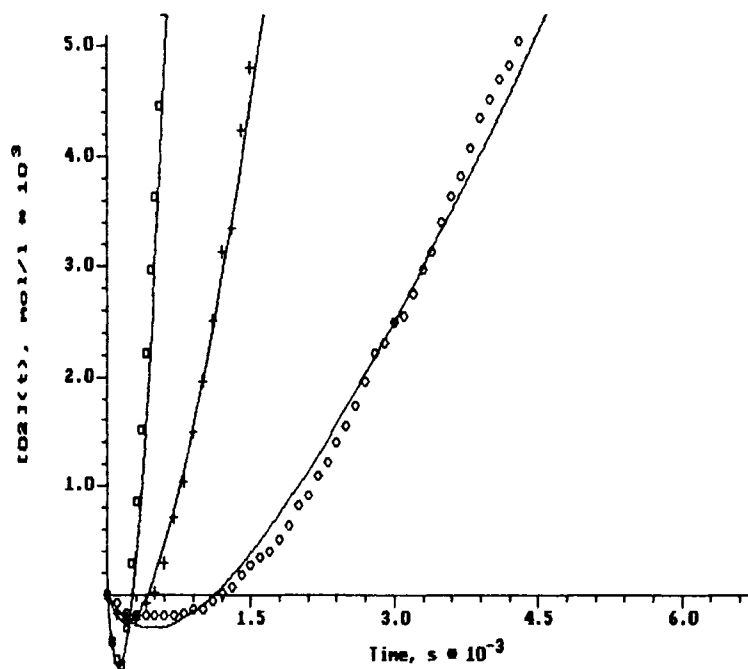
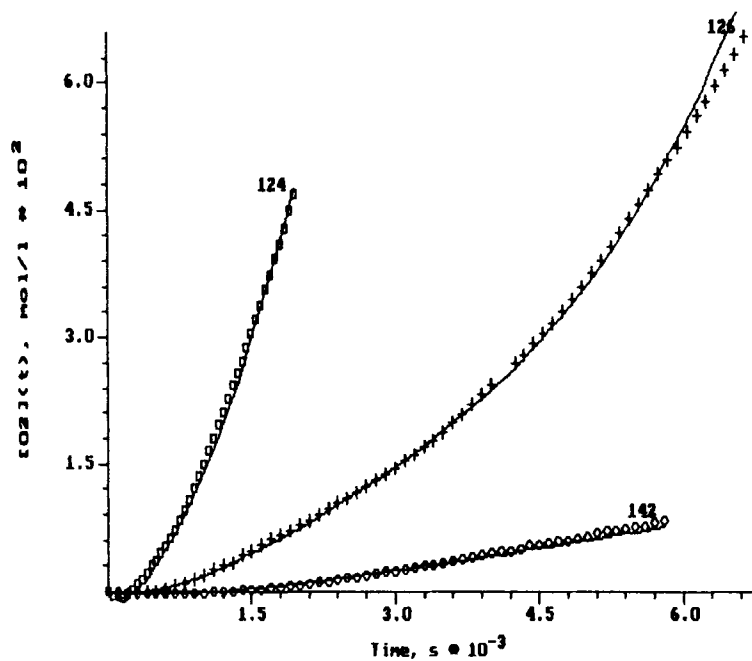
TABLE I

Values of kinetic parameters of investigated inhibitors in oxidizing *n*-hexadecane at $T = 140^\circ\text{C}$

$P_j \setminus \text{InH}$	Naugard 1-4	Naugard R	Naugalube 640	Naugalube 680
$P_{7.0}$	$2 \cdot 10^4$	$1.5 \cdot 10^4$	$5.6 \cdot 10^3$	$5.3 \cdot 10^3$
$P_{7.2}$	347.5	359.2	40.6	10.0
P_8	1.0	1.0	1.0	1.0
P_9	$\approx 1 \cdot 10^{-6}$	$\approx 1 \cdot 10^{-6}$	$\approx 1 \cdot 10^{-6}$	$\approx 1 \cdot 10^{-6}$
P_{10}	$\leq 1 \cdot 10^{-8}$	$\leq 1 \cdot 10^{-8}$	$1.8 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$
P_{-7}	$3 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$
$P_{-7}^{(1)}$	$\approx 1 \cdot 10^{-5}$	$\approx 1 \cdot 10^{-5}$	$\approx 1 \cdot 10^{-5}$	$\approx 1 \cdot 10^{-5}$
$P_7^{(1)}$	$1.0 \cdot 10^3$	$1.0 \cdot 10^3$	$0.6 \cdot 10^3$	$0.6 \cdot 10^3$
$P_8^{(1)}$	0.05	0.05	0.03	0.03
K_w	$1.55 \cdot 10^5$	$1.55 \cdot 10^5$	$2 \cdot 10^2$	$2 \cdot 10^2$
$k_{12}/k_{0.1}$	1.29	0.89	≈ 1.0	≈ 1.0
e_2/e	0.385	0.493	0.450	0.440
k_g	0.15	0.40	-	-
P_{p1}	-	-	$2.0 \cdot 10^3$	$1.5 \cdot 10^3$
k_{p2}	-	-	$1.8 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
$w_z(0)$	-	-	-	$2.05 \cdot 10^{-6}$
K_z	-	-	-	$7.5 \cdot 10^{-4}$

to these dependences, inhibitors of the second group have no expressed induction period: the rates increase from the very beginning—monotonously, nearly linearly—with the depth of oxidation. In the framework of the scheme (7.0)–(10.0), it can be explained by a large value of rate constant k_{-7} .

We shall estimate parameters $P_{7.0}$, P_8 , P_9 and P_{-7} from the initial parts of $v(t)$ dependences in the considered series, and parameters $P_{7.2}$ and P_{10} from the results of the preliminary identification (item 4.2). Let's calculate $v(t)$ dependences on $[\text{InH}]_0$ in the series and compare them with the experimental findings (Figure 49). The coincidence of the calculation data with the experiment data takes place at a certain initial part, after which the calculated value raises sharply, i.e. inhibition in calculation ends much earlier than in the experiment. It is easy to ensure that it is impossible to increase duration of retardance in the frames of the scheme (7.0)–(10.0), for example, by changing the P_8 parameter without changing qualitative character of the $v(t)$ dependences. Large duration of retardance can be provided by a product of transformation of the initial inhibitor, possessing the inhibitorial properties of either. The most probable product with such properties in the scheme (7.0)–(10.0) is InOOR, formed in reaction:

FIGURE 39 Naug_1-4 Auto-oxidation $\text{InH} = 8e-4$ experiment & calculation.FIGURE 40 Naug_1-4 auto-oxidation $\text{InH} = 8e-4$ experiment & calculation.

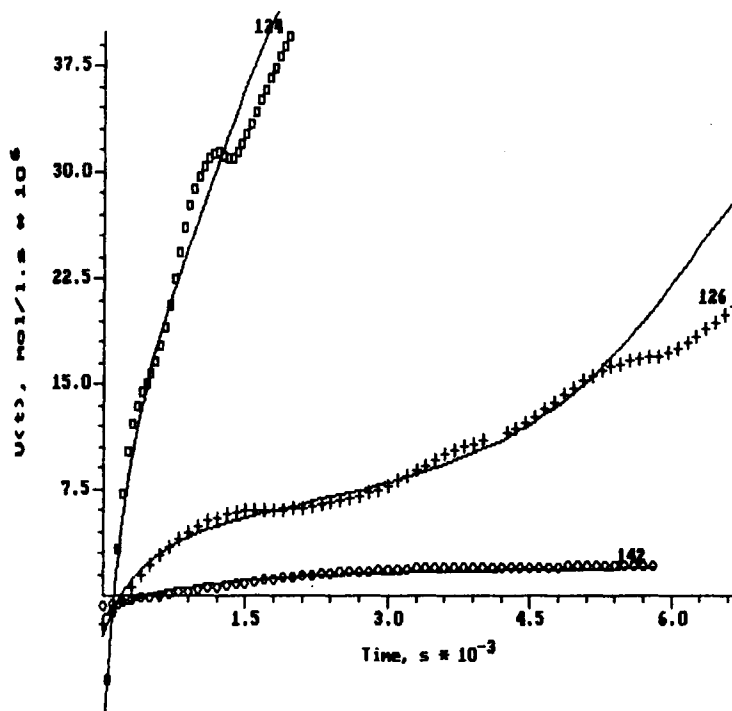


FIGURE 41 Naug_1-4 auto-oxidation $\text{InH} = 8e-4$ experiment & calculation.



Several alternative mechanisms of retardant action of the product have been considered, the choice was the following:



The principal stage here is the formation of In^{\cdot} radical in the reaction that provides nearly unlimited duration of retardance. From the point of view of formal description of the considered experiment, there is no difference which radical interacts with the product: R^{\cdot} or RO_2^{\cdot} . But after consideration of inhibited auto-oxidation of the initial sample, the selection of radical R^{\cdot} appears favorable. Along with inhibiting properties, the product InOOR can have initiating ones:



The totality of reactions (P.1)–(P.2) allows to improve sufficiently the correspondence of experiment to calculation Figure 50.

Another feature of the inhibitors of the Naugalube group lies in the fact that

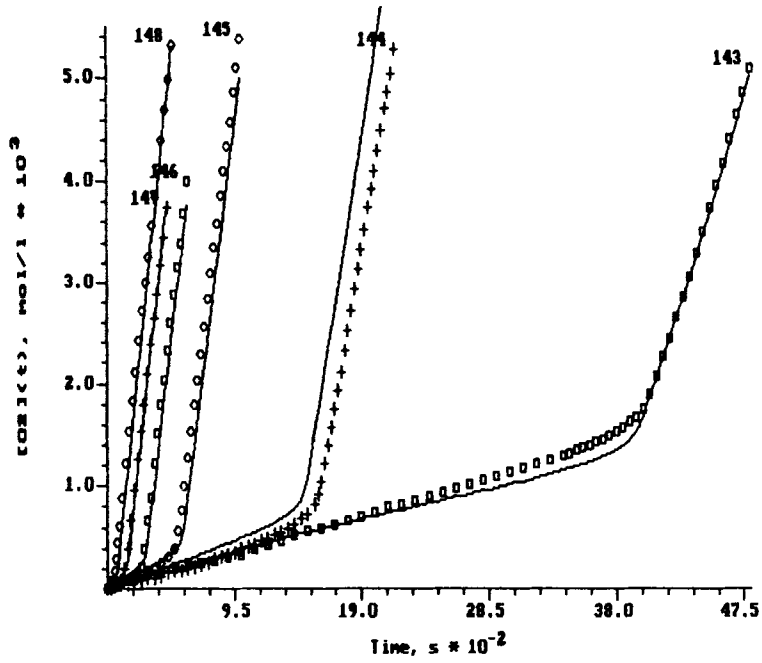


FIGURE 42 Naug₁₋₄ W₁ = 1e-6 lnH = (0.25-50)e-4 experiment & calculation.

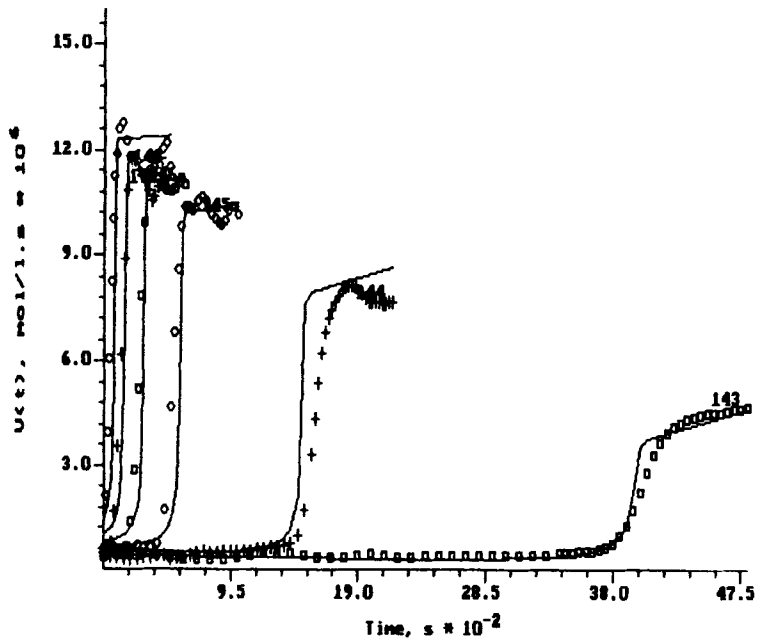


FIGURE 43 Naug₁₋₄ W₁ = 1e-6 lnH = (0.25-50)e-4 experiment & calculation.

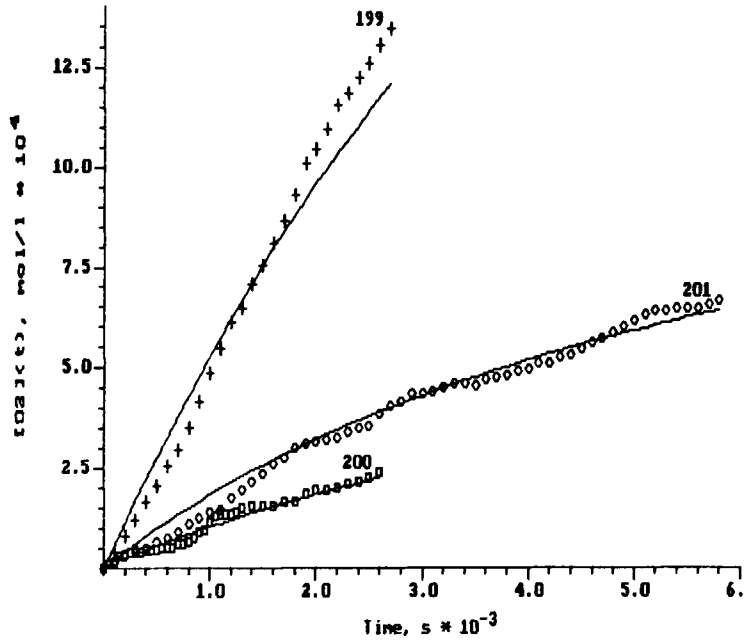


FIGURE 44 Naug-1-4 InH = $5e-3$ $W_i = (0.5, 1, 3)e-6$ experiment & calculation.

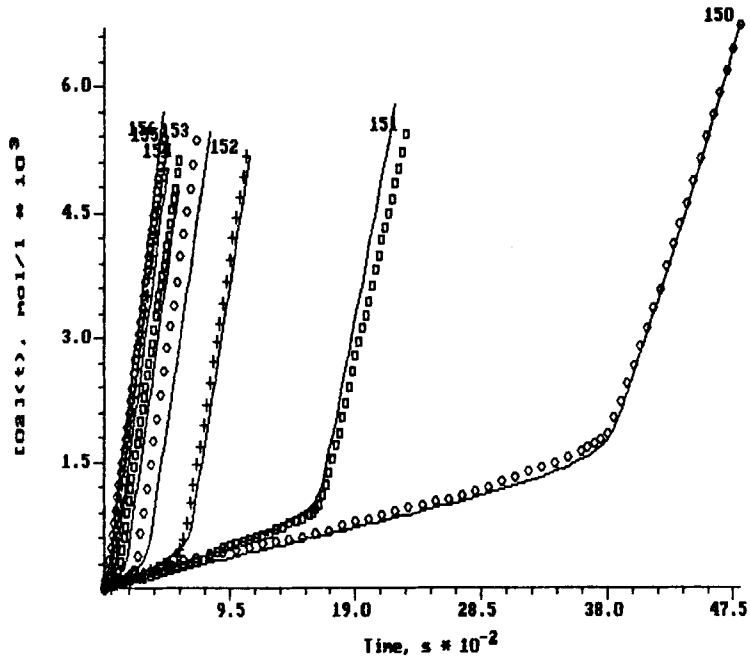


FIGURE 45 Naug-R $W_i = 1e-6$ InH = $(0.1-50)e-4$ experiment & calculation.

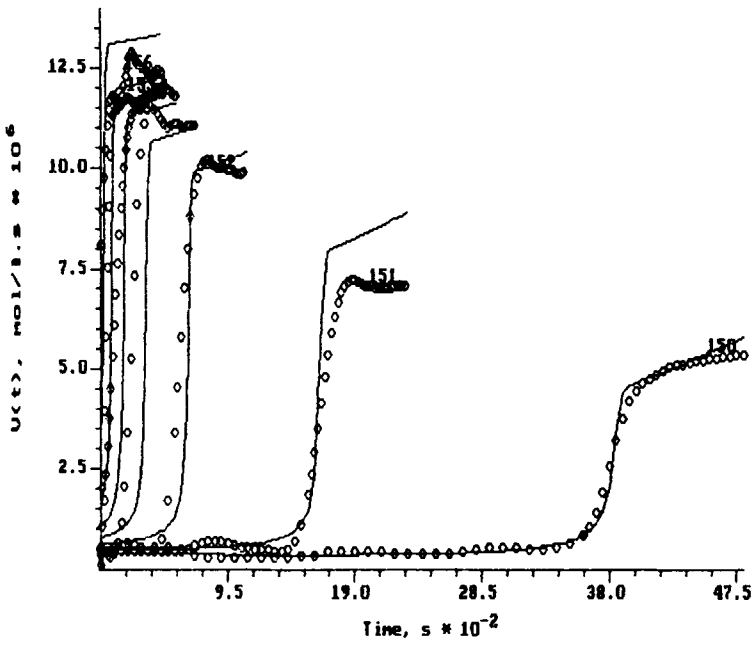


FIGURE 46 Naug_R $W_i = 1e-6 \text{ InH} = (0.1-50)e-4$ experiment & calculation.

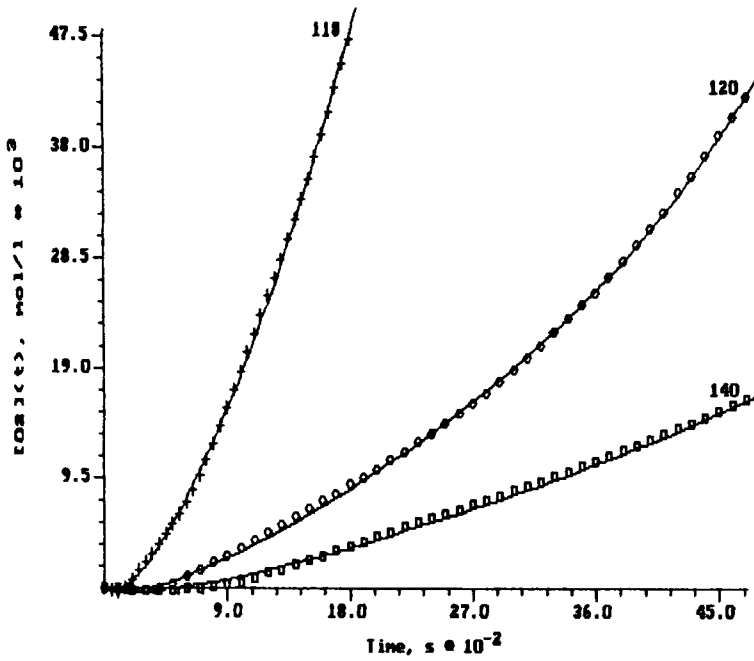


FIGURE 47 Naug_R auto-oxidation $\text{InH} = 5e-4$ experiment & calculation.

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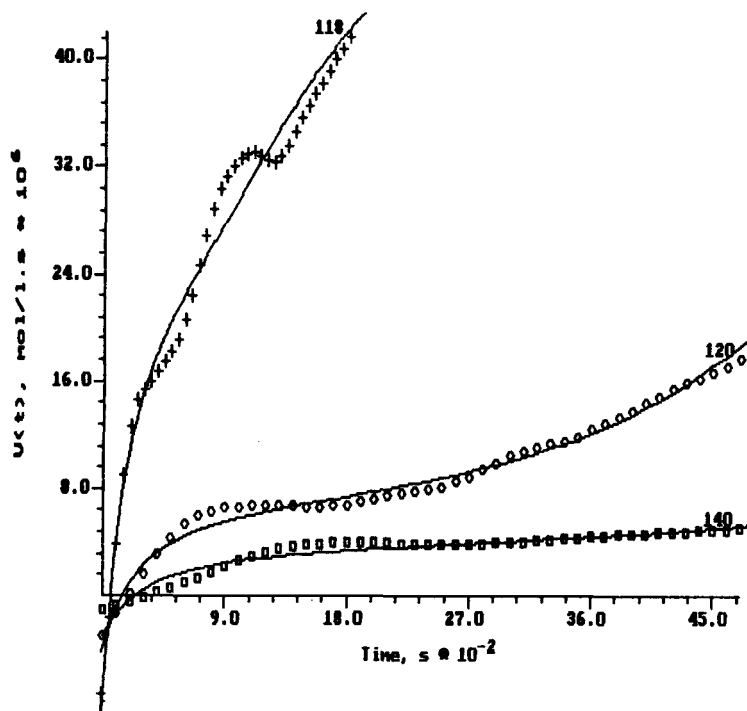


FIGURE 48 Naug-R auto-oxidation $\text{InH} = 5e-4$ experiment & calculation.

the dependence of the rate of initiation on inhibitor concentration is essentially weaker than for Naugard group. Quantitatively it is expressed by the fact that the equilibrium constant K_w for Naugalube 640 is sufficiently smaller than for the first two inhibitors. Thus, calculations presented in Figures 49 and 50 were made using the following values of constants:

$$K_w = 2 \cdot 10^2, \quad K_p = 2 \cdot 10^2, \quad K_i = 0,9 \cdot 10^2.$$

Let us now consider a series of experimentes on auto-oxidation of oxidized samples shown in Figures 26 and 27. From comparison of these experimental data with analogous ones for Naugard 1-4 and Naugard R, it follows that oxidation in the presence of Naugalube 640 flows without gas isolation. In the rest of aspects, for inhibitors of both groups, qualitative behavior of experimental dependences of this series is similar. That is why it was not difficult to describe this experiment in the framework of the mechanism, considered above for Naugard group. We would remind the reader that according to this mechanism in the experiments under consideration, breaking is performed mainly by the product of reaction (-7.1). Its influence is characterized by two parameters: $P_7^{(1)}$ and $P_8^{(1)}$, which define the intensity and duration of retardant action of the product, respectively. For inhibitors from the Naugalube group we have considered that only a part of inhibitor is transformed to a product during heating. This is connected with the fact that the rate of inhibitor expense from Naugalube group is lower than that for Naugard

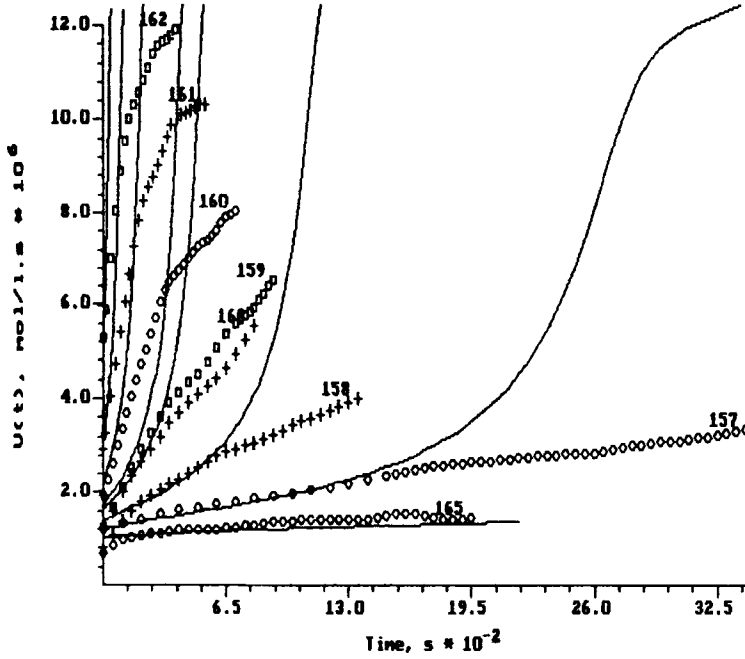


FIGURE 49 Naug_640 $W_i = 1e-6 \ln H = (0.2-20)e-4$ no product.

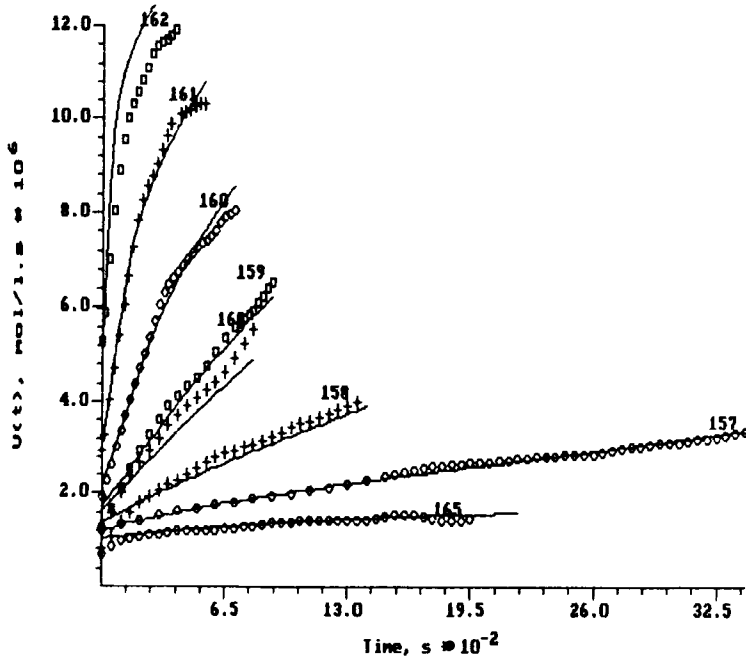


FIGURE 50 Naug_640 $W_i = 1e-6 \ln H = (0.2-20)e-4$ InOOR: inhibitor & initiator.

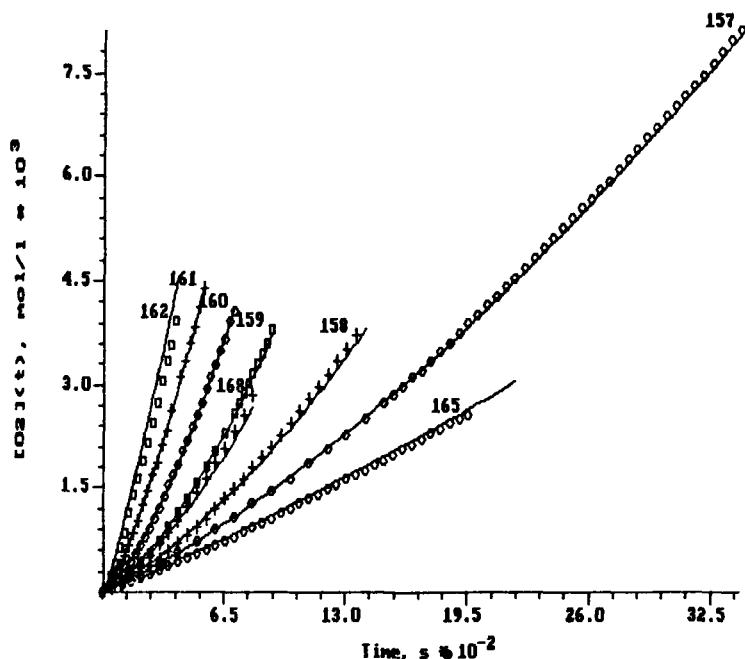


FIGURE 51 Naug₆₄₀ $W_i = 1e-6$ $\text{InH} = (0.2-20)e-4$ experiment & calculation.

one. However, calculations have shown a weak dependence of the result on unexpended concentration of inhibitor: in the oxidized sample the initial inhibitor is bad for retardance because of strong reversibility of reaction (-7.0).

To conclude the investigation of Naugalube 640 inhibitor, general optimization of kinetic parameters by all the experimental data has been performed. Final values of P_i are presented in Table I, and the comparison of calculation and experiment are shown in Figures 52–55.

Let us reconsider last of the four selected inhibitors, Naugalube 680. Experimental data for this inhibitor are practically similar to those for Naugalube 640 in two series of experiments: initiated oxidation of different $[\text{InH}]_0$ (Figures 15 and 16) and auto-oxidation of oxidized samples (Figures 28 and 29). So the main rules of retardant influence and values of kinetic parameters for these inhibitors are close. The general difference between them is observed at concentration $[\text{InH}]_0 = 5 \cdot 10^{-2}$ mole/l: at this value the initial rate of oxidation has increased sharply in experiments with Naugalube 680 (Figure 20). If you determine values of kinetic parameters from the first two series of experiments and calculate dependences $[\text{O}_2](t)$ for the third one, calculated values will lie sufficiently lower than experimental ones (Figure 56).

To explain this dispersion and difference of Naugalube 680 from Naugalube 640, we maintained that inhibitor Naugalube contained an admixture of initiating character. Its quantity in the system is proportional to inhibitor concentration, and that is why at small $[\text{InH}]_0$ it is practically ineffective and becomes apparent only if $[\text{InH}]_0$ increased from $5 \cdot 10^{-3}$ up to $5 \cdot 10^{-2}$ mole/l (Figure 15).

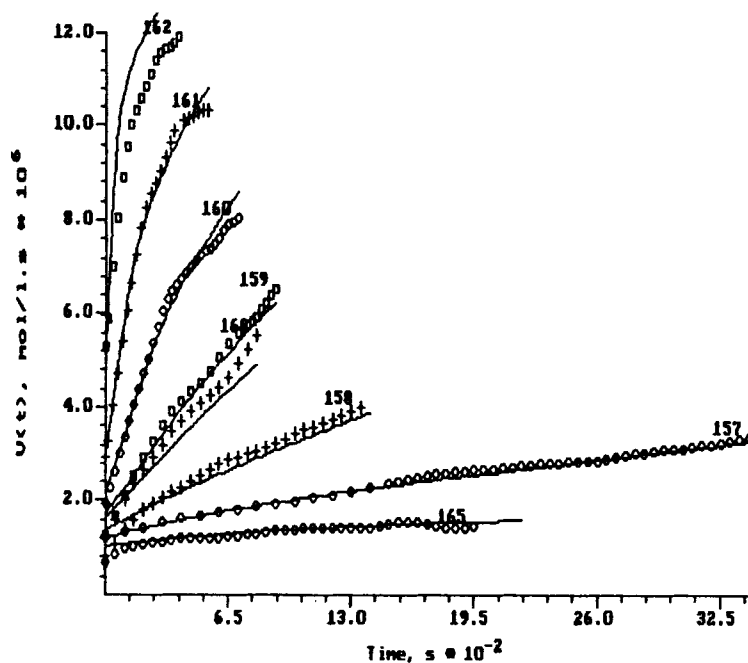


FIGURE 52 Naug₆₄₀ $W_1 = 1e-6$ InH = $(0.2-20)e-4$ experiment & calculation.

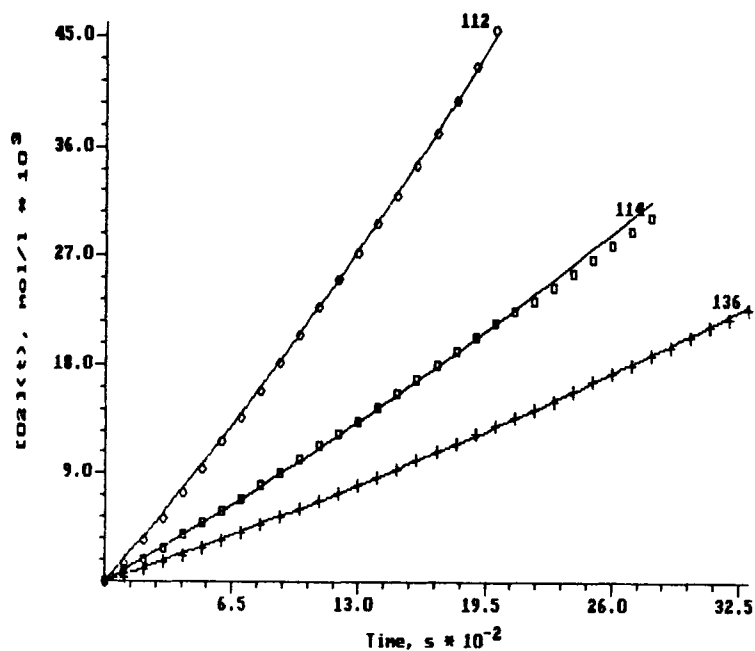


FIGURE 53 Naug₆₄₀ auto-oxidation InH = $5e-4$ experiment & calculation.

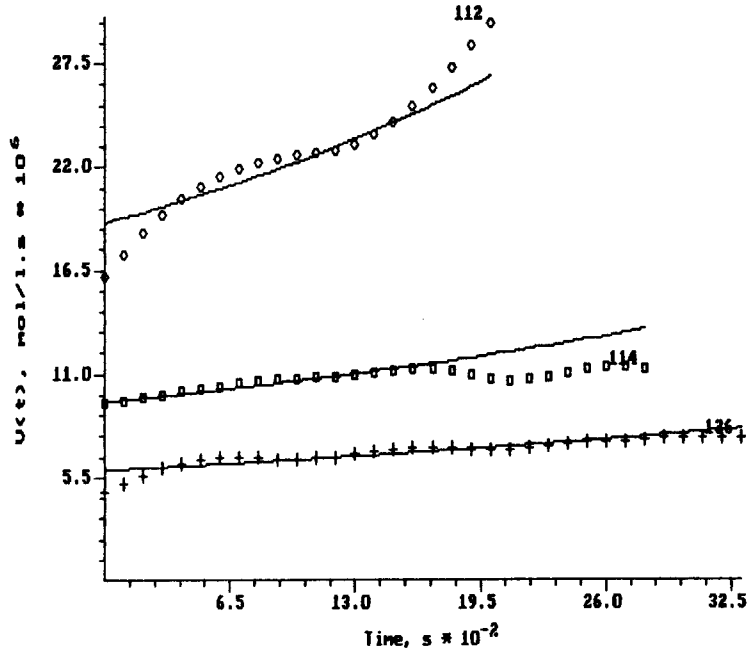


FIGURE 54 Naug_640 auto-oxidation $InH = 5e-4$ experiment & calculation.

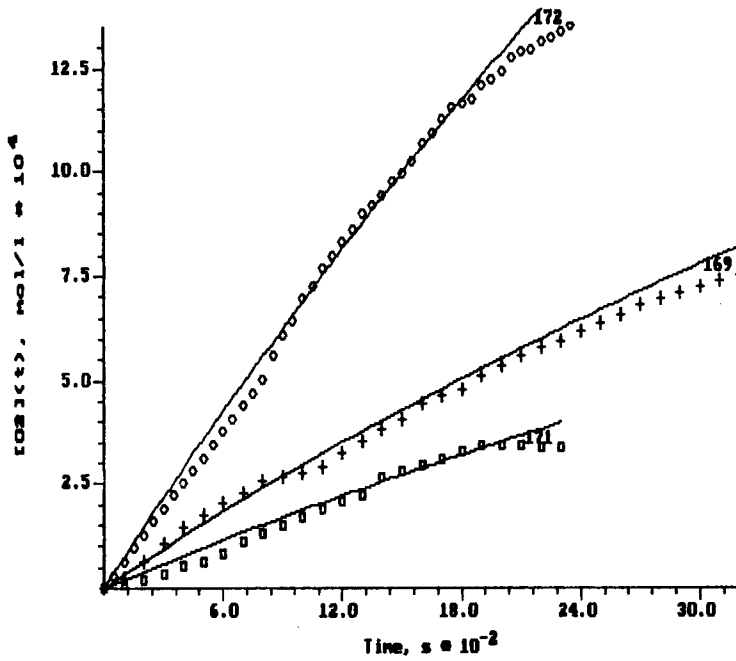


FIGURE 55 Naug_640 $InH = 5e-2$ $W_i = (0.5, 1, 3)e-6$ experiment & calculation.

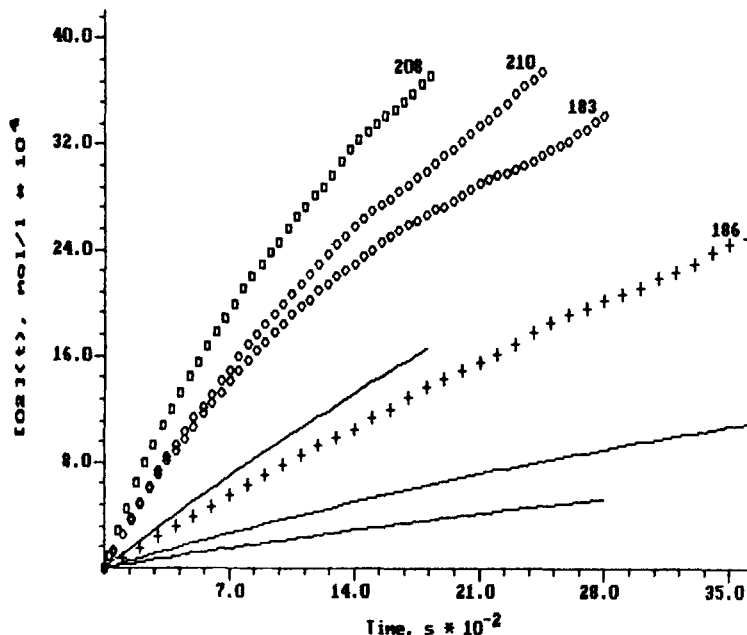


FIGURE 56 Naug_680 InH = $5e-2$ $W_i = (0.5, 1, 3)e-6$ 186: (air $W_i = 1e-6$).

The most simple mechanism of initiation can be written as follows:

$$w_z = w_z(0) \exp(-K_z t) \quad (31)$$

The unknown parameters are: $w_z(0)$ —start rate of initiation; K_z —constant of admixture expense.

It is possible to easily determine the values of these parameters, describing the experiment satisfactorily (Figure 57). For all this, it appeared that for the description of experiment 186, performed in air, the values of parameters $w_z(0)$ and K_z should be decreased by five times. It witnesses for the following mechanism of initiation:



According to reaction (Z.1), expressions for parameters $w_z(0)$, K_z are the following:

$$w_z(0) = 2 \cdot e \cdot k_z \cdot [I_2]_0 \quad (32)$$

$$K_z = k_z \cdot [O_2] \quad (33)$$

Reaction (Z.1) explains another feature of inhibitor Naugalube 680, mentioned above (item 4.2): just for it the decrease of oxygen partial pressure leads to the decrease of oxidation rate. This decrease appears because of reaction (Z.1), and

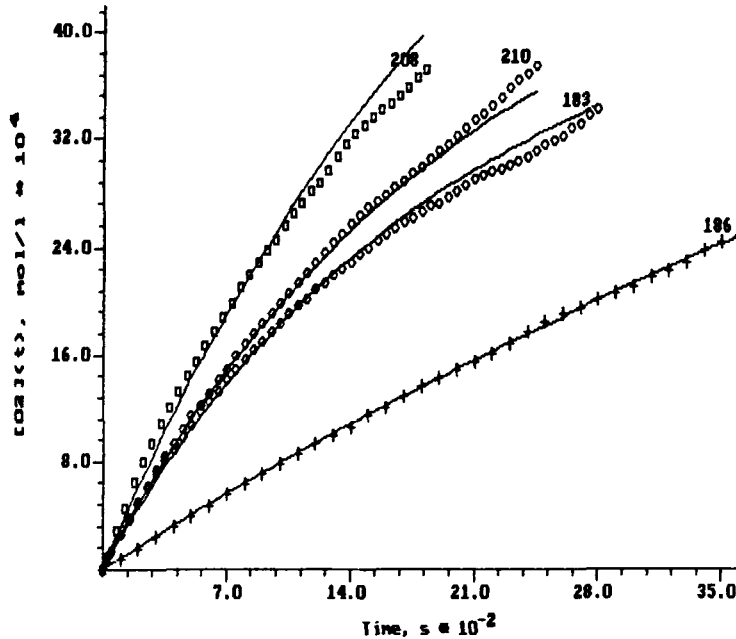


FIGURE 57 Naug_680 InH = $5e-2$ $W_i = (0.5, 1, 3)e-6$ admixture—initiator 186: air.

not (7.1)—one that could be hardly explained by changes of structure in the row of inhibitors under consideration.

Unfortunately, we can't say anything about a physical nature of the supposed admixture. Its presence might be connected, evidently, with the technologic features of the process of inhibitor Naugalube 680 production.

Comparison of experimental and calculated data for Naugalube 680 are presented in Figures 58–61. The calculation was made after final optimization of parameters. Corresponding values of P_j are presented in Table I.

This finishes the investigation of four selected inhibitors: Naugard 1–4, Naugard R, Naugalube 640 and Naugalube 680 in oxidizing *n*-hexadecane at 140°C. The main rules of retardant influence of these inhibitors have been explained and corresponding quantitative characteristics determined. The results have allowed description of all the existing experimental data.

DISCUSSION

The main result of the investigation is a mathematical model of the action mechanism of considered inhibitors. Let us analyze the general properties of the received model. First of all, let us underline that the final mechanism of inhibiting includes nearly all the reactions of the classical scheme (7.0)–(10.0). As a result of investigation, the initial scheme had to be supplemented essentially by reactions, which can be divided by generalization order into following groups:

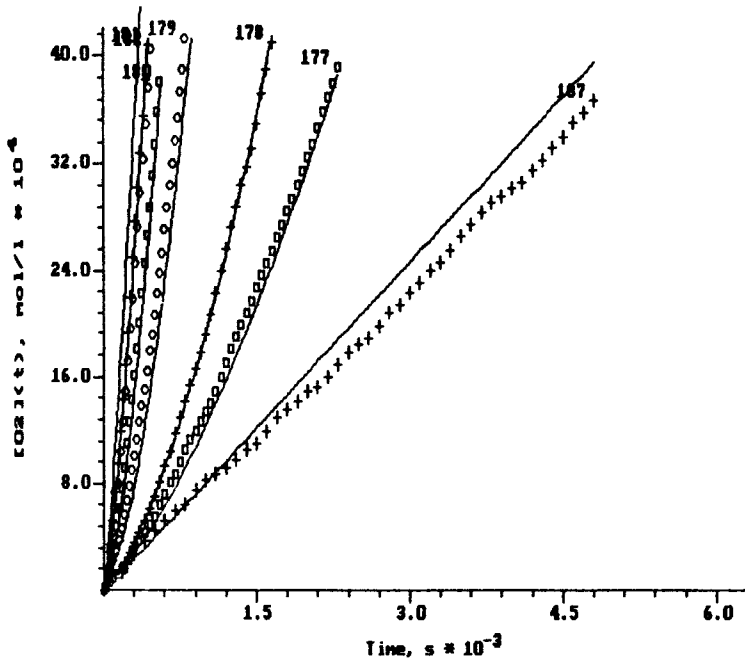


FIGURE 58 Naug-680 W, = $1e-6$ InH = $(0.2-50)e-4$ experiment & calculation.

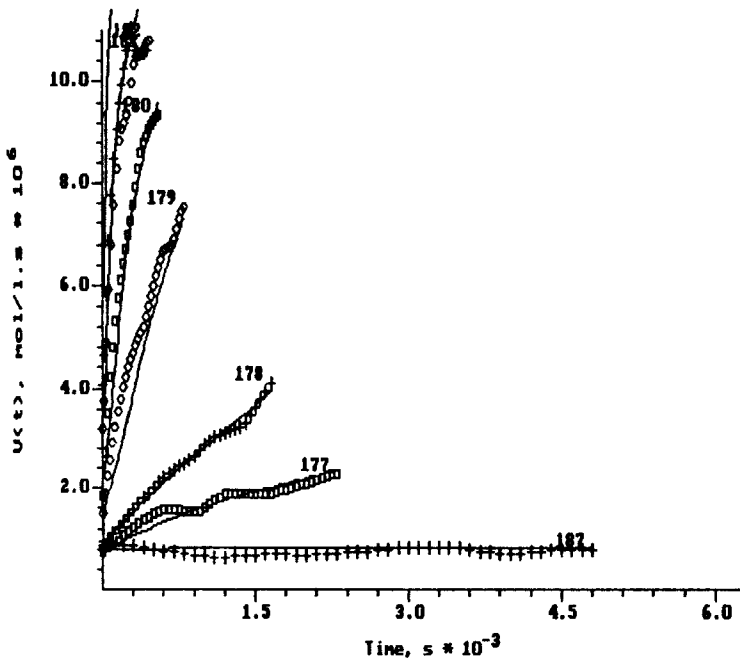


FIGURE 59 Naug-680 W, = $1e-6$ InH = $(0.2-50)e-6$ experiment & calculation.

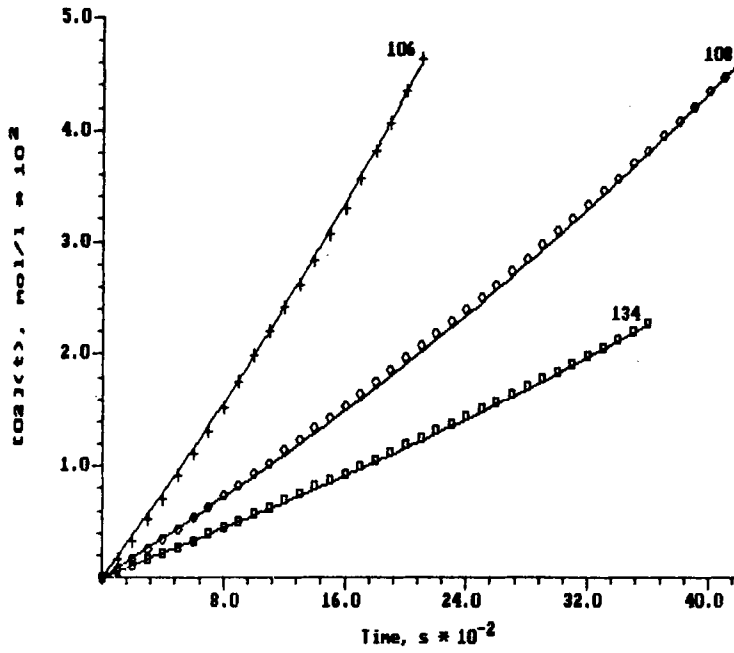


FIGURE 60 Naug_680 auto-oxidation $\text{InH} = 5e-4$ experiment & calculation.

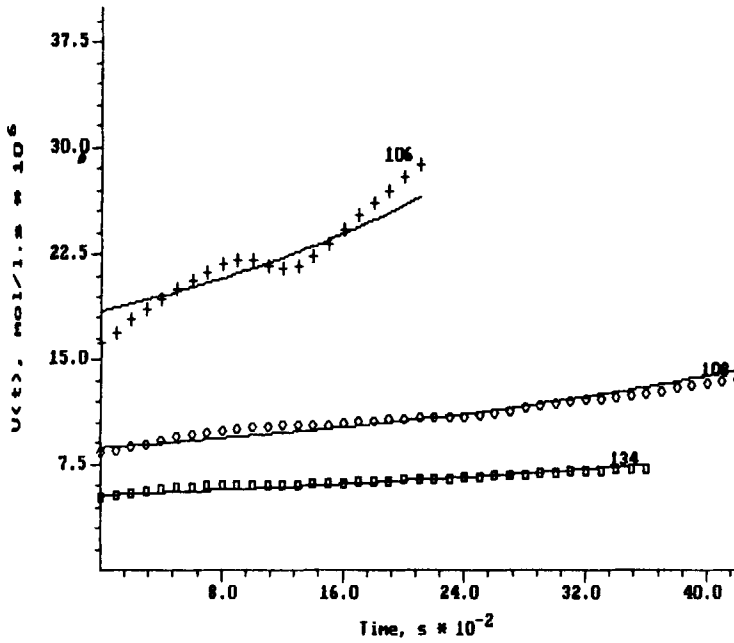


FIGURE 61 Naug_680 auto-oxidation $\text{InH} = 5e-4$ experiment & calculation.

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Reactions Characteristic for All the Investigated Inhibitors

Firstly, the retardant mechanism of auto-oxidation of oxidized samples of hexadecane by the product of transformation of initial inhibitor should be attributed to the reactions characteristic for all the investigated inhibitors. The product is formed according to reaction (–7.1), and its effect is characterized by two kinetic parameters, $P_7^{(1)}$ and $P_8^{(1)}$, which define the intensity and the duration of retardance.

Secondly, the effect on the rate of initiation by cumylperoxide appeared to be the general property of all the inhibitors: inhibitors of the given structure change conditions of initiator decomposition (reaction (W.1)).

Reaction Characteristic for Inhibitors of Naugard Group

Auto-oxidation of oxidized samples of hexadecane in the presence of inhibitors of the Naugard group at a certain initial stage is accompanied by gas isolation according to reaction (G.1).

Reactions Characteristic for Inhibitors of Naugalube Group

An important role in initiated oxidation is played by the product of transformation of the initial inhibitor InOOR, formed according to reaction (8.0). This product has both inhibiting (P.1) and initiating (P.2) properties.

Reactions Characteristic for Some Inhibitors

The reaction (Z.1) of additional initiation that is observed in the presence of large concentration of Naugalube 680 inhibitor ($[InH]_0 = 5 \cdot 10^{-2}$ mole/l) should be attributed to reactions characteristic for some inhibitors.

Taking into account all these additional reactions, the system of equations describing the considered process of inhibited oxidation look as follows:

$$v = v_1 - 0,5 \cdot P_6 v_2^2 + 0,5 \cdot w_0 - k_g \cdot y_2^2 \quad (34)$$

$$v_1 = (1 - q) \cdot v_2 + P_6 v_2^2 + P_{7,0} v_2 z - P_{-7} xy + v_2 x + 2 \cdot P_7^{(1)} v_2 z_1 \quad (35)$$

$$w_s = P_6 v_2^2 + 2 \cdot v_2 x + P_9 x^2 + 2 \cdot P_7^{(1)} v_2 z_1 \quad (36)$$

$$P_{7,0} v_2 z + P_{7,2} w_i z / (1 - q + P_{7,2} z) + P_{p1} v_1 z_2 = (P_{-7} + P_{-7}^{(1)}) xy + v_2 x + P_9^2 x + P_{10} (1 - q) x \quad (37)$$

$$\dot{y} = P_2 (1 - q) \cdot v_2 - k_{s1} y - 2 \cdot k_{s2} y^2 + P_{7,0} v_2 z + P_7^{(1)} v_2 z_1 - (P_{-7} + P_{-7}^{(1)}) xy \quad (38)$$

$$\dot{z} = -(P_8 v_2 x + P_9 x^2) + P_{p1} v_1 z_2 - P_{-7}^{(1)} xy \quad (39)$$

$$\dot{q} = (0.5 w_o + v_1 + P_{p1} v_1 z_2) / [\text{RH}]_o \quad (40)$$

$$\dot{z}_1 = P_{-7}^{(1)} xy - P_7^{(1)} P_8^{(1)} v_2 z_1 \quad (41)$$

$$\dot{z}_2 = P_8 v_2 x - P_{p1} v_1 z_2 - k_{p2} z_2 \quad (42)$$

$$\dot{y}_2 = -k_g y_2^2 \quad (43)$$

$$y(0) = y_o; \quad z(0) = z_o; \quad q(0) = 0 \quad (44)$$

$$z_1(0) = z_1^o; \quad z_2(0) = z_2^o; \quad y_2(0) = y_2^o \quad (45)$$

Along with the former notations the following ones are introduced here:

$$z_1 = [\text{InOH}]; \quad z_2 = [\text{InOOR}]; \quad y_2 = [\text{ROOH}_2] \quad (46)$$

$$P_{-7}^{(1)} = k_{-7}^{(1)} \frac{k_2 [\text{RH}]_o}{k_{8,0} + k_{8,1}}; \quad P_{p1} = \frac{k_{p1}}{k_1 [\text{O}_2]} \quad (47)$$

All the calculation data for final comparison with experimental data were received from the solution of this system of equations, values of the kinetic parameters were taken from Table I.

The received results together with data from Table I, in particular, allow comparison of the efficiency of effect of considered inhibitors and explain the behavior of experimental data. Let us compare kinetic parameters of inhibitors of Naugard and Naugalube groups.

1) Values of $P_{7,0}$ and $P_{7,2}$, which define the intensity of retardance, are several times higher for Naugard than for the Naugalube group. Moreover, Naugard inhibitors are sufficiently stronger in decreasing the rate of initiation: equilibrium constant K_w is 2–3 degrees higher for Naugard than for Naugalube. As a result, at similar concentration $[\text{InH}]_o$ inhibitors of the Naugard group decrease the rate of oxidation stronger and hold it constant for a longer time, i.e. brightly expressed induction period is characteristic for them Figures 62 and 63.

2) A large value of P_{-7} parameter of inhibitors of the Naugalube group decreases their efficiency strongly in presence of hydroperoxides: the rate of oxidation grows fast with increase of $[\text{ROOH}]$ concentration. The stage with constant rate disappears from the kinetic curve, and it is being "linearized" (Figure 62).

3) The presence of an active product InOOR for inhibitors of the Naugalube group increases the duration of retardance: slow growth of oxidation rate is being observed for a long period of time.

4) A comparatively large P_{10} value for inhibitors of the Naugalube group leads to the fact that initial rate of oxidation decreases only until a definite level with

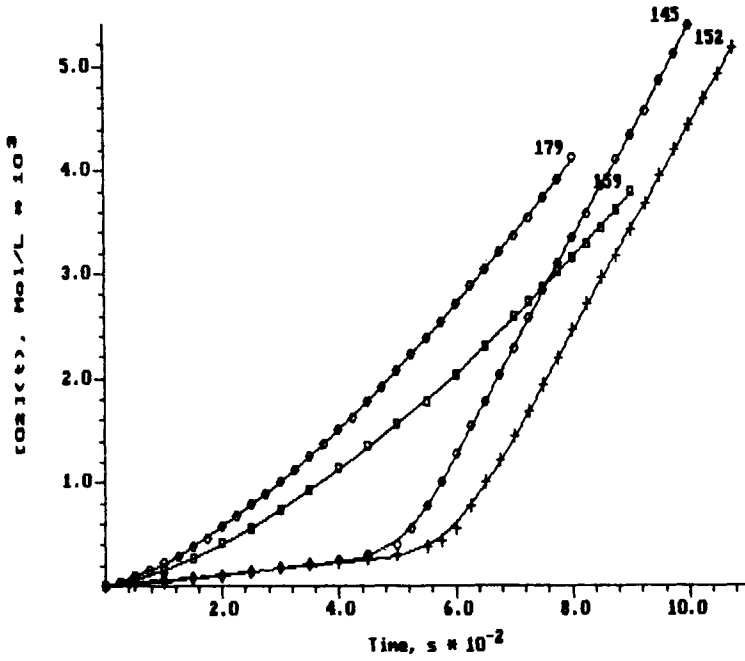


FIGURE 62 Hexadecane $T = 140$ $W_1 = 1e-6$ $InH = 2e-4$.

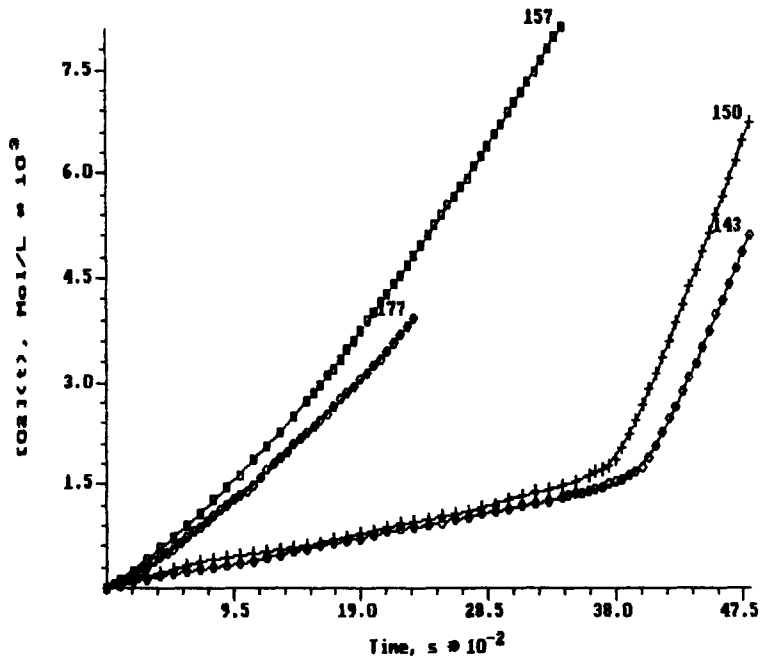


FIGURE 63 Hexadecane $T = 140$ $W_1 = 1e-6$ $InH = 1e-3$.

the growth of $[\text{InH}]_o$ concentration. Relative difference between rates of oxidation grows with the increase of concentrations of Naugalube and Naugard inhibitors (Figures 62 and 63).

5) The process of auto-oxidation retardance of oxidized samples is defined by InH product. $P_7^{(1)}$, $P_8^{(1)}$ parameters of this product for all the inhibitors are close, consequently, kinetic curves are close as well. The difference is present only at the initial stage, where gas isolation is observed in the presence of Naugard inhibitors.

The main conclusions, which can be made on the basis of data from Table I, are well illustrated by Figures 62 and 63. These figures perform the comparison of experimental kinetic curves for all the investigated inhibitors at two values of $[\text{InH}]_o$: $2 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$ mole/l.

The mathematical model allows the features of the investigated process by calculation to be studied. For example, the behavior of experimental data of Figure 62 at longer time periods is of interest. The results of a corresponding computation are present in Figures 64 and 65. It can be seen that at a defined concentration $[\text{InH}]_o$, inhibitors of the Naugalube group are integrally more effective than the Naugard ones: the quantity of oxygen absorbed in their presence at $t > 0.8 \cdot 10^3$ sec becomes lower than in the presence of the Naugard group of inhibitors.

Mathematical modeling allows control of the change of concentrations of different substances and rates of reactions with time. Calculated curves of the expense of Naugard 1–4 and Naugalube 640 inhibitors, and the storing of InOOR—the product of Naugalube 640 transformation—are present in Figures 66 and 67 which, show kinetic curves of hydroperoxide storing in those very experiments. Different ways of retardance of radicals according to Equation (36) are shown in Figure 67.

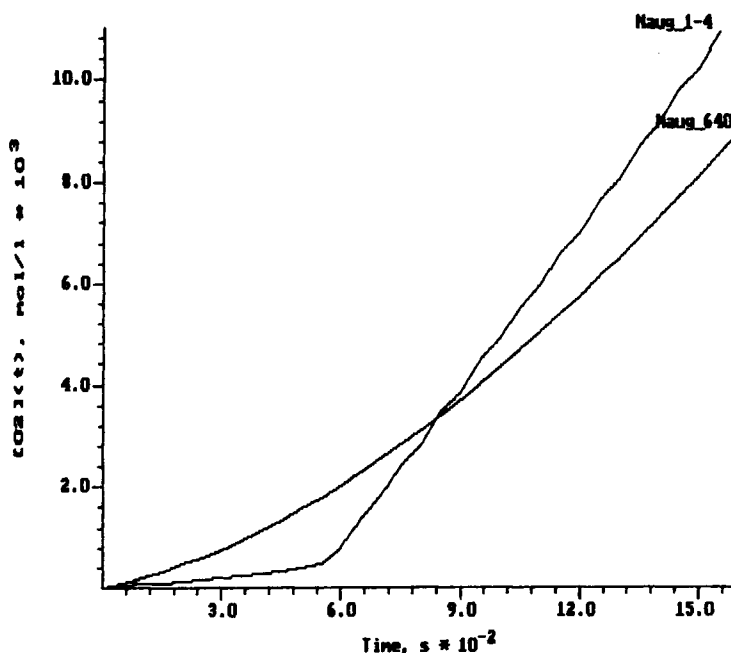


FIGURE 64 Hexadecane $T = 140$ $W_i = 1e-6$ $\text{InH} = 2e-4$ calculation.

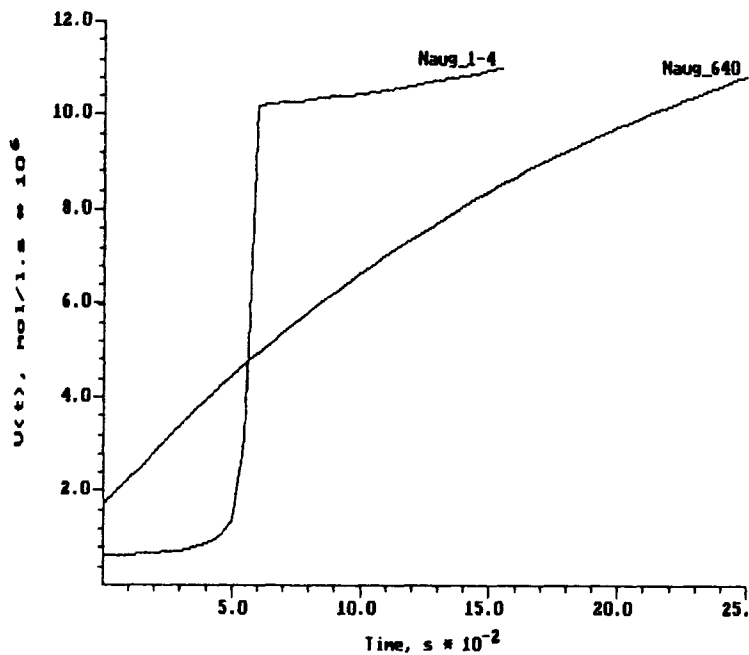


FIGURE 65 Hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = 2e-4$ calculation.

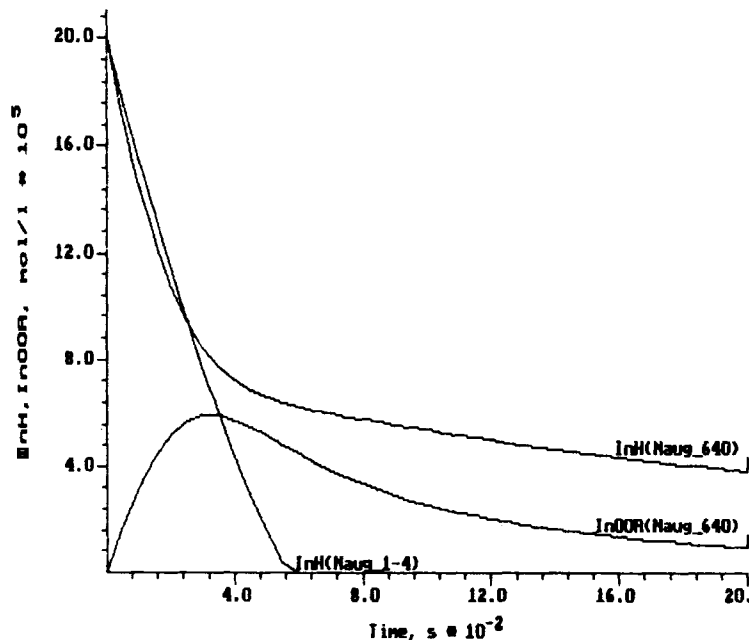


FIGURE 66 Hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = 2e-4$ calculation.

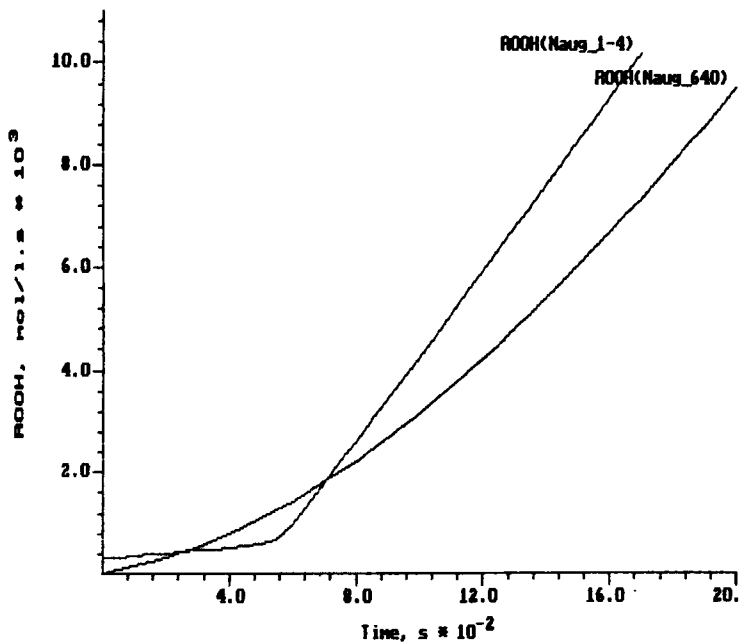


FIGURE 67 Hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = 2e-4$ calculation.

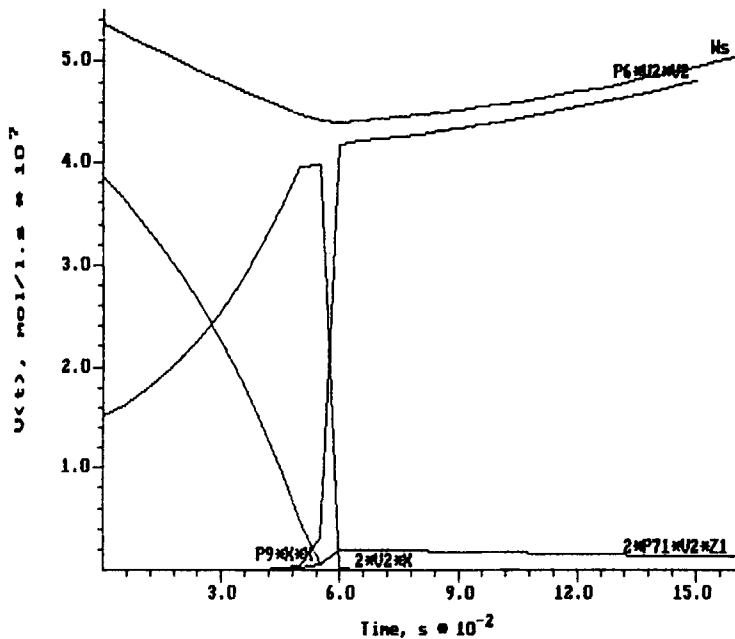


FIGURE 68 Naug_1-4 hexadecane $T = 140$ $W_1 = 1e-6$ $\ln H = 2e-4$ calculation.

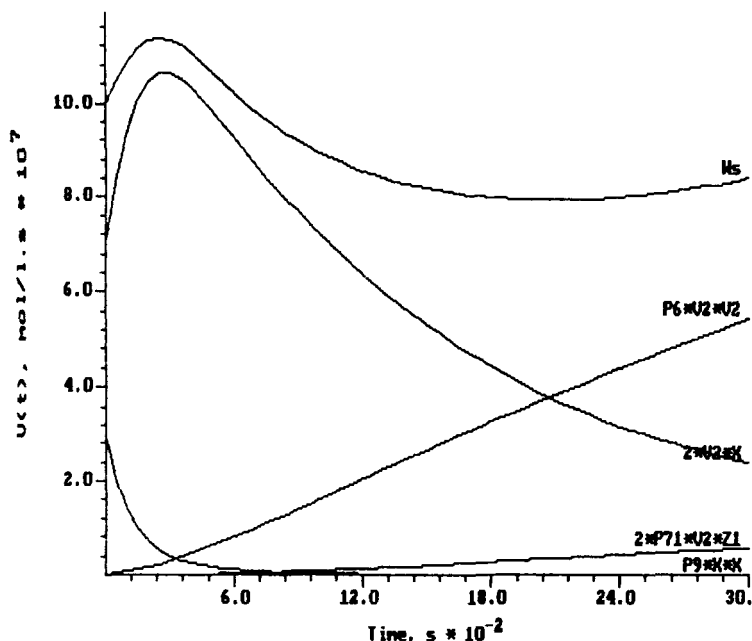


FIGURE 69 Naug_640 hexadecane $T = 140$ $W_i = 1e-6$ $\ln H = 2e-4$ calculation.

These data allow control of the change of correlation of different ways of terminating radicals with time in the considered process of inhibited oxidation.

Thus, mathematical modeling of the process gives the possibility of explaining the behavior of experimental data, comparing the efficiency of the effect of different inhibitors on a quantitative level, and clearing up the cause of difference or similarity of their efficiencies. It allows calculation of the behavior of the system in conditions, different from experimental ones, to control the change of concentrations of substances and rates of reactions, defining the process of retardation.

CONCLUSIONS

1) Kinetic rules of inhibited oxidation of *n*-hexadecane have been investigated at 140°C in presence of the following inhibitors: Naugard 1–4, Naugard R, Naugalube 640, Naugalube 680. The investigation was performed under conditions of auto-oxidation and initiated oxidation at different rates of initiation in a wide interval of concentration changes of inhibitors and hydroperoxides at different oxygen partial pressures.

2) A mathematical model of the investigated process has been worked out that characterizes quantitatively its main rules, describes all the existing experimental data.

3) The results of our investigation allow us to divide four considered inhibitors into two groups: Naugard 1–4 and Naugard R and Naugalube 640 and Naugalube 680. Inhibitors of the first group have a large intensity of retardance (large values

of parameters $P_{7,0}$ and $P_{7,2}$). Intensity of retardance of the second group of inhibitors is lower, because of lower $P_{7,0}$ and $P_{7,2}$ and larger P_{-7} and P_{10} ; however, the presence of an active product of transformation (supposedly InOOR) increases duration of their retardant effect.

4) For the investigated inhibitors, the mechanism of retardance of auto-oxidation of the preliminary oxidized samples differs qualitatively from that present under conditions of initiated oxidation. In oxidized medium, inhibiting is caused mainly by the product of transformation of initial inhibitor (supposedly InOH). Properties of this product are weakly dependent on the structure of the initial inhibitor: the product of all the inhibitors has a low intensity and very long duration of retardance.

5) In the presence of inhibitors of the Naugard group auto-oxidation of oxidized samples is followed by gas isolation on a certain initial stage. The supposition has been put forward that gas isolation appears during decomposition of hydroperoxides of a definite structure under influence of inhibitor molecules able to structurize oxidizing medium.

6) The influence of investigated inhibitors on initiating properties of cumylperoxide has been found: in presence of inhibitors the rate of initiation decreases. This property is the most potent for the Naugard group and lower for the Naugalube one. This phenomenon is evidently connected with structurizing ability of nitrogen containing molecules of these inhibitors.

7) A sharp increase of oxidation rate has been observed at maximal concentration of Naugalube 680 inhibitor $[InH]_0 = 5 \cdot 10^{-2}$ mole/l. The supposition has been made that it is connected with the presence of an admixture possessing initiating properties. Kinetic characteristics of this admixture–initiator and of its quantity have been estimated ($\approx 2,7\%$ of Naugalube 680 concentration).

RESUME

The results received in the present work lead us to formulate the problem of the connection of structure of antioxidants with the efficiency of their action in a new way. Two new aspects of this problem were pointed out:

1) It is necessary to take into account both the formal-kinetic characteristics of inhibitors (totality of reactions of inhibited oxidation and numerical values of kinetic parameters, characterizing these reactions), as well as other characteristics. For example, physical–chemical properties of molecules of antioxidants and, in particular, their ability to affect the properties of oxidizing medium.

2) One should be careful in attempts to predict the efficiency of antioxidant effect at deep stages of oxidation on the basis of quantitative characteristics of action of these antioxidants received at the initial stages of oxidation. This is also correct for predicting of the efficiency of antioxidants in complicated technical mixtures (fuels, oils, lubricants, polymer materials, etc.) on the basis of quantitative characteristics of their action in pure hydrocarbons. Some more details for items 1 and 2 follow.

Item 1

From very general positions, the physical sense of the phenomenon discovered seems simple. In non-polar hexadecane even weakly polar oxygen-containing molecules, for instance, peroxides and hydroperoxides, are being concentrated around the inhibitor molecule. It happens under the effect of nitrogen atoms. It is well-known in principle that nitrogen- and sulfur-containing compounds form labile micellae in oxidizing benzenes, reactive and diesel fuels, promoting fall-out formation. However, until now the ability of antioxidant molecules for structurizing of the oxidizing medium was not considered as the factor influencing the efficiency of their action. Now a problem arises of working out the methods and parameters of identification and quantitative characterization of this property of antioxidants. Inhibitors of the Naugard group may serve a convincing example of this. Here we are not talking about certain corrections of the characteristics of their efficiency. It is impossible to receive mathematical model of their effect without taking into account structurizing properties of these molecules.

Item 2

It was found that the initial molecules of inhibitor in an oxidized medium can transform fast and completely into other compounds which possess inhibiting (or any other) activity. In the present work we have met the fact that for the initial molecules of antioxidants with different structure and properties, the products of their transformation had practically similar efficiencies. Kinetic curves of oxygen absorption in oxidized samples of hexadecane appeared close for all the four initial structures. In general, this is not obligatory: the products of transformation of different initial antioxidants can have different efficiencies as well. The fact is of principle here that it is necessary to know all of this while predicting both the change of efficiency of antioxidant action along with the depth of substrate oxidation and their efficiency in media initially containing the products of oxidation.

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