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**Abstract**

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## ON THE PARTICIPATION OF AN INHIBITOR IN THE ACT OF DEGENERATE CHAIN BRANCHING

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In previous works ([1],[2]) we suggested that, in the oxidation reaction of a hydrocarbon, inhibitors participate not only in chain termination and initiation, but also in the act of degenerate chain branching. In doing so, we assumed that different inhibitors change in different ways the number of chains initiated, on average, as a result of the decomposition of one hydroperoxide molecule. To verify the correctness of this assumption, we studied the oxidation of isotactic polypropylene in the presence of a mixture of two inhibitors—alkylphenols. Let us write the equation for the development of a branched chain reaction with chain termination on two inhibitors ($IH'$ and $IH''$) in the following form ($x$ is the concentration of active centers):

$$\frac{dx}{dt} = W_0 + \varphi x - k'[IH']x - k''[IH'']x. \qquad \text{(I)}$$

This equation is also valid for a degenerate-branched reaction, such as the oxidation reaction of a hydrocarbon, if the lifetime of the branching product is small compared with the time of development of the reaction. Under the conditions of our experiments, i.e., at 200°, the time of development of the reaction is measured in tens or hundreds of minutes, whereas the branching product (hydroperoxide) decomposes by 50% in approximately 9 sec (extrapolation from the data of work ([3])). The critical concentration of inhibitor, i.e., the concentration below which the reaction proceeds nonstationarily, with self-acceleration, and above which it proceeds stationarily ([4],[5]), is determined from the condition:

$$\varphi x = k'[IH']x + k''[IH'']x. \qquad \text{(II)}$$

In the case of one inhibitor ($[IH''] = 0$)

$$[IH']_{cr} = \frac{\varphi}{k'}, \qquad \text{(III)}$$

and the critical concentration of one inhibitor ($IH'$) in the presence of the other ($IH''$) is equal to

$$[\mathrm{IH}']_{\mathrm{cr}} = \frac{\varphi}{k'} - \frac{k''}{k'}[\mathrm{IH}'']. \qquad \text{(IV)}$$

If the critical concentration of the first inhibitor increases in the presence of the second, i.e.,

$$\frac{\partial[\mathrm{IH}']_{\mathrm{cr}}}{\partial[\mathrm{IH}'']} = \frac{1}{k'}\frac{\partial\varphi}{\partial[\mathrm{IH}'']} - \frac{k''}{k'} > 0 \qquad \text{(V)}$$

then, since

$$\frac{k''}{k'} > 0,$$

this means that the self-acceleration factor of the reaction under consideration increases in the presence of this second inhibitor, i.e.,

$$\frac{\partial\varphi}{\partial[\mathrm{IH}'']} > 0.$$

In the region of nonstationary course of the reaction, the inhibitor is consumed considerably more rapidly than in the stationary region; as a result, the boundary between these regions, i.e., the critical concentration, appears on the curve of the dependence of the induction period on the inhibitor concentration in the form of a sharp bend ([6]), and thus can be determined directly from experiment.

In the present work we studied the influence of the inhibitor 2,6-di-(1,1-dimethylhexyl)-4-methylphenol, hereinafter called, for short, "monophenol," on the magnitude of the critical concentration of another inhibitor, 2,2′-methylene-bis-(4-methyl-6-tert-butylphenol), "biphenol." Earlier we showed that biphenol is an effective inhibitor of the oxidation of polypropylene, whereas monophenol is not only in itself a weak inhibitor, but also lowers the effectiveness of the inhibitor—biphenol—if a mixture of both inhibitors is introduced into the oxidizing polypropylene ([2]). It could be thought that both the low effectiveness of the monophenol itself and the lowering of the effectiveness of biphenol in its presence are explained by an increase in the self-acceleration factor under the influence of monophenol.

The procedure for carrying out the experiment has been described in our papers ([1], [2]).

In Fig. 1 is shown the dependence of the induction period of oxidation of isotactic polypropylene on the concentration of biphenol in the absence (curve 1) and in the presence of monophenol, 0.01 mole/kg (curve 2), at a temperature of 200° and an oxygen pressure of 300 mm Hg. It is seen from the figure that the critical concentration of biphenol in the absence of monophenol, equal to

Fig. 1. Dependence of the induction period of polypropylene oxidation on the concentration of 2,2-methylene-bis-(4-methyl-6-tert.-butylphenol) at 200°, $P_{O2} = 300$ mm Hg. 1—in the absence and 2—in the presence of 2,6-di-1,1-dimethylhexyl-4-methylphenol.

Figure 1: Fig. 1. Dependence of the induction period of polypropylene oxidation on the concentration of 2,2-methylene-bis-(4-methyl-6-tert.-butylphenol) at 200°, $P_{O2} = 300$ mm Hg. 1—in the absence and 2—in the presence of 2,6-di-1,1-dimethylhexyl-4-methylphenol.

$1.3 \cdot 10^{-3}$ mole/kg, in the presence of monophenol increases to $4 \cdot 10^{-3}$ mole/kg. It is interesting that in the absence of monophenol the value of the critical concentration of biphenol increases with increasing oxygen pressure, i.e.

$$\frac{\partial [\mathrm{IH}']_{\mathrm{cr}}}{\partial [\mathrm{O}_2]} > 0$$

(Fig. 2).

**Fig. 1.** Dependence of the induction period of polypropylene oxidation on the concentration of 2,2-methylene-bis-(4-methyl-6-tert.-butylphenol) at 200°, $P_{\mathrm{O}_2} = 300$ mm Hg. 1—in the absence and 2—in the presence of 2,6-di-1,1-dimethylhexyl-4-methylphenol.

Thus, it follows from the experiment that the magnitude of the self-acceleration factor increases in the presence of the monophenol inhibitor and increases with increasing oxygen pressure.

Leaving open the question of the initiating stage of the oxidation process, let us write the scheme for the development of the oxidation reaction of the hydrocarbon (polypropylene) in the following form:

$$\mathrm{R}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{RO}_2^{\cdot} \tag{1}$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\cdot} \tag{2}$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{IH} \rightarrow \mathrm{ROOH} + \mathrm{I}^{\cdot} \tag{3}$$

$$\mathrm{ROOH} + \mathrm{RH} \xrightarrow{\mathrm{IH}, \mathrm{O}_2} \delta \cdot \mathrm{RO}_2^{\cdot} + \text{inactive products.} \tag{4}$$

From this scheme (assuming $[\mathrm{R}^{\cdot}] \ll [\mathrm{RO}_2^{\cdot}]$, $\frac{d[\mathrm{RO}_2^{\cdot}]}{dt} = 0$, $\frac{d[\mathrm{ROOH}]}{dt} = 0$) we find an expression for the critical concentration of the inhibitor:

Fig. 2. Dependence of the induction period of polypropylene oxidation on the concentration of 2,2-methylene-bis-(4-methyl-6-tert.-butylphenol) at 200°, $P_{O2} = 150$ (1), 300 (2), and 600 mm Hg (3).

Figure 2: Fig. 2. Dependence of the induction period of polypropylene oxidation on the concentration of 2,2-methylene-bis-(4-methyl-6-tert.-butylphenol) at 200°, $P_{O2} = 150$ (1), 300 (2), and 600 mm Hg (3).

$$[\mathrm{IH}]_{\mathrm{cr}} = \frac{\delta k_2 [\mathrm{RH}]}{(1-\delta)k_3}, \tag{VI}$$

Comparing (3) and (6), we obtain an equation relating the self-acceleration factor $\varphi$ to the constants of the above scheme:

$$\varphi = \frac{\delta}{1-\delta} k_2 [\mathrm{RH}]. \tag{VII}$$

This equation is valid only for a stationary reaction, i.e., for the case $\delta < 1$. Since the maximum value of the total concentration of inhibitors in our experiments did not exceed 0.7% by weight (0.02 mole/kg), the quantity [RH] may be regarded as constant. The only quantity that depends on the concentration of monophenol and on the oxygen pressure may be the probability of degenerate branching $\delta$ (i.e., the probability of chain initiation upon decomposition of one hydroperoxide molecule). It follows from equation (VII) that, in the case where the value of $\delta$ approaches unity, the critical inhibitor concentration will increase without bound. This apparently explains the absence of critical phenomena in the oxidation of polypropylene in the presence of a single monophenol.

**Fig. 2.** Dependence of the induction period of polypropylene oxidation on the concentration of 2,2-methylene-bis-(4-methyl-6-tert.-butylphenol) at 200°, $P_{O2} = 150$ (1), 300 (2), and 600 mm Hg (3).

Apparently, as we have already written ([1,2]), a large part of the free radicals formed in the decomposition of the branching product (hydroperoxide) is destroyed by intracage recombination, for example:

$$\mathrm{ROOH} \rightarrow \mathrm{RO}^{\cdot} + {}^{\cdot}\mathrm{OH}, \qquad \mathrm{RO}^{\cdot} + \mathrm{R_1H} \rightarrow \mathrm{ROH} + \mathrm{R_1^{\cdot}},$$

$$\mathrm{R_1^{\cdot}} + {}^{\cdot}\mathrm{OH} \rightarrow \mathrm{R_1OH}.$$

An inhibitor that removes one of the two free radicals (for example, ${}^{\cdot}$OH) will hinder intracage recombination and thereby stimulate chain branching. Conversely, an inhibitor capable of removing both radicals will suppress branching or, at any rate, stimulate it to a much lesser extent. Therefore the number of

active functional groups in the inhibitor molecule is one of the most important factors determining whether a given inhibitor will stimulate pronounced chain branching or not. It is precisely in this respect, i.e., in the number of active functional groups in the molecule, that the inhibitors we have studied—alkylphenols—differ from one another.

An oxygen molecule, entering the "cage," converts the radical $R^{\cdot}$ into $RO_2^{\cdot}$ and thereby increases the probability of chain initiation, if only because among the products of recombination of $RO_2^{\cdot}$ with other radicals there will be peroxide compounds.

As a result of the investigation it has been shown that the self-acceleration factor of the oxidation reaction of a high-molecular hydrocarbon, polypropylene, depends on the oxygen pressure and depends strongly on the concentration of the inhibitor—monophenol, 2,6-di-(1,1-dimethylhexyl)-4-methylphenol.

The increase in the self-acceleration factor of the oxidation reaction in the presence of the inhibitor—monophenol—can be explained by participation of the inhibitor in the act of degenerate chain branching.

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*Note: Figure translations are in progress. See original paper for figures.*