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Simultaneous determination of the content and activity of sterically hindered phenolic and amine stabilizers by means of an oxidative model reaction

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Abstract

Measurements of the reduced post-induction oxygen consumption rate in a model system comprising cumene initiated oxidation performed in the presence of the hindered amine stabilizer (HAS) Chimassorb 2020 offers the possibility of determining the state of the stabilizer type related to polymers.

The rate of the post-induction oxidation depends linearly on the reciprocal square root of the concentration of the antioxidant over a sufficiently wide range thereby allowing reliable determinations to be made. The presence of the basic, sterically hindered phenolic stabilizer (Irganox 1010) usually used for polymer stabilization has no influence on the post-induction phase of cumene oxidation and conversely the HAS tested did not change the induction time and the rate constant induced by Irganox 1010.

The rate constant for the addition of cumyl $R^{\cdot}$ radicals to Chimassorb 2020 was determined to be $k_{(333\ K)} = (1.5 \pm 0.2)\cdot 10^7\ M^{-1}\ s^{-1}$.

Thus the model reaction of initiated oxidation of cumene may be considered as a promising method for the simultaneous determination of phenolic and HAS-functionalities of stabilizers in polymers and their potential interactions.

Keywords: Model oxidation; Antioxidants; Stabilizers; Rate constant; Induction time; Oxidation rate

1. Introduction

The intrinsic resistance of polyolefin materials to themooxidative ageing is extremely low and, therefore the use of stabilizers is necessary to ensure high polymer performance. In general, a mixture of stabilizers is used for the most effective stabilization of polyolefins—that is a package of stabilizers, containing basic, secondary and combined light stabilizers (HAS) are commonly employed [1].

Sterically hindered phenols and secondary aromatic amines are usually related to the basic stabilizers. They manifest a high stabilizing effect and nowadays are of importance as stabilizers for polyolefins [2]. The basic antioxidants are scavengers of peroxy macroradicals and therefore hinder the formation of hydroperoxide reaction sequences and the scission of primary bonds [3–5].

The secondary stabilizers are stabilizers of secondary action, which act by destroying hydroperoxides with no concomitant formation of radicals forming molecular, inert products. Phosphities, sulfides, thioethers and others are used as secondary stabilizers for polyolefins [6,7].

In addition to these two types of stabilizers, hindered amine stabilizers (HAS) based on 2,2,6,6-tetramethylpiperidine derivatives have been recently proposed as light, and partially heat, stabilizers with significant long-term stabilization effects [8–13].

It is an established fact that the efficiency of stabilizers in polyolefins governs the useful life-time of polyolefin materials [14]. The efficiency of the stabilizer is one useful source of information for assessing the

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consumption of stabilizers by different processes during their production, storage, weathering exposure and exposure under special application conditions. It will therefore be important for questions of effective compounding be it for special long-term applications or recycling. Hence, these facts highlight the importance of the availability of methods for the analysis of stabilizer content and activity control during the ageing of polymers, e.g. (a) in what way is the initial content of stabilizer reduced and therefore what is the real residual content of stabilizers related to the definite time of the ageing? (b) is there some post-action of stabilizers due to functional changes in the molecular structure of the stabilizer? (c) What is the correlation between the changes and rheology of polymer materials?

It should be noted that the spectral methods (FTIR, NMR, UV) commonly used for studying of stabilizers [15,16] are often suitable only for the analysis of the initial state of the stabilizer in polymeric materials since they often suffer from problems by interference with other spectral signals of the already exposed polymer materials. In addition, these methods require expensive equipment and may not be routinely performed. It is important, therefore, to have methods available with different prerequisites for quantitative studies.

Kinetic approaches to these problems are noteworthy, in particular, investigation of the use of model oxidative reactions. One of these reactions—radical initiated oxidation of cumene has been employed for the analysis of antioxidants in complex organic compositions for some time [17,18]. The validity of this model reaction for analysis of the effects of phenolic stabilizers has been shown previously [17,19,20], however, this work was not developed further and only recently has become the focus of further work [21,22].

In spite of the great importance of HAS stabilizers there is to date a lack of simple quantitative methods for the monitoring of the state of the stabilizers in polymeric materials. In the present paper the results of an investigation of a commercial phenolic Irganox 1010 and HAS-Chimassorb 2020 stabilizers by the aid of the model cumene initiated reaction are shown, and the possibility of their simultaneous determination is considered.

2. Theoretical considerations

Without any inhibiting additives the model reaction of the initiated oxidation of cumene proceeds under steady state conditions, the kinetic chains are fairly long (e.g. at the rate of initiation $W_i = 6.8 \cdot 10^{-8}$ mol/l s and temperature 60 °C the length of chains is about 100), hydroperoxide does not contribute additionally to the initiation of oxidation and air oxygen pressure is sufficient to not limit the process [$P_{O_2} = 0.2$ bar (10^{-3} mol O_2 l^{-1})].

For this reaction a scheme may be represented in the following form (Scheme 1):[1]

Chain initiation: generation of $R^{\cdot}$ radicals (W_i is initiation rate),

initiator$\rightarrow$ radicals of initiator $r^{\cdot}$ and

$rO_2\bullet\ (k_i) \rightarrow$ cumylalkyl radicals $R\bullet(k_i)$

Chain propagation: $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ (rate constant k_2)

$RH + RO_2^{\cdot} \rightarrow ROOH + R^{\cdot}$ (rate constant k_3)

Chain termination: $2\,RO_2^{\cdot} \rightarrow$ inactive products(rate constant k_6)

Scheme 1

with RH: cumene, $\dot{R}$: cumylalkyl radical, $\dot{RO_2}$: cumylperoxy radical, ROOH: cumylhydroperoxide.

According to this scheme the kinetics of oxygen absorption is, as shown in Fig. 1(1). For the scheme the reaction rate is described as:

$$W_{O_2} = W_i^{1/2} k_3 k_6^{-1/2} [RH] \tag{1}$$

with W_{O_2}—rate of uninhibited oxidation, W_i—initiation rate, k_3 and k_6—the rate constants, [RH]—concentration of cumene.

In the presence of a phenolic inhibitor (InH), even in low concentrations such as $\sim 10^{-4}$–10^{-6} mol/l) Scheme 1 and consequently Fig. 1(1) and the expression (1) are changed to Fig. 2 and to the expression (2) of the inhibited oxidation rate:

$$W_{\text{inh}\,O_2} = W_{i(0)} k_3 [RH] \{fnk_7[InH]\}^{-1} \tag{2}$$

where $W_{\text{inh}\,O_2}$—rate of inhibited oxidation, $W_{i(0)}$—start initiation rate; n—number of functional groups in one molecule of a stabilizer; f—inhibition coefficient, representing

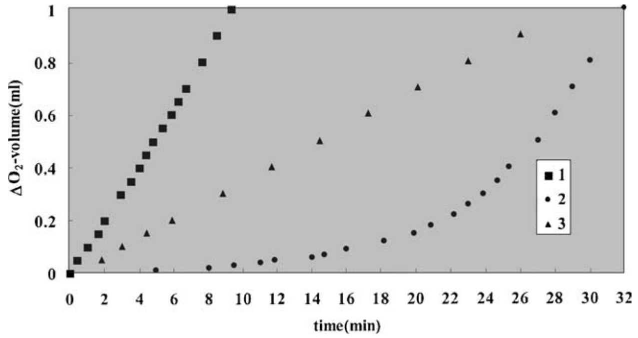

Fig. 1. Kinetic dependences of oxygen consumption for cumene initiated oxidation. Initiator is 2,2′-azobisisobutyronitrile (AIBN), $W_i = 6.8 \cdot 10^{-8}$ mol/l s, 60 °C. (1) Uninhibited oxidation, [InH] = 0, (2) [sterically hindered phenol example (Irganox 1330)] = $1.5 \cdot 10^{-5}$ mol/l [25], (3) [sterically hindered amine example (Climassorb 944)] = $7.2 \cdot 10^{-4}$ mol/l [19].

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[1] Using the currently accepted rate constant numbering for elementary oxidation reactions [3,23].

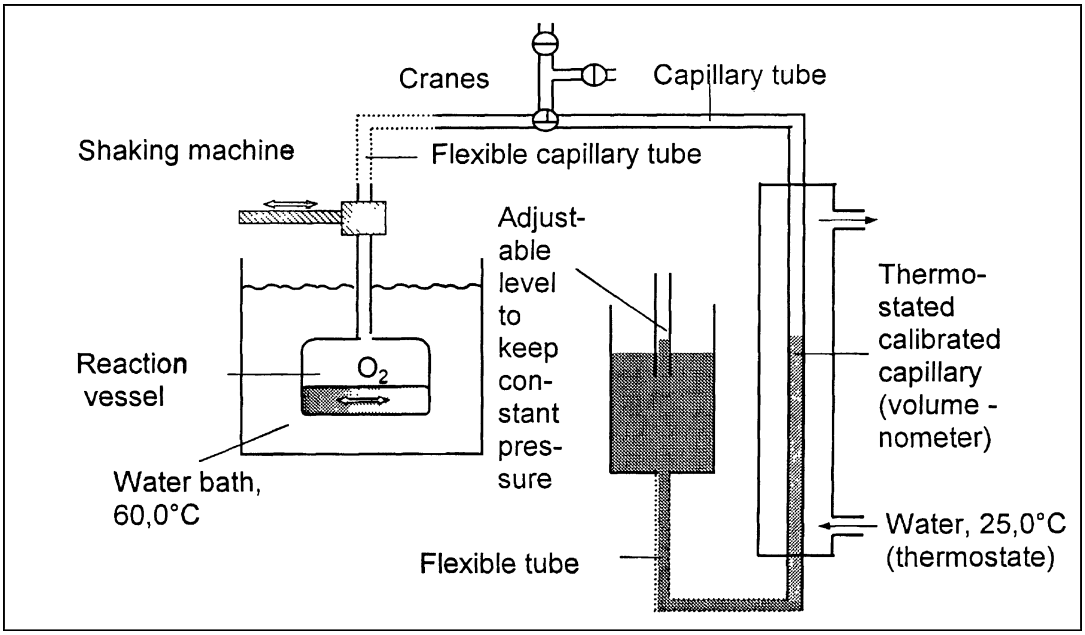

Fig. 2. Schematic diagram of measuring equipment for oxygen consumption at constant pressure.

the number of $RO_2^{\bullet}$ peroxy radicals deactivated by each antioxidant functional group of one molecule of stabilizer or how many oxidation chains are terminated by one antioxidant group of one molecule of stabilizer; [InH]—concentration of a stabilizer; k_7—rate constant of the reaction $InH + RO_2^{\bullet} \rightarrow ROOH + In^{\bullet}$ (see Scheme 2) [2]

Chain initiation: Initiation including formation of cumylalkyl radicals $R^{\bullet}$ (initiation rate is W_i) [1]

Chain propagation:

$R^{\bullet} + O_2 \xrightarrow{k_2} RO_2^{\bullet}$ [2]

$RO_2^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet}$ [3]

Chain termination:

$RO_2^{\bullet} + InH \xrightarrow{k_7} ROOH + In^{\bullet}$ [7]

$RO_2^{\bullet} + In^{\bullet} \xrightarrow{k_8}$ inactive products [8]

$In^{\bullet} + In^{\bullet} \xrightarrow{k_9}$ inactive products [9]

Scheme 2

with InH—phenolic inhibitor (stabilizer); $In^{\bullet}$—radical of the stabilizer.

The inhibited oxidation proceeds with an induction period [see Fig. 1(2)]. The length of the induction period depends on the concentration of the inhibitor and the rate of initiation and is calculated according to the expression:

$$\tau = f[\mathrm{InH}](W_i)^{-1} \qquad (3)$$

with τ—induction period which is usually evaluated from kinetic curves of the oxidation [21].

In accordance with Scheme 2 the following important relationship along with (3) was derived in [18,24] for the total chemical deactivating interaction of one functional inhibitor group with $RO_2^{\bullet}$ peroxy radicals

$$\Delta(O_2)/[RH] = -k_3\ \mathrm{In}(1 - t/\tau)/k_7 \qquad (4)$$

with t—reaction time; $\Delta(O_2)$—volume of consumed or absorbed oxygen.

The induction period τ is evaluated from the kinetic curve [Fig. 1(2)]. The inhibitor content [InH], in equivalents per litre, can be calculated by using W_i from the experimental conditions [25,26] and a first assumed provisional value of f for expression (3).

According to Scheme 2 given for phenolic stabilizers with one inhibiting group at 60 °C values of $f = 1$ to $f = 2$ are expected due to the possible efficiency of reaction [9]. The recombination reaction [9] will depend strongly on the structure of the antioxidant [3,24]. Therefore, for unknown phenolic stabilizers it is reasonable to assume provisionally $f = 1.5$ as long as further knowledge about the stabilizer is lacking.

For graphic evaluation of the kinetic data a semi-logarithmic transformation of data of oxygen absorption due to relationship (4) is convenient. The inhibition rate constant k_7 is given by the slope of this plot.

Let us consider a scheme of reactions for initiated cumene oxidation in the presence of the hindered amine

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[2] Using the currently accepted rate constant numbering for elementary reactions of an inhibited oxidation of hydrocarbons [3,23].

stabilizers (HAS) based on 2,2,6,6-tetramethylpiperidine derivatives. According to the literature information available [27] and based upon the authors' experimental data [Fig. 1(3)] [22] may be simplified as follows (Scheme 3):

Chain initiation:

Initiation including formation of cumylalkylradicals $R^{\cdot}$ (initiation rate is W_i)

Chain propagation: $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ (k_2)
$RO_2\bullet + RH \rightarrow ROOH + R\bullet$ (k_3)

Chain termination: $R_1{-}NH$ + active radical → inert molecular products(k_5)
$2\,RO_2^{\cdot} \rightarrow$ inactive products(rate constant k_6)

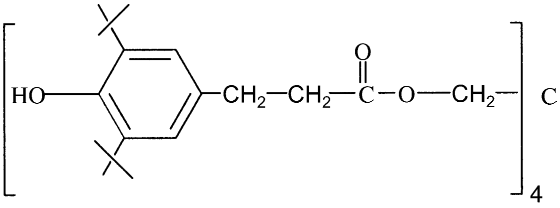
Scheme 3

with $R_1{-}NH$—hindered amine stabilizer.

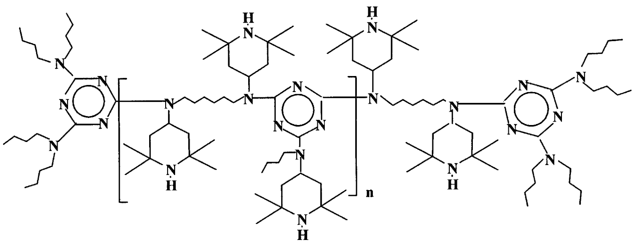
3. Experimental procedures

The model oxidation of cumene was performed under the most acceptable conditions used for phenolic stabilizers [17,18,21,24,28–30]: initiation rate $W_i = 3.4$–$6.8 \cdot 10^{-8}$ mol/l s, temperature (60 ± 0.02) °C and pressure $P_{O_2} = 0.2$ bar (air) with 2,2′-azobisisobutyronitrile (AIBN) as the initiator. The volume of the reaction mixture was 10 cm^3 (25 °C). For the given initiation rate 10 mg of AIBN had to be added [25].

Stabilizers were (all from Ciba Specialty Chemicals, Basel, Switzerland): tetrakis[methylene(3,5-di-tert-butyl-4 hydroxyhydrocinnamate)]methane—(Irganox 1010):



Sterically hindered amine stabilizer based on 2,2,6,6-tetramethylpiperidine—(Chimassorb 2020):



The rate of oxidation was evaluated from the amount of oxygen consumed, which was measured volumetrically as described in [18] with the simple equipment shown in Fig. 2.

4. Results and discussion

In Fig. 3 the kinetic oxygen absorption dependences for cumene initiated oxidation in the presence of the Chimassorb 2020 are presented. It is clearly seen that the reaction rate is substantially reduced. The inhibited oxidation proceeded without an initial induction period, which is in good agreement with Scheme 3, and with the steady rate which linearly depends on the second root of the (Chimassorb 2020) concentration (over the concentration range $1.7 \cdot 10^{-4}$–$6.7 \cdot 10^{-4}$ mol/l) i.e. $W_{\text{inh}\,O_2} \sim [\text{Chimassorb 2020}]^{1/2}$.

Fig. 4 shows the dependence between the rate of oxidation and concentration of Chimassorb 2020. This implies that the reaction $RO_2^{\cdot} + R_1{-}NO^{\cdot}$ does not take place, at least in the conditions of the experiment, and the nitroxyl radical $-NO^{\cdot}$ of Chimassorb 2020 mainly interacts with cumylalkyl radicals $R^{\cdot}$ and thereby the reaction $R_1{-}NO^{\cdot} + R^{\cdot}$ competes with the reaction $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$. Indeed, according to the literature data [31] the rates of these reactions are comparable.

It is well known that even well-purified hydrocarbons originally contain some concentration $\sim 10^{-6}$–10^{-4} mol/l of hydroperoxides [3,23,32]. For the easily oxidized cumene we assumed the value 10^{-4} mol/l of cumylhydroperoxide contained in cumene before the experiment. In addition, as a simple calculation shows, the concentration of cumylhydroperoxide for the experiments at steady state condition (60 °C, $P_{O_2} = 0.2$ bar (air) (reaction [3] of the schemes) for the time of reaction (for 2–3 h maximum) reaches the values $5 \cdot 10^{-4}$–10^{-3} mol/l in total, which is stoichiometrically comparable with concentrations of SHA added to reveal the inhibiting function.

Nitroxyl radicals are typical oxygen-centred π-radicals with a high oxidation potential (for example the potentials of half-wave of oxidation in acetonitrile is +0.21 to +0.51 V, in water is +0.791 to +1.09 V) and

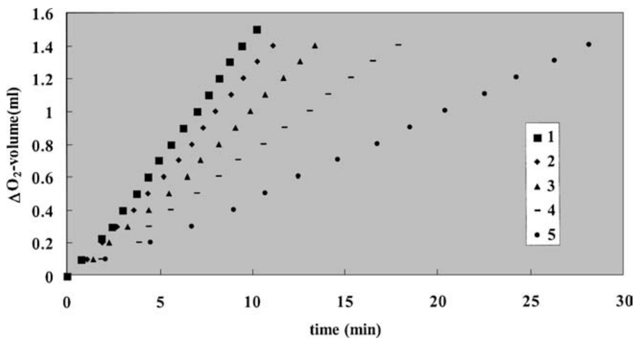


Fig. 3. Kinetic dependences of oxygen consumption for cumene initiated oxidation in the presence of hindered amine stabilizer (Chimassorb 2020). Reaction mixture volume = 20 ml, $W_i = 3.4 \cdot 10^{-8}$ mol/l s (AIBN); (1) [InH] = 0, (2) $1.7 \cdot 10^{-4}$, (3) $3.3 \cdot 10^{-4}$, (4) $6.7 \cdot 10^{-4}$, (5) $1.3 \cdot 10^{-3}$ mol/l.

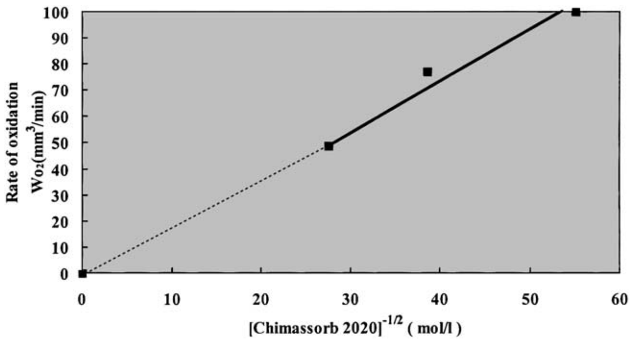


Fig. 4. Oxidation rate for cumene vs concentration of hindered amine stabilizer Chimassorb 2020. $W_{i(AIBN)} = 3.4 \cdot 10^{-8}$ mol/l s, 60 °C.

they are not able to be oxidized (by strong oxidizing agent at specific conditions only) [33]. Therefore, they do not add dioxygen and are not even sensitive towards peroxy radicals, at least in the condition of the experiments. Really the stable nitroxyl radicals are widely presented in the literature as active $R^{\cdot}$ radical acceptors to be used as a stabilizer for polymers, active inhibitors of radical polymerization and thermooxidative degradation or spin scavengers—free radical traps for a study of radical reactions, etc. [33–38]. In addition, the nitroxyl radicals readily interact with hydroperoxides to form nitrone and molecular products which are inert in the conditions of the cumene model oxidation to allow to make correct determination [8,10–12,27].

Thus, the experimental data obtained confirm the proposed Scheme 3 and specify it as Scheme 4.

Chain initiation:

$\mathrm{AIBN} \rightarrow \mathrm{r}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot$ (initiation rate W_i) [1]

Chain propagation:

$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2^{\cdot}}$ (rate constant k_2) [2]

$\mathrm{RO_2}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot$ (rate constant k_3) [3]

Formation of nitroxyl radicals:

$\mathrm{R_1{-}NH} + \mathrm{ROOH} \rightarrow \mathrm{R_1{-}NO}\cdot +$ molecular products [4]

Chain termination:

$\mathrm{R}\cdot \mathrm{R_1{-}NO}\cdot \rightarrow \mathrm{R_1{-}NOR} +$ inert products(rate constant k_5) [5]

$2\,\mathrm{RO_2^{\cdot}} \rightarrow$ inactive products (rate constant k_6) [6]

Scheme 4

The steady state condition for cumene oxidation is established very fast: in general, an interval of an unsteady stage of oxidation is 0.01–100 s [38]. It is calculated according to an expression $t = (2k_6 W_i)^{-1/2}$ and for the initiated cumene oxidation at 60 °C and $P_{O_2} = 0.2$ bar (air), it equals 40 s.

At steady state conditions the rates of forming and losing of radicals of oxidation chain become equal—$dR^{\cdot}/dT = 0$ and $d\mathrm{RO}_2^{\cdot}/dT = 0$. Using the method of stationary concentrations [23,32] for Scheme 4 we obtain:

$$\mathrm{dR}^{\cdot}/\mathrm{d}T = W_i - k_2[\mathrm{R}^{\cdot}][\mathrm{O_2}] + k_3[\mathrm{RO}_2^{\cdot}][\mathrm{RH}] - k_5[\mathrm{R}^{\cdot}][\mathrm{R_1{-}NO}^{\cdot}] = 0$$

$$\mathrm{dRO}_2^{\cdot}/\mathrm{d}T = k_2[\mathrm{R}^{\cdot}][\mathrm{O_2}] - k_3[\mathrm{RO}_2^{\cdot}][\mathrm{RH}] - k_6[\mathrm{RO}_2^{\cdot}]^2 = 0$$

Adding together these two equations we obtain the following expressions:

$$W_i - W_5 = k_6[\mathrm{RO}_2^{\cdot}]^2 \text{ and } [\mathrm{RO}_2^{\cdot}] = [(W_i - W_5)/k_6]^{1/2},$$

where $k_5[\mathrm{R}^{\cdot}][\mathrm{R_1{-}NO}^{\cdot}] = W_5$. Thus for the rate of oxidation we have:

$$W_{1(O_2)} = k_3[\mathrm{RO}_2^{\cdot}][\mathrm{RH}] = (W_i - W_5)^{1/2} k_3 k_6^{-1/2}[\mathrm{RH}] = W_{i1}^{1/2} k_3 k_6^{-1/2}[\mathrm{RH}] \quad (5)$$

where

$$W_{i1} = W_i - W_5 \quad (6)$$

W_{i1}—rate of initiation in the presence of Chimassorb 2020, W_i—initiation rate in the absence of Chimassorb 2020 and W_5—rate of reaction between cumyl $\mathrm{R}^{\cdot}$ radicals and Chimassorb 2020($-\mathrm{NO}^{\cdot}$) [stage [5] of Scheme 4] equal to:

$$W_5 = k_5[\mathrm{R}^{\cdot}][\text{Chimassorb 2020}(-\mathrm{NO}^{\cdot})] \quad (7)$$

From Eq. (7) the rate constant k_5 for addition of cumyl radicals ($\mathrm{R}^{\cdot}$) to the nitroxyl radicals ($-\mathrm{NO}^{\cdot}$) generated from Chimassorb 2020 can be calculated.

In steady state conditions of oxidation in the presence of Chimassorb 2020 for fairly long chains the following equations are valid [23,32]:

$$k_2[\mathrm{R}^{\cdot}][\mathrm{O_2}] = k_3[\mathrm{RO}_2^{\cdot}][\mathrm{RH}] = W_{1(O_2)} \quad (8)$$

From Eqs. (5)–(8), using the known magnitudes of the constants for cumene oxidation [23,39,40]: $k_{3(333\,K)} = 1.75$, $k_{6(333\,K)} = 1.84 \cdot 10^5$, $k_2 = 10^9$ 1/mol s; [RH] = 6.9, $[\mathrm{O_2}] = 10^{-3}$ mol/l, one can obtain the following expressions for calculations of k_5:

$$[\mathrm{R}^{\cdot}] = W_{1(O_2)}/k_2[\mathrm{O_2}] = W_{1(O_2)}/10^6 \text{ and}$$
$$k_5 = 10^6(W_i - W_{i1})/[\text{Chimassorb 2020}(-\mathrm{NO}^{\cdot})]\,W_{1(O_2)} \quad (9)$$

The k_5 value calculated from Eq. (9) for $[\text{Chimassorb 2020}(-\mathrm{NO}^{\cdot})] \leq 7 \cdot 10^{-4}$ mol/l is $k_{5(333\,K)} = (1.5 \pm 0.2) \cdot 10^7$ 1/mol s.

Now it is possible to consider the scheme of cumene initiated oxidation in the simultaneous presence of the phenolic and amine stabilizers.

Kinetic curves of oxygen absorption and their semilogarithmic transformation for radical initiated cumene oxidation in the simultaneous presence of the phenolic

Irganox 1010 and the hindered piperidine Chimassorb 2020 are presented in Figs. 5 and 6.

Table 1 shows results of the kinetic curves (Fig. 5) and its semilogarithmic plot (Fig. 6) treatment and corresponding calculations by Eqs. (3), (4), (7) and (9).

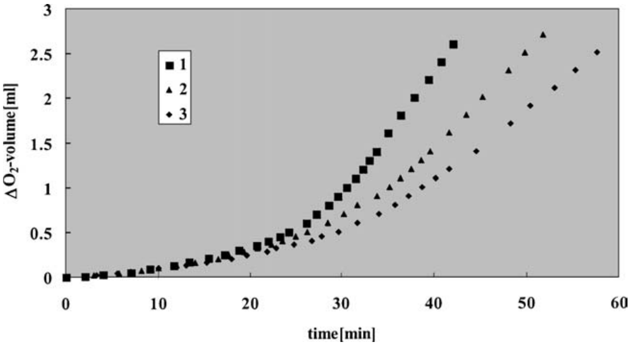


Fig. 5. Kinetic curves of oxygen consumption for cumene initiated oxidation in the simultaneous presence of the phenolic Irganox 1010 and the amine Chimassorb 2020. $W_i = 3.4 \cdot 10^{-8}$ mol/l s (AIBN), 60 °C. (1) [Irganox 1010] = $8.0 \cdot 10^{-6}$ mol/l; (2) [Irganox 1010] = $8.0 \cdot 10^{-6}$ + [Chimassorb 2020] = $3.3 \cdot 10^{-4}$ mol/l; (3) [Irganox 1010] = $8.0 \cdot 10^{-6}$ + [Chimassorb 2020] = $6.7 \cdot 10^{-4}$ mol/l.

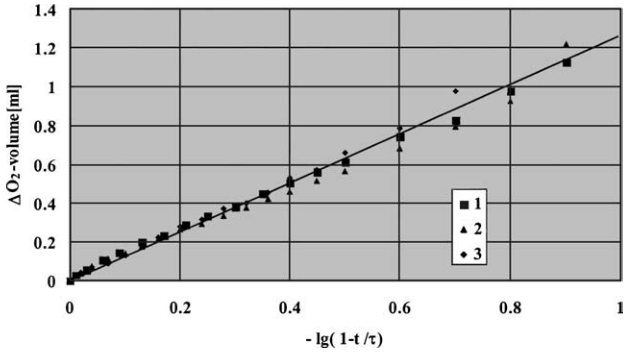


Fig. 6. Semilogarithmic transformation of the kinetic curves of oxygen consumption for cumene initiated oxidation in the simultaneous presence of the phenolic Irganox 1010 and the amine Chimassorb 2020. $W_i = 3.4 \cdot 10^{-8}$ mol/l s (AIBN), 60 °C. (1) [Irganox 1010] = $8.0 \cdot 10^{-6}$ mol/l; (2) [Irganox 1010] = $8.0 \cdot 10^{-6}$ + [Chimassorb 2020] = $3.3 \cdot 10^{-4}$ mol/l; (3) [Irganox 1010] = $8.0 \cdot 10^{-6}$ + [Chimassorb 2020] = $6.7 \cdot 10^{-4}$ mol/l.

It is observed from the data plot that the presence of Chimassorb 2020 does not interfere with the induction period and rate constant values k_7 of Irganox 1010 and conversely, the presence of phenolic inhibitor and its conversion products have a minor influence on the inhibiting action of the amine HAS-inhibitor which is manifested after the phenolic inhibitor is consumed. The general scheme of the oxidation in the simultaneous presence of HAS and phenolic antioxidant may be summed up as Scheme 5.

Chain initiation:

$$\mathrm{AIBN} \rightarrow \mathrm{r}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot \ \text{(initiation rate } W_i\text{)} \qquad [1]$$

Chain propagation:

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2^{\cdot}} \ \text{(rate constant } k_2\text{)} \qquad [2]$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot \ \text{(rate constant } k_3\text{)} \qquad [3]$$

Formation of nitroxyl radicals:

$$\mathrm{R_1{-}NH} + \mathrm{ROOH} \rightarrow \mathrm{R_1{-}NO}\cdot + \text{ molecular products} \qquad [4]$$

Chain termination:

$$\mathrm{R}\cdot + \mathrm{R_1{-}NO}\cdot \rightarrow \mathrm{R_1{-}NOR} + \text{ inert products (rate constant } k_5\text{)} \qquad [5]$$

$$2\,\mathrm{RO_2^{\cdot}} \rightarrow \ \text{inactive products (rate constant } k_6\text{)} \qquad [6]$$

$$\mathrm{RO_2^{\cdot}} + \mathrm{InH} \rightarrow \mathrm{ROOH} + \mathrm{In^{\cdot}} \text{(rate constant } k_7\text{)} \qquad [7]$$

$$\mathrm{RO_2^{\cdot}} + \mathrm{In^{\cdot}} \rightarrow \ \text{inactive products (rate constant } k_8\text{)} \qquad [8]$$

$$\mathrm{In^{\cdot}} + \mathrm{In^{\cdot}} \rightarrow \ \text{inactive products(rate constant } k_9\text{)} \qquad [9]$$

Scheme 5

The expressions (2) and (5) fit this mechanism of the inhibition realized in sequence within an induction and for post-induction period, respectively.

Thus, the dependences established, along with data obtained previously [22,41] show a remarkable opportunity to determine simultaneously the effective concentration of the active functional groups of hindered piperidine and phenolic stabilizers by means of the one model reaction of cumene oxidation.

Table 1
The kinetic parameters of model reaction of cumene initiated oxidation in the absence, separate and simultaneous presence of inhibitors (Irganox 1010) and (Chimassorb 2020) $W_{i(\mathrm{AIBN})} = 3.4 \cdot 10^{-8}$ mol/l s, 60 °C

Inhibitor//[InH] · 10^5, mol/l	Induction time (τ), min	Rate of inhibited oxidation $W_{1(\mathrm{O_2})}$, mm^3/min	Post-induction oxidation rate, mm^3/min		Inhibition rate constant, $\mathrm{M^{-1}\,s^{-1}}$	
			$W_{\mathrm{O_2}}$	$W_{1(\mathrm{O_2})}$	$k_7 \cdot 10^{-4}$	$k_1 \cdot 10^{-7}$
0	0	–	146	–	–	–
Chimassorb 2020//33	0	100	–	–	–	1.7
Chimassorb 2020//67	0	77	–	–	–	1.5
Irganox 1010//0.8	32	–	144	–	1.7	–
Irganox 1010 + Chimassorb 2020//0.8 + 33	36	–	–	104	1.75	1.6
Irganox 1010 + Chimassorb 2020//0.8 + 33	38	–	–	80	1.65	1.4

Acknowledgements

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