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# Inhibition Mechanisms of Sterically Hindered Phenols in Oxidizing Low-Density Polyethylene Melt: Mathematical Modelling

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The kinetic investigation of the inhibition mechanisms of 2.6-di-ferf-butylphenol and 2,6-di-ferf-butyl-4-metylphenol in low-density polyethylene melt oxidizing at 120, 130, 140°C has been carried out and the mathematical models of the mechanisms were developed. At each temperature the key reactions in the mechanisms of action of antioxidants were identified and the corresponding kinetic parameters were determined. The comparison of the efficiencies of these antioxidants and **2,4,6-tri-ferf-butylphenol**  studied earlier has been carried out.

KEY WORDS Phenols, sterically hindered phenols, oxidation, polyethylene melt, low density polyethylene, inhibition, mathematical modelling.

#### **INTRODUCTION**

We previously discussed the problem of the quantitative investigation of complex processes of inhibited oxidation of hydrocarbonic materials and considered one of the possible approaches to its solution.' The approach is based on the experimental measurement of kinetics of the oxygen absorption, using a highly sensitive differential manometric device developed for this purpose. The device allows us to measure the rate of oxidation with high accuracy and in a wide range of the experimental conditions. Special mathematical tools were also developed for identification of action mechanisms of antioxidants and determination of kinetic parameters. These tools include the methods, algorithms and programs for fast and advanced treatment of the experimental data with the help of computer.

The suggested method was applied for the detailed investigation of the mecha-

nism of inhibiting action of **2,4,6-tri-tert-butylphenol** in the oxidating melt of polyethylene of low density at 120, 130, **140°C.** 

The aim of the present paper is to continue these investigations with the study of the mechanisms of action of 2,6-di-tert-butylphenol and **2,6-di-terf-butyl-4-meth**ylphenol in the same conditions and to compare the efficiency of action of three investigated spatially-impeded phenols by means of mathematical models.

## **THE PROBLEM**

The investigation of the mechanism of inhibited oxidation of hydrocarbonic materials is performed in two stages. The first stage involves a detailed study of the mechanism of oxidation of hydrocarbonic medium. The second stage involves the study of the mechanism of action of antioxidants in this medium. It was shown in the paper,<sup>1</sup> that the initial stages of oxidation of low density polyethylene at  $120-$ **140°C** are satisfactorily described by the following scheme of transformations:

$$
RH + O_2 \xrightarrow{k_{0.0}} 2 \cdot r
$$
 (0.0)

$$
I \xrightarrow{k_{0,1}} 2e \cdot r_i \tag{0.1}
$$

$$
I \xrightarrow{k_{0.1}} 2e \cdot r_i
$$
 (0.1)  
RH + r<sup>'</sup>  $\xrightarrow{k_{0.2}} R'$  + rH (0.2)  
RH + r<sup>'</sup>  $\xrightarrow{k_{0.3}} R'$  + r,H (0.3)

$$
RH + r_i \xrightarrow{k_{0.3}} R' + r_i H \qquad (0.3)
$$

$$
O_2 + R' \xrightarrow{k_1} RO_2
$$
 (1.0)

$$
RH + RO_2 \xrightarrow{k_2} R^{\cdot} + ROOH \tag{2.1}
$$

$$
ROOH \xrightarrow{k_{3,1}} 2 \cdot r
$$
  
ROOH  $\xrightarrow{k_{3,3}}$  molecular product (3.1)

**(3.3)** 

$$
ROOH \xrightarrow{\kappa_{3,3}} \text{molecular product}
$$
\n(3.3)\n
$$
RO_{2} + RO_{2} \xrightarrow{k_{6,0}} O_{2} + \text{molecular product}
$$
\n(6.0)

Here RH = oxidative medium,  $I =$  initiator,  $e =$  the probability of the initiator radicals outlet entering into the volume,  $\mathbf{r}$  = radical of any structure, different from  $r_i$ , R', RO<sub>2</sub>. Constants of initiator  $k_{0,1}$ , *e* must first be determined by an independent experiment. They are set known in the further investigation.

The present process proceeds in quasi stationary regime in relation to the concentrations of radicals which are fully characterized by four kinetic parameters:

$$
W_0 = 2 \cdot k_{0.0} \cdot [\text{O}_2][\text{RH}]_0; \quad P_6 = \frac{2 \cdot k_6}{(k_2[\text{RH}]_0)^2}; \quad k_{3.1}; \quad k_{s1} = k_{3.1} + k_{3.3}
$$

The values of these parameters at 120, 130 and 140°C were determined in the paper. '

The next stage involves the investigation of the mechanism of antioxidants action. The next stage involves the investigation of the incentains of antioxidants action.<br>We use the following scheme of transformations as the initial approximation for<br>antioxidants of spacially-impedes phenols class:<br> $\text{InH} +$ antioxidants of spacially-impedes phenols class:

$$
InH + RO_2 \xrightarrow{k_7} In^{\cdot} + ROOH \tag{7.0}
$$

$$
InH + RO2 \xrightarrow{k_7} In + ROOH
$$
 (7.0)  
ROOH + In<sup>'</sup> \xrightarrow{k\_7} InH + RO<sub>2</sub> (-7.0)  
InH + R<sup>'</sup> \xrightarrow{k\_{7,1}} In' + RH (7.1)

$$
InH + R^{2} \xrightarrow{k7.1} In^{2} + RH
$$
 (7.1)

$$
InH + R' \xrightarrow{k7.1} In' + RH
$$
 (7.1)  

$$
InH + r'_i \xrightarrow{k7.2} In' + r'_iH
$$
 (7.2)

$$
\text{In}^{\cdot} + \text{RO}_{21} \xrightarrow{k_{8.0}} \text{InOOR} \tag{8.0}
$$
\n
$$
\text{In}^{\cdot} + \text{RO}_{2}^{\cdot} \xrightarrow{k_{8.1}} \text{InH} + \text{molecular product} \tag{8.1}
$$

$$
\text{In}^{\cdot} + \text{RO}_{2}^{\cdot} \xrightarrow{\kappa_{8.1}} \text{InH} + \text{molecular product} \tag{8.1}
$$

$$
i \xrightarrow{k_{8,1}} InH + molecular product
$$
 (8.1)  
In' + In'  $\xrightarrow{k_9}$  In-In (9.0)

$$
\text{In}^{\cdot} + \text{In}^{\cdot} \xrightarrow{k_9} \text{In-In}
$$
\n
$$
\text{In}^{\cdot} + \text{RH} \xrightarrow{k_{10}} \text{InH} + \text{R}^{\cdot}
$$
\n
$$
(10.0)
$$

The process  $(7.0)$ - $(10.0)$  proceeds in quasi stationary regime in relation to the concentration of In' radical and is characterized quantitatively by seven kinetic parameters:

$$
P_{7.0} = \frac{k_7}{k_2[\text{RH}]_0}; \quad P_{7.1} = \frac{k_{7.1}}{k_1[\text{O}_2]}; \quad P_{7.2} = \frac{k_{7.2}}{k_{0.3}[\text{RH}]_0}; \quad P_{-7} = k_{-7} \cdot C
$$
\n
$$
P_8 = \frac{k_{8.0}}{k_{8.0} + k_{8.1}}; \quad P_9 = 2 \cdot k_{9.0} \cdot C^2; \quad P_{10} = k_{10} \cdot [\text{RH}]_0 \cdot C
$$

Definition:  $C = k_2[RH]_0/(k_{8.0} + k_{8.1}).$ 

The study of the mechanism of the particular antioxidant action requires establishing which of the supposed reactions  $(7.0)$ - $(10.0)$  play a significant role. This requires identifying the mechanism of deceleration experimentally, and to determining the values of the corresponding kinetic parameters.

## **EXPERIMENTAL**

Polyethylene of low density was applied as oxidative substrate, and dicumylperoxide-as the initiator. Methods of purification of substances and physico-chemical properties of **PELD** are presented in the paper.'

The investigation was performed at **120,** 130 and 140°C. We experimentally measured the kinetics of the oxygen absorption of the oxidizing polymer with the help of a highly sensitive differential manometric device.<sup>2</sup> The content of hydroperoxides was iodometrically determined.

According to the developed procedure for identifying the mechanism of antioxidants action and determining the kinetic parameters at each 'temperature four series of experiments were performed, measuring kinetics of the oxygen absorption *[O,](t)* as a function of:

- -the partial oxygen pressure at sufficiently high concentration of antioxidant  $[InH]_0$ ;
- -the rate of initiation at the definite and sufficiently high  $[InH]_0$ ;
- -the initial concentration of antioxidant  $[InH]_0$  at the definite rate of initiation;
- —the concentration of hydroperoxides  $[ROOH]_0$  in specially oxidated samples of the substrate at the definite  $[InH]_0$ .

## **MATHEMATICAL**

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Treatment of the experimental data starts with smoothing and differentiating of the initial kinetic curves of the oxygen absorption  $[O_2](t)$ . As a result we obtain the dependences of the oxidation rate on time  $v(t) = d[O_2]/dt$ , which are applied then for identification of the process mechanism and for the determination of the kinetic parameters.

The first step in the investigation of antioxidants is the preliminary identification of the mechanism. This step is concluded in a direct experimental verification of the presence of the reactions (7.1). *(7.2),* and (10.0). To estimate the role of these reactions it is necessary to perform two series of oxygen absorption experiments in the initiated oxidation at sufficiently high concentration of antioxidant  $[InH]_0$ : 1. At different partial pressures of the oxygen, 2. At different rates of initiation.

In the presence of the reaction (7.1) the decrease of dissolved oxygen concentration in the medium leads to the decrease of the oxidation rate. The investigations showed [ 11, that **2,6di-re~t-butyl-4-methylphenole, 2,6-di-tert-butylphenole** and **2,4,6**  tri-tert-butylphenole exhibit no clear dependence of the oxidation rate on partial pressure of the oxygen. **As** an illustration, the Figure **1** shows kinetic curves obtained in the atmosphere of oxygen and air at 140°C. Thus, the role of the reaction (7.1) for the investigated spatially-impeded phenols is negligibly small under conditions of present investigations.



**FIGURE** 1 **The kinetic curves of the oxygen consumption in initiated oxidation** of **low-density polyethylene melt at 140°C in presence 2,6-di-ferf-butyl-4-methylphenol(l, 2) and 2,6-di-ferf-butylphenol**   $(3, 4)$ . The concentration  $[\text{InH}]_0 \cdot 10^2$  mol/l: 1, 2-0.83; 3, 4-8.0. The initiation rate  $W_i = 2.75 \cdot 10^{-6}$ **moll1 's. The oxygen partial pressure** %: 1, **4- 100; 2, 3-21,** 

To identify the reactions (7.2), (10.0) we performed a series of experiments with different rates of initiation  $w_i$  at one and sufficiently high concentration  $[InH]_0$ . At these conditions the dependence of  $v(O)/w_s^{0.5}$  value on  $w_i/w_s^{0.5}$  represents the straight line with the tangent equal to  $1/(1 + P_{7,2}[InH]_0)$  with a ordinate axis cut-off of  $P_{10}/P_9^{0.5}$  (where  $w_s =$  total rate of initiation by means of decomposition of the initiator and hydroperoxides). For comparison, the Figure 2 shows the corresponding dependences for all the investigated phenols at 140°C. The tangent of all the straight lines is less than unity. This confirms the presence of the reaction (7.2). The presence of the ordinate axis cut-off means that the reaction (10.0) plays under the considered conditions a significant role in the mechanism of spacially-impeded phenols.

After the preliminary identification of the mechanism of antioxidant action, the next step of the investigation is the determination of numerical values of kinetic parameters. This is performed by iterations, i.e. the values of  $P_i$  are refined step by step. Parameters on each iteration are calculated from a sequence of the **ex**perimental data obtained under conditions at which the values of the corresponding  $P_i$  are determined with the maximum accuracy. To determine parameters the dependences of  $v(t)$  are used, calculated in different series of experiments.

At first the values of  $P_7$ ,  $P_8$  are determined from the dependences  $v(t)$  in the experiments with low initial concentrations of antioxidant  $\text{[InH]}_0 \approx 10^{-5} - 10^{-6}$ mole/l. Then  $P_9$  value is determined from the experiments with the average con-



**FIGURE 2** The dependences  $v(0)/w_s^{0.5}$  on  $w_t/w_s^{0.5}$  in polyethylene melt at 140°C for: 1-2,4,6-tri**rert-butylphenol, 2-2,6-di-rerr-butyl-4-methylphenol. 3-2,6-di-rerf-butylphenol. The concentration**   $[InH]_0.10^2$  mol/l:  $1-1.0$ ;  $2-0.83$ ;  $3-8.1$ .

centrations of  $\text{[InH]}_0 \leq 10^{-3}$  mole/l. To determine  $P_{-7}$  parameter special series of experiments is performed on the inhibited oxidation of preliminarily oxidated samples of polyethylene containing sufficiently big amount of hydroperoxides. Then, the parameters  $P_{7,2}$  and  $P_{10}$  are determined from the series of experiments with different rates of initiation  $w_i$  at sufficiently high concentration of antioxidant [InH]<sub>0</sub>  $\approx 10^{-2}$  mole/l. Thus, each parameter is determined at conditions at which the influence of not yet determined parameter is minimal; the values of such "secondary" parameters are taken from previous iterations. If the analysis of the experimental data is carried out correctly, the calculating process converges after **3- 4** iterations.

By means of this method, the values of kinetic parameters were determined for 2,6-di-ferf-butylphenol and **2,6-di-fert-butyl-4-methylphenol** at 120, **130** and **140°C.**  The values  $P_i$ , obtained are shown in the Table I. The Table I also shows for comparison the parameters for **2,4,6-tri-terr-butylphenol** from the paper.'

#### **VERIFICATION OF THE EXPERIMENTAL RESULTS**

The last stage of the experimental data treatment is the verification of the obtained results. According to the parameter values obtained it is necessary to calculate

#### TABLE I'



Kinetical parameters of inhibition for 2,6-di-ferf-butylphenol (DTBPh), 2.6-di-ferf-butyl-4 methylphenol (ionole) and 2,4,6-tri-tert-butylphenol (TTBPh) in melt conditions at  $120-140^{\circ}$ C for polyethylene of low density

kinetic curves of the oxygen absorption and to compare them with the experimental ones. The Figures 3 and 4 show the comparison of the experimental points and the calculated continuous lines of kinetic curves  $[O_2](t)$  of the initiated oxidation at 140°C for 2,6-di-tert-butylphenol and **2,6-di-tert-butyl-4-butylphenol.** 

The system of equations corresponding to the scheme  $(0.0)$ – $(10.0)$ , with the obtained values of kinetic parameters by means of mathematical models of action mechanisms of the investigated antioxidants allow us to describe satisfactorily all the existing experimental data for 2,6-di-tert-butylphenol and nearly all—for 2,6**di-tert-butyl-4-methylphenol.** The exceptions are the experiments with sufficiently high concentration  $\text{[InH]}_0$ . There the experimental induction period is longer than the calculated one (Figure 5, curves 1, 2).

Additional increases of the deceleration time with the increase of 2,6-di-tertbutyl-4-methylphenol concentration may be explained by the formation of products of recombination of In' radicals which also exhibit inhibiting properties $3-5$ : e deceleration time with the increase of 2,6-di-tert-<br>
ration may be explained by the formation of products<br>
als which also exhibit inhibiting properties<sup>3-5</sup>:<br>
In<sup>+</sup> + In<sup>+</sup>  $\xrightarrow{k_9}$   $\delta$ ·InH<sub>1</sub> (9.0)

$$
\text{In}^{\cdot} + \text{In}^{\cdot} \xrightarrow{k_9} \delta \cdot \text{InH}_1 \tag{9.0}
$$

It is a success to estimate the value of **6** by the existing experimental data: the Figure 5 shows the curves 1', 2' calculated at  $\delta = 0.5$ . As for the action mechanism of InH, product, the existing data are insufficient for its reliable identification. We assumed, that this mechanism includes the main reactions of the initial inhibiting scheme. We also estimated some kinetic parameters. Calculation of curves l', 2' in the Figure 5 was performed using the following values:

$$
P_{7,0}^{(1)} = 200;
$$
  $P_{-7}^{(1)} = 1 \cdot 10^{-4};$   $P_8^{(1)} = 0.5$ 



**FIGURE 3 The comparison of thc experimental and theoretical kinetic curves** of **the oxygen consumption in initiated oxidation** of **low-density polyethylene melt in presence 2.6-di-tert-butyl-4-methylphenol at 140°C. The initiation rate**  $W_i = 2.75 \cdot 10^{-6}$  **mol/l.s. The concentration**  $[\text{InH}]_0 \cdot 10^4$  **mol/l:** 1-1.3; 2-2.0: *3-3.5;* **3-7.0;** 5-9.0; **6-18;** 7-82,

Although the present values represent estimates, the qualitative result is of sufficient interest:  $InH<sub>1</sub>$  product decelerates less effectively than the initial 2,6-di*tert*-butyl-4-methyl-phenol. This is because  $\text{InH}_1$  possesses a lower  $P_{7,0}^{(1)}$  and a higher  $P_{-7}^{(1)}$  than InH. However, it possesses a longer period of deceleration  $(P_8^{(1)} < 1)$ . Apparently, the value  $P_{8}^{(1)} = 0.5$  is explained by bifunctional structure of InH<sub>1</sub>, when both --OH groups participate in the deceleration:



#### **DISCUSSION**

Using the data from the Table I, let us perform the comparative analysis of the efficiency of the investigated antioxidants action. We will use the common notation: DTBPh--2,6-di-tert-butylphenol, ionole-2,6-di-tert-butyl-4-methylphenol, **TTBPh-2,4,6-tri-tert-butylphenol.** 



**FIGURE 4 The comparison of the experimental and theoretical kinetic curves of the oxygen** con**sumption in initiated oxidation** of **low-density polyethylene melt at 140°C in presence 2,6-di-rerr-butylphenol.** The concentration  $\text{[InH]}_0 \cdot 10^3$  mol/l:  $1 - 0.05$ ;  $2 - 0.45$ ;  $3 - 1.5$ ;  $4 - 4.4$ ;  $5 - 6.0$ ;  $6 - 40$ ;  $7 -$ **80. The initiation rate**  $W_i = 2.75 \cdot 10^{-6}$  **mol/l · s.** 

The efficiency of antioxidants action is characterized by two main components: the intensity and duration of deceleration of the oxidation process. The intensity of deceleration is defined by the following factors:

1. Parameters  $P_{7.0}$ ,  $P_{7.1}$ ,  $P_{7.2}$ . The higher are the values of these parameters, the lower is the oxidation rate in the presence of antioxidant. As it was shown above, the role of the reaction (7.1) is negligibly small under conditions of this study. The values of  $P_{7,0}$  are approximately equal for ionole and TTBPh and are significantly higher than those for DTBPh. Based on the value of  $P_{7,2}$  parameter the investigated antioxidants may be placed in the following sequence: DTBPh < TTBPh < ionole (Table I).

2. Parameters  $P_{-7}$ ,  $P_{10}$ , decrease the intensity of deceleration. The reaction  $(-7.0)$  does not play a significant role for any of the investigated phenols. Threshold values of the parameter  $P_{-7}$  shown in the Table I are defined by the accuracy of the corresponding experimental data. The reaction (10.0) plays a more significant role. The values of the corresponding  $P_{10}$  parameter for the investigated antioxidants differ insignificantly. Nevertheless, it should be noted, that  $P_{10}$  of ionole is a little smaller at all temperatures, than that of TTBPh. At equal  $P_{7,0}$  values this should lead to higher intensity of deceleration for ionole in comparison with 'ITBPh.

The duration of decelerating action of antioxidants is defined by the existence of active products of transformation and by the values of  $P_8$  and  $P_9$  parameters.



**FIGURE** *5* **The inhibiting effect of derivatives of 2,6-di-rerr-butyl-4-methylphenol on initiated oxi**dation of low-density polyethylene melt at 140°C. The concentration  $[\text{InH}]_0$ , 10<sup>3</sup> mol/l: 1,1'-4.13; 2, **2'**, 3,  $3' - 8.3$ . The initiation rate  $W_i$ : 10<sup>6</sup> mol/l·s: 1,  $1' - 2.75$ ; 2, 2', 3,  $3' - 4.13$ . **1'**,  $2' -$ the reaction In'  $+$  In'  $\rightarrow \delta$ . InH<sub>1</sub> is taken into account. 3,3'—the reaction InOOR  $\rightarrow$  2 $\delta$ .r' is taken into account **too.** 

We found that the products of transformation play a significant inhibiting role only with ionole, while the values of other parameters are close to those of other investigated phenols. Therefore, the highest duration of deceleration is observed with ionole.

Thus, the data presented in the Table I allow us to rank the investigated spacially inhibited phenols according to the efficiency of their action:

$$
DTBPh < TTBPh < \text{ionole}.
$$

Mathematical models of the action mechanisms of antioxidants, obtained in the present work allow us to perform numerical investigations of the features of the inhibited oxidation in conditions, different from the conditions of the experiment. Figure 6 shows the results of calculation of the oxygen absorption kinetics in conditions of autooxidation at 140°C in presence of the investigated antioxidants at two different concentrations of  $[\text{InH}]_0:1 \cdot 10^{-3}$  and  $1 \cdot 10^{-2}$  mole/l. The relative position of kinetic curves in this Figure correlates with the above efficiency sequence. In this case even without taking into account the inhibiting product (curves **3,6)** ionole possesses higher efficiency in comparison with 7TBPh. This is explained by the fact, that  $P_{10}$  value for ionole is lower than that for TTBPh. It should be



**FIGURE 6 The calculated kinetic curves of the oxygen consumption in autoxidation of low-density polyethylene melt at 140°C in presence DTBPh (1, 5), TTBPh** (2, *6).* **ionole (3, 4, 7, 8, 9, 9'). The concentration**  $[\text{InH}]_0 \cdot 10^3$  **mol/l:**  $1-4-1.0$ ;  $5-9'-10.4$ ,  $8$ —the reaction  $\text{In'} + \text{In'} \rightarrow 8 \cdot \text{InH}_1$  is taken into account. 9, 9'-the reaction InOOR  $\rightarrow$  28 $\cdot$  r' is taken into account too.

also noted that this correlation of efficiencies holds in the entire range of concentrations  $[InH]_0$  considered in this study.

Finally, let us consider the question about the completeness of the performed investigation. Are there any important reactions we neglected, in the initial transformation scheme **(7.0)-(10.0)?** If in the stage of verification of the results there is a systematic, qualitative difference between the calculation and the experiment, then the initial scheme should include additional reactions, the characteristics of which could be estimated on the basis of this difference.<sup>6</sup> This approach was carried out for the investigations of ionole.

For example, with regard to the reaction

Find the class of this therefore, 
$$
1 \text{ and } 4 \text{.}
$$
 (12.0)

\nIn H + O<sub>2</sub>  $\xrightarrow{k_{12}}$  In  $^{\circ}$  + HO<sub>2</sub>

\n(12.0)

it may be stated, that it does not play a significant role in the considered conditions, it may be stated, that it does not play a significant role in the considered conditions, because the rate constant of this reaction is  $k_{12} \sim 10^{-4}$  l/mole $\cdot$ s,<sup>7-10</sup> and consebecause the rate constant of this reaction is  $k_{12} \sim 10^{-4}$  l/mole·s,<sup>7-10</sup> and consequently, the rate  $k_{12}$  [InH][O<sub>2</sub>]  $\sim 10^{-4} \cdot 10^{-2} \cdot 10^{-2} = 10^{-8}$  mole/l·s-is sufficiently lower than the rate of initiation. This conclusion has a direct experimental proof, namely there is no observed dependence of the oxidation rate on partial oxygen pressure in the experiment (Figure 1).

Another important example is in the decomposition of quinolidic peroxides,<br>
rmed according to the reaction (8.0):<br>  $\text{InOOR} \xrightarrow{k_{11}} 2 \cdot \text{r}$  (11.0) formed according to the reaction **(8.0):** 

$$
InOOR \xrightarrow{k_{11}} 2 \cdot r
$$
 (11.0)

It is clear that at sufficiently high rate constant  $k_{11}$  this reaction will play a significant role in the mechanism of the antioxidant action. Unfortunately, the existing literature data<sup>11</sup> do not allow us to calculate  $k_{11}$  for the conditions of the present work with required accuracy. It is however, possible to estimate the value of  $k_{11}$ , at which the role of the reaction (11.0) will become significant. Figure 6 shows the curve 9, calculated for  $k_{11} = k_{3,1} = 3 \cdot 10^{-5} \text{ s}^{-1}$ , the rest of parameters were the same, as for the curve 8. The present value of  $k_{11}$  influences sufficiently the initiated oxidation also (Figure 5, curve 3). Consequently, if the role of quinolidic peroxides under the considered conditions would be very high, this should be experimentally observed. However, the role of the reaction (11.0) may be insignificant not only because  $k_{11}$  is small, but also because of the additional consumption of quinilidic peroxides in real conditions of oxidation. This is illustrated in Figure 5 (curve 3) and Figure 6 (curve 9) showing the results of calculation with high value of  $k_{11}$  =  $5.10^{-4}$  and the constant of total quinolidic peroxides consumption  $k<sub>s</sub> = 5.10^{-3}$  $S^{-1}$ .

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