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The Mathematical Model for the Inhibition Mechanism of 2,4,6-Tri-*tert*-butylphenol in Low-Density Polyethylene Melt Oxidizing at 120–140°C

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The inhibition mechanism of 2,4,6-tri-*tert*-butylphenol in low-density polyethylene melt oxidizing at 120, 130, 140°C was studied using the procedures developed to study complicated processes of chain oxidation and inhibition in hydrocarbon materials. At each temperature the key reactions of antioxidant action were identified and the corresponding kinetic parameters determined. The analysis showed how the effectiveness of tri-*tert*-butylphenol changes as a function of temperature.

INTRODUCTION

Two types of approaches have been proposed to investigate the complex processes of inhibited oxidation of organic substances. The scope of the first type approach is limited to the study of separate reactions and determination of the changes of their rate constants.^{1–5} This type of investigations produced the basis for many aspects of modern theory of inhibited oxidation.

However, the data obtained by this type of investigations are insufficient to fully characterize the antioxidant efficiency in various concrete conditions. The efficiency of an antioxidant is the result of a large number of reactions proceeding simultaneously. Therefore, this efficiency cannot be characterized with satisfactory accuracy using incomplete fragmental presentation of the mechanism of antioxidant action. Therefore, special experimental investigation methods are necessary, to

accurately identify the mechanism of inhibited oxidation and the quantitative determination of its characteristics.

The development of the second type of approach represents a new direction in the investigation of inhibited oxidation processes. These approaches include in addition to development of new experimental methods and special equipment, also a great deal of computations. These combined experimental-computational allowed us to solve satisfactorily a number of specific cases.⁶⁻¹⁰

However, because of the complexity of the problem, the application of general methods is not successful in every case.

In this respect, the development of a quantitative investigation method of antioxidant action activity is of great importance. On one hand the method should reflect the specificity of inhibited oxidation processes, and on the other, its universal character. In addition, the method should also be applicable for the investigation of antioxidants at various oxidation conditions. The most universal index is the rate of oxygen absorption by the oxidizing substance, because it reflects the final result of all main reactions in proceeding the system. In References 11 and 12 a method was worked out for the identification of mechanisms of antioxidant action and determination of kinetic parameters based on oxygen absorption kinetics $[O_2](t)$ measured experimentally using a high-sensitive differential manometric device.¹³

The method was based on the determination of initial oxidation rate $v(O) = d[O_2]/dt|_{t=0}$ at various concentrations of antioxidant, initiator, hydroperoxides, solved oxygen.

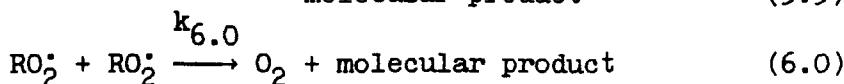
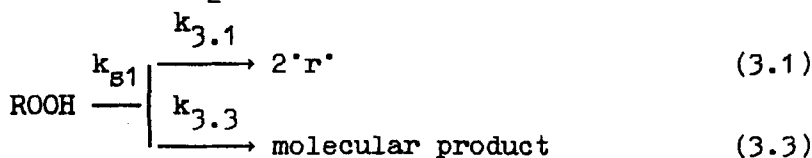
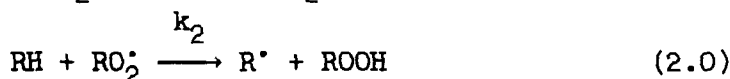
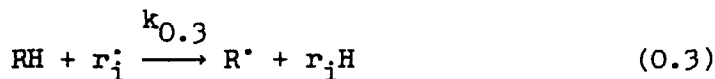
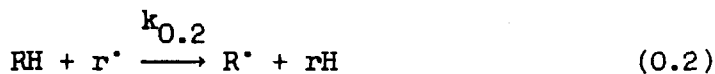
Thus, only initial part was used for $v(O)$ determination from total kinetic curve of inhibited oxidation. This minimized the role of initial antioxidant transformation products, with inhibiting and initiating properties.

By means of this method the investigations were performed on reaction mechanisms of a number of antioxidants of complicated phenols and aromatic amines.¹⁴⁻¹⁵ One important result of these studies was the finding that under the conditions of investigations, the products of transformation of antioxidants did not influence significantly the oxidation process. This allows us to use the complete kinetic $[O_2](t)$ curve and not only its initial part for the study of this class of antioxidants.

In the present paper, this modified method is used to investigate the inhibiting mechanism of tri-*tert*-butylphenol of low-density polyethylene melts oxidized at 120, 130 and 140°C.

TASK

Before investigating the mechanism of antioxidant action in a specific oxidizing medium, it is necessary to determine accurately the oxidation mechanism in this medium. In present work we used the low-density polyethylene (M.M. = 2000) as the hydrocarbon medium. The initial stages of its oxidation are fully described by the following set of transformations¹⁶:



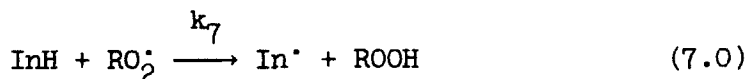
Here RH = oxidizing medium, I = initiator, e = probability of initiator radical appearing in the reaction volume, $r \cdot$ = radical of any structure different from $r_i \cdot$, $R \cdot$, $\text{RO}_2 \cdot$. Initiator constants $k_{0.1}$ and e should be determined by independent experiments and are therefore known.

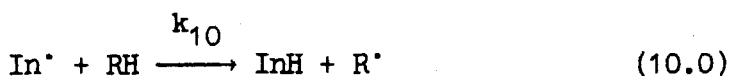
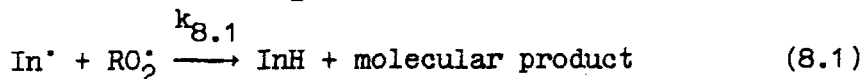
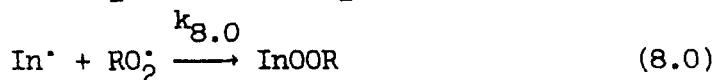
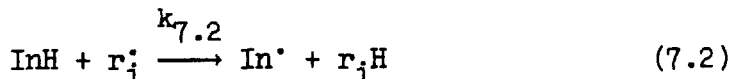
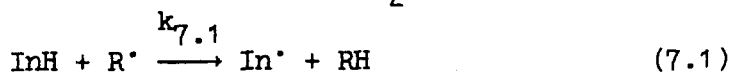
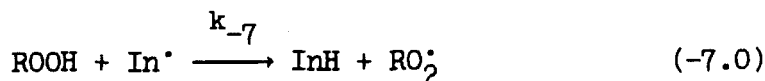
This process proceeds in a quasistationary regime in relation to the concentration of radicals and is fully characterized by the following kinetic parameters:

$W_0 = 2k_{0.0}[\text{O}_2][\text{RH}]_0$ = radical formation rate without taking into account ROOH degradation; $P_6 = 2k_6/(k_2)^2[\text{RO}_2 \cdot]_0$ = parameter of quadratic break of $\text{RO}_2 \cdot$ radicals; $P_{3.1} = k_{3.1} \cdot P_2$ = parameter of degenerated 1-st order branching corresponding to ROOH; $k_{s1} = k_{3.1} + k_{3.3}$ = constant of total 1-st order hydroperoxide consumption.

First, it is necessary to determine the values of these parameters at 120, 130, 140°C. For this purpose it is required to perform one antioxidation experiment at each temperature using the initial polyethylene (in this experiment the oxidation depth must be fairly large). In addition, 2–3 experiments of initiated oxidation at quite high rate of initiation are required.¹⁷

The next stage is the study of the mechanism of antioxidant action. The following classic inhibition scheme¹⁸ represents the basis for the proposed method:





Process (7.0)–(10.0) proceeds in quasistationary regime relative to In^\bullet radical concentration and is characterized quantitatively by kinetic parameters as follows:

$P_{7.0} = k_7/k_2[\text{RH}]_0$ = parameter, characterizing activity of InH molecule according to RO_2^\bullet radical; $P_{7.1} = k_{7.1}/k_1[\text{O}_2]$ = parameter, characterizing the activity of InH molecule according to radical R; $P_{7.2} = k_{7.2}/k_{0.3}[\text{RH}]_0$ = parameter, characterizing the activity of InH molecule according to initiator radical r_i^\bullet ; $P_8 = k_{8.0}/k_{8.0} + k_{8.1}$ = regeneration parameter of InH molecule in chain breaking acts; $P_{-7} = k_{-7} \cdot C$ = parameter, characterizing In^\bullet radical activity with respect to ROOH molecule; $P_9 = 2k_{9.0} \cdot C^2$ = parameter of quadratic break of In^\bullet radicals; $P_{10} = k_{10} \cdot [\text{RH}]_0 \cdot C$ = parameter, characterizing In^\bullet radical activity with respect to RH substrate; Designation: $C = k_2[\text{RH}]_0/(k_{8.0} + k_{8.1})$.

To identify the mechanism of antioxidant action and to determine kinetic parameters using this method, it is necessary to perform 4 series of experiments at each temperature. In these experiments kinetics of oxygen absorption $[\text{O}_2](t)$ is measured as a function of the following parameters:

- (i) Partial oxygen pressure at rather high $[\text{InH}]_0$.
- (ii) Initiation rate at rather high inhibitor concentration $[\text{InH}]_0$.
- (iii) Initial inhibitor concentration $[\text{InH}]_0$ at a given initiation rate.
- (iv) Hydroperoxide concentration $[\text{ROOH}]_0$ in specially oxidated substrate samples at a given $[\text{InH}]_0$.

Using this data the key reactions in the mechanisms (7.0)–(10.0) are determined at each temperature and the values of corresponding kinetic parameters for antioxidant investigated are determined.

The last stage of the investigation is the verification of the results. This is done by comparing the calculate kinetic curves of oxygen absorption (using the values of parameters obtained through calculations) with the experimental curves. A good agreement between the calculations and experimental results in a wide range of experimental conditions would indicate that the mechanism of the process was identified correctly and the values of kinetic parameters determined accurately.

EXPERIMENTAL

Low-density polyethylene was purified by reprecipitation and partial fractionation from CCl_4 . Polymer obtained showed the following characteristics: M.M. = 2000, viscosity at 135° – 65 spz., density 0.775 g/cm^3 (135°) and 100–150 branchings per each 1000 chains.

Cumylperoxide applied as initiator was twice recrystallized from ethanol. The rest of the reagents and solvents were purified using standard procedures.

Investigations were performed at 120, 130 and 140°C . Kinetics of oxygen absorption by oxidizing polymer was measured experimentally using a special high-sensitive differential manometric device.¹³ The content of hydroperoxides was determined by iodine-metric method.

At the end of each test preliminary treatment of experimental data was performed using differentiation and smoothing of kinetic curves of oxygen absorption. Based on the data of each test we calculated the dependence of oxidation rate on time $v(t)$, that was used for identification of process mechanism and determination of kinetic parameters.

CALCULATIONS

The investigation of process mechanism started with determination of kinetic parameters of polyethylene oxidation. First, the dependences of oxidation rate on time $v(t) = d[\text{O}_2]/dt$ were calculated by differentiating and smoothing the data of experiments with initiated and autooxidized polyethylene in absence of tri-*tert*-butylphenol. The values of parameters W_0 , P_6 , $P_{3,1}$, k_{s1} at 120, 130 and 140°C were determined from these relationships using previously developed procedures to investigate the oxidizability of hydrocarbons¹⁸ (Table I).

The first step in the investigation of the effect of tri-*tert*-butylphenol is preliminary identification of its mechanism. Direct experimental testing indicates the presence of the following reactions: (7.1), (7.2), (10.0). Two series of experiments, at rather high antioxidant concentration $[\text{InH}]_0$ should be performed on oxygen absorption in initiated oxidation to estimate the importance of these reactions. The first series involves the experiments at various partial pressures of oxygen, and the second includes experiments at various rates of initiation.

In presence of the reaction (7.1) a decrease of concentration of oxygen, solved in medium, should lead to a decrease of oxidation rate. Figure 1 shows kinetic

TABLE I
Parameters of oxidation of low density polyethylene at 120–140°C

$P_j/T^\circ\text{C}$	120	130	140
$P_6 \cdot 10^{-3}$	4.37 ± 0.03	2.38 ± 0.05	1.06 ± 0.04
$W_0 \cdot 10^8$	0.87 ± 0.06	1.81 ± 0.13	10.4 ± 0.8
$P_{3,1} \cdot 10^5$	0.81 ± 0.09	1.53 ± 0.11	3.02 ± 0.24
$k_{s1} \cdot 10^3$	1.52 ± 0.16	3.12 ± 0.30	5.87 ± 0.42

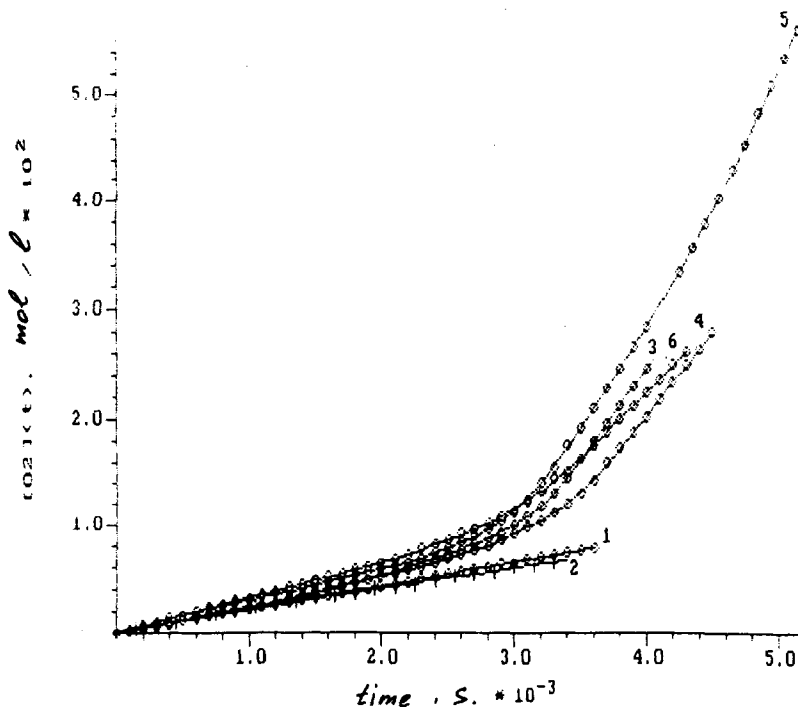


FIGURE 1 The kinetic curves of the oxygen consumption in initiated oxidation of low-density polyethylene melt at 130°C (1, 2) and 140°C (3–6) in presence tri-*tert*-butylphenol. The concentration of TTBP $[InH]_0 = 1 \cdot 10^{-2}$ mol/l. The oxygen partial pressure %: 1, 3—100, 4—77, 5—43, 2, 6—21.

curves, obtained at various partial pressures of oxygen at 120, 130 and 140°C. At 120°C the results of tests in oxygen and air are similar. At 130°C the same situation is observed. Thus, for tri-*tert*-butylphenol we observed no clear dependence of oxidation rate on partial oxygen pressure at any temperature of investigation. Consequently, under conditions of present experiments the role of reaction (7.1) can be neglected.

The identification of reactions (7.2), (10.0) is based on the results of a series of tests with various initiation rates w_i . At rather high inhibitor concentration, the dependence of $v(O)/w_s^{0.5}$ on $w_i/w_s^{0.5}$ falls on straight lines with the slope of $1/(1 + P_{7.2}[InH]_0)$ and ordinate axis intersect at $P_{10}/P_9^{0.5}$ (here $w_s =$ total initiation rate due to the degradation of initiator and hydroperoxides).

Figure 2 shows the corresponding relationships for tri-*tert*-butylphenol at three temperatures. All straight lines have a slope whose tangent is less than unity. This indicates the presence of reaction (7.2). The observed ordinate axis intersection means, that the reaction (10.0) plays a significant role in the mechanism of tri-*tert*-butylphenol action. Quantitative treatment of these relationships gives the following initial approximations for the respective parameter values (at 120, 130 and 140°C):

$$P_{7.2} = (50.2, 55.6, 41.8) \quad P_{10}/P_9^{0.5} \cdot 10^4 = (2.6, 3.8, 5.3)$$

The next step of the investigation is determination of numerical values of kinetic

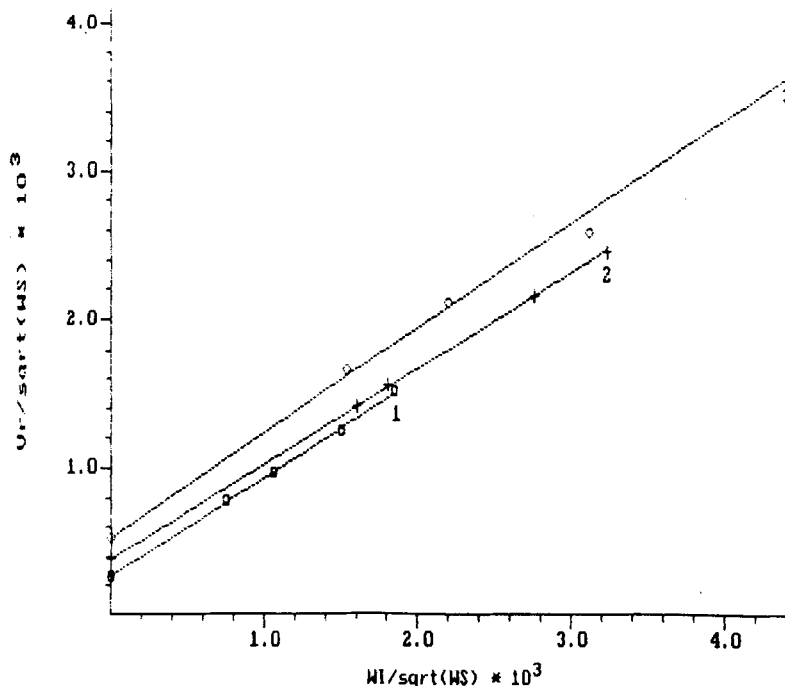


FIGURE 2 The dependences $v(O)/w_s^{0.5}$ on $w_i/w_s^{0.5}$ for tri-*tert*-butylphenol in polyethylene melt at the temperature °C: 1—120, 2—130, 3—140. The concentration of TTBP $[InH]_0 = 1 \cdot 10^{-2}$ mol/l.

parameters. It is performed by an iteration process. At each iteration the parameters are calculated as follows:

$$P_7, P_8, \rightarrow P_9 \rightarrow P_{-7} \rightarrow P_{7.2} \rightarrow P_{10}$$

Dependences $v(t)$, calculated in various series of tests, are used for determination of parameters. Each parameter is determined from the experimental data obtained under conditions, in which the influence of parameters not yet established is minimal. The values of such "unimportant" parameters are taken from previous iteration. The parameter values are determined from the parts of kinetic curves where their influence is maximal.

Thus the group of parameters P_7, P_8 is determined from the initial parts of $v(t)$ dependences in tests with low initial concentrations of antioxidant $[InH]_0 \approx 10^{-5} - 10^{-4}$, $P_9 =$ at $[InH]_0 \leq 10^{-3}$ and $P_{7.2} =$ at $[InH]_0 \approx 10^{-2}$ mole/l. Parameter P_{-7} is determined from a special series of tests on inhibited oxidation of preliminarily oxidized polyethylene samples containing a rather large amount of hydroperoxides. The series of tests with various initiation rates w_i at rather high antioxidant concentration $[InH]_0 \approx 10^{-2}$ mole/l is used for determination of P_{10} parameter.

By means of this treatment of experimental data we obtained the values of kinetic parameters for tri-*tert*-butylphenol at three temperatures listed in Table II.

TABLE II
Kinetic parameters of inhibition for 2,4,6-tri-*tert*-butylphenol in low density polyethylene at 120–140°C

$P_i/T^\circ\text{C}$	120	130	140
$P_{7.0} \cdot 10^{-3}$	1.25 ± 0.03	1.03 ± 0.08	0.77 ± 0.02
$P_{-7} \cdot 10^5$	≈ 2	≈ 4	≈ 6
$P_{7.2}$	55.0 ± 3.3	46.4 ± 2.8	45.1 ± 4.1
P_8	0.70 ± 0.03	0.88 ± 0.07	1.00 ± 0.05
$P_9 \cdot 10^6$	1.16 ± 0.08	2.25 ± 0.19	6.26 ± 0.58
$P_{10} \cdot 10^7$	2.32 ± 0.15	5.43 ± 0.77	14.3 ± 1.3

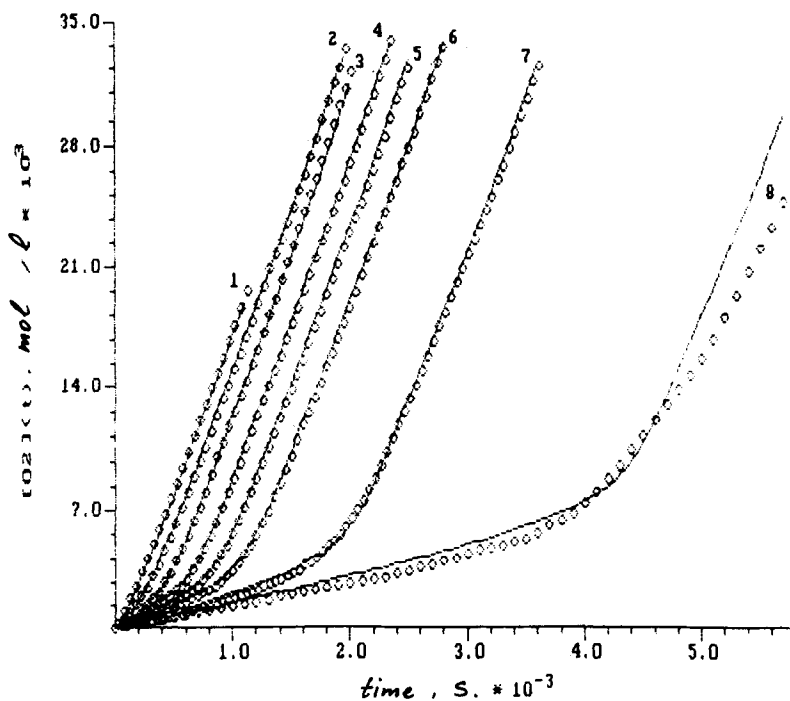


FIGURE 3 The comparison of the experimental and theoretical kinetic curves of the oxygen consumption in initiated oxidation of low-density polyethylene melt in presence tri-*tert*-butylphenol at 120°C. The initiation rate $w_i = 1.14 \cdot 10^{-6}$ mol/l·s. The concentration of TTBP $[\text{InH}]_0 \cdot 10^4$ mol/l: 1—0.38, 2—1.0, 3—2.0, 4—3.0, 5—4.0, 6—5.0, 7—10.0, 8—25.0.

DISCUSSION

The complete set of the obtained data shows, that the mechanism of inhibiting action of tri-*tert*-butylphenol includes all the reactions from (7.0) to (10.0), excluding (7.1). Under investigated conditions, the role of the last reaction is negligible. Reaction (–7.0) influences weakly the rate of the process. Consequently, the values of P_{-7} parameter are only approximate. The rest of parameters are estimated quite accurately with a relatively small error.

An important state of the investigation is the evaluation of the results. This is

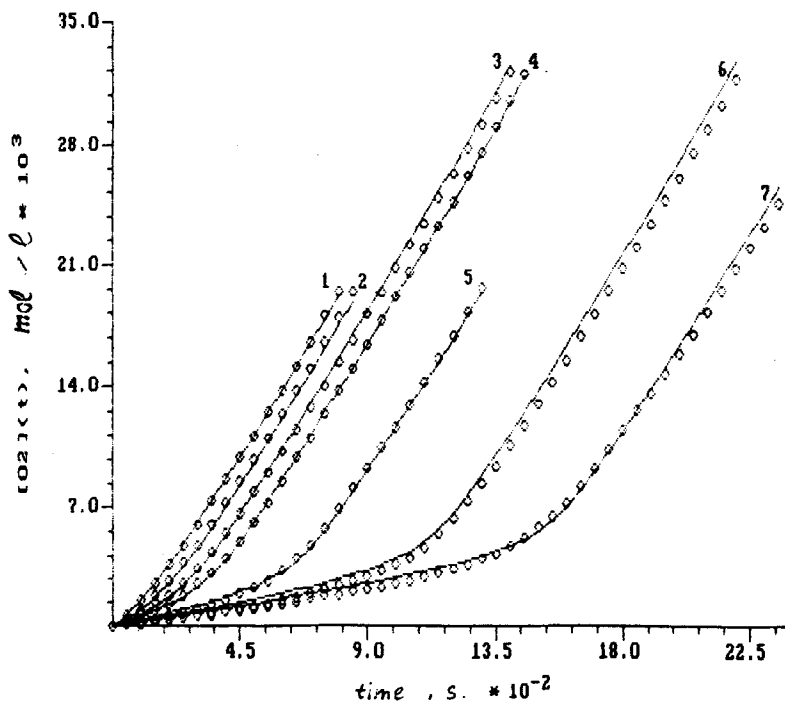


FIGURE 4 The comparison of the experimental and theoretical kinetic curves of the oxygen consumption in initiated oxidation of low-density polyethylene melt in presence tri-*tert*-butylphenol at 130°C. The initial rate $w_i = 1.25 \cdot 10^{-6}$ mol/l·s. The concentration of TTBP $[\text{InH}]_0 \cdot 10^4$ mol/l: 1—0.5, 2—1.0, 3—1.5, 4—2.0, 5—4.0, 6—7.0, 7—10.0.

accomplished by substituting the values of determined parameters into the system of equations corresponding to the full scheme of reactions (0.0)–(10.0), and calculating the kinetic curves of oxygen absorption and comparing these curves with the experimental ones. Figures 3–5 show the comparison of experimental (points) and calculated (continuous lines) kinetic curves $[\text{O}_2](t)$ at initiated oxidation for various concentrations of tri-*tert*-butylphenol at 120, 130, 140°C. The satisfactory agreement between the calculations and experiments proves that the mechanism of the process has been correctly identified, and the parameter values are fairly accurate.

Let us now analyze the data from Table II. Parameter $P_{7.0}$ has a negative temperature dependence, because the expression for $P_{7.0}$ includes the ratio of the rate constants $k_{7.0}/k_2$, and the activation energy for $P_{7.0}$ is lower, than that for k_2 . Activation energy $E(P_{7.0})$ of $P_{7.0}$ parameter equals approximately the difference $E(k_{7.0}) - E(k_2)$ and can be calculated from the data of Table II: $E(P_{7.0}) = -32.6 \pm 3.8$ kJ/mole.

Parameter $P_{7.2}$ has no distinct temperature dependence. Apparently, the difference of activation energies $E(k_{7.2}) - E(k_{0.3})$ is too small, and measurements in wider temperature interval are necessary for its reliable determination. Nevertheless, the obtained result allows us to conclude that in the temperature range between 120–140°C values of $P_{7.2}$ parameter fall between 45–55 l/mole.

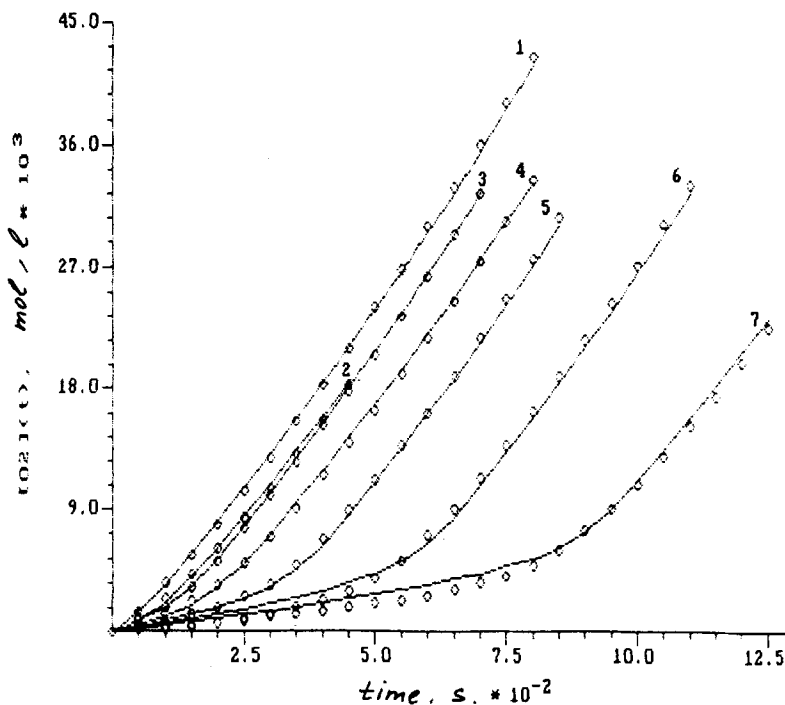


FIGURE 5 The comparison of the experimental and theoretical kinetic curves of the oxygen consumption in initiated oxidation of low-density polyethylene melt in presence tri-*tert*-butylphenol at 140°C. The initiation rate $w_i = 1.82 \cdot 10^{-6}$ mol/l·s. The concentration of TTBP $[InH]_0 \cdot 10^4$ mol/l: 1—0.5, 2—1.0, 3—1.5, 4—2.0, 5—4.0, 6—7.0, 7—10.0.

The value of P_8 parameter at 120 and 130°C is less than unity. This suggests on the basis of the scheme (7.0)–(10.0) the regeneration of antioxidant molecules in the process of chain breaking. It follows from the Table II that the ability for regeneration of tri-*tert*-butylphenol in polyethylene is not high, and it decreases with increasing temperature.

Parameters P_9 and P_{10} show positive temperature dependence, and corresponding activation energies can be determined from the data of Table II: $E(P_9) = 113 \pm 16$ kJ/mole; $E(P_{10}) = 123 \pm 7$ kJ/mole.

The obtained estimates of activation energies allow us to calculate the values of kinetic parameters at other temperatures, for example, at 100 and 150°C. This provides the efficiency estimates of tri-*tert*-butylphenol in a wider temperature interval.

In conclusion, the key parameters defining the efficiency of tri-*tert*-butylphenol in the temperature interval of 120–140°C, are $P_{7.0}$, $P_{7.2}$, P_8 , P_9 , and P_{10} . The efficiency of antioxidant increases with increasing values of $P_{7.0}$ and P_8^{-1} and decreasing values of P_9 and P_{10} . With the increasing temperature the first two parameters decrease, while the other two—increase abruptly. This leads to an abrupt decrease of the antioxidant efficiency.

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