

Decomposition of Polypropylene Hydroperoxides Induced by Nitric Oxide: New Concept of Reaction Mechanism

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ABSTRACT: NO-induced decomposition of hydroperoxides in solid polypropylene and cumyl hydroperoxide, dissolved in *n*-decane, at 25°C was studied. Analysis of kinetic regularities of hydroperoxide decomposition and nitroxide radical accumulation leads to the conclusion that both in solids and in solutions these reactions have the autoaccelerated character. The induction periods are determined by trace amounts of impurities (probably of higher nitrogen oxides). The maximum rate of the process depends on the NO pressure. The possible reaction mechanisms are supposed, and the key role is assigned to the formed nitrosocompounds. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 407–414, 2001

Key words: hydroperoxide decomposition; nitric oxide; nitrogen dioxide; nitrosocompound; nitroxide radical; polypropylene

INTRODUCTION

At present, there is a huge rise in studies of nitric oxide reactions with different classes of organic compounds. NO is the essential part of aggressive gases polluting the urban atmosphere. It plays also an important role in biochemical processes. Nitric oxide can interact with hydroperoxides accumulated in polymer materials in the course of their processing and exploitation. It is surprising that mechanism of this reaction is not yet established. The phenomenon of NO-induced hydroperoxide decomposition was investigated by some researchers.^{1–3} The molecule of nitric oxide has an unpaired electron and it was *a priori* expected that it decomposed hydroperoxides with the formation of nitrogen-containing inorganic compounds and organic free radicals.

Shelton and Kopczewski³ postulated the primary decomposition step to be



Carlsson et al.² supposed that NO reacts with ROOH forming peroxide radicals:



At high hydroperoxide concentrations in solution the process was described as decomposition of hydroperoxide dimers by nitric oxide:³



The above-mentioned mechanisms of the primary step were based on analyses of reaction products only. There are no data on kinetic regularities of reaction.

Pryor et al. gave evidence, that NO₂, a more active than NO free radical, cannot decompose hydroperoxides in solutions directly, and the primary step is nitrosation of hydroperoxide by a nonparamagnetic dimer N₂O₄.⁴ This study casts doubts on the conclusions about the relatively

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simple mechanism of the reaction of $\text{NO} + \text{ROOH}$ and the free radicals role in this process, especially in the case of solid polymers.

The purpose of this work was to study the kinetic regularities of interaction of nitric oxide with hydroperoxides, to establish the formation of free radicals in this reaction in solid polypropylene (PP) and in model system of *n*-decane + cumyl hydroperoxide by ESR, and to make some conclusions about the mechanism of the process.

EXPERIMENTAL

Polypropylene

Experiments were performed with commercial isotactic PP (grade 0.5-P 10/20) with $M_w = 2.3 \times 10^5$ and a powder density of 0.464 g/cm^3 . The polymer was washed repeatedly with methanol in a Soxhlet extractor to remove stabilizers. Hydroperoxides in PP were produced by oxidizing the polymer in air at 90°C for 15 h.

Cumyl Hydroperoxide

To receive pure cumyl hydroperoxide the commercial product was converted into sodium salt. The crystals obtained were rinsed several times with small portions of purified benzene. The salt was dissolved in equivalent amount of water and turned into ROOH by bubbling CO_2 through the solution. Hydroperoxide was separated from aqueous solution of Na_2CO_3 , washed by distilled water, and dried in vacuum for 6–8 h. The content of active oxygen in purified hydroperoxide was $(95 \pm 5)\%$.

n-Decane

n-Decane (chemically pure grade) was purified in accordance with standard methods.⁵

Nitric Oxide

Nitric oxide was obtained by the conventional method⁶ in reaction of nitric acid (density $d^{20} = 1.1\text{--}1.5 \text{ g/cm}^3$) with copper chips. To remove the NO_2 admixture, the gas was bubbled through 5% NaOH solution and then dried by melted KOH. The possible admixture of nitrogen was removed by a threefold repeated cycle: freezing at 77 K, evacuation of gas phase, thawing out. Obtained in such a way, gas solidified at 77 K to form

colorless powder with no traces of blue tint characteristic of N_2O_3 . The absorption spectra of the gas measured in UV and visible regions exhibited only bands belonging to NO (200 Torr pressure, 5 cm optical path length).

Nitrogen Dioxide

Nitrogen dioxide was obtained by thermal decomposition of lead nitrate and dried by passing over fresh P_2O_5 .⁷

To prevent the penetration of trace amounts of O_2 during exposure of samples to NO-containing atmosphere, the experiments were performed in all-glass devices.

The experimental procedure was as follows. The samples of oxidized PP powder ($\sim 70 \text{ mg}$) or of cumyl hydroperoxide solution in decane (0.2 mL; $[\text{ROOH}]$ varies from 0.01 to 0.2 mol/L) were placed into ampoules for ESR measurements jointed with glass spheres ($V = 100 \text{ cm}^3$). These devices were sealed to the vacuum system and degassed. The powder samples were evacuated at a pressure of $\sim 10^{-4}$ Torr and 25°C for 1 h to remove O_2 dissolved in polymer. Liquid solutions were degassed by threefold repeated cycle: freezing at 77 K, evacuation of gas phase, thawing out. After the air had been removed, the necessary amount of nitric oxide was injected into ampoules. In some experiments we used nitric oxide with small admixture of NO_2 . The gas-filled ampoules were sealed off from the vacuum system. The exposure of samples to NO-containing atmosphere was performed at 25°C . Because it is known⁴ that NO_2 causes an efficient decomposition of hydroperoxides, the exposed samples assigned for determination of residual hydroperoxide concentration were opened in vacuum. The gaseous reaction products were thoroughly pumped out together with unreacted nitric oxide to avoid the oxidation of NO by oxygen of air.

The concentration of hydroperoxide in PP was determined by iodometric titration in a mixture of chloroform with glacial acetic acid.⁸ The content of liberated iodine was measured with a spectrophotometer by determining the optical density of I_3^- (at $\lambda 360 \text{ nm}$ $\epsilon = 2.76 \times 10^4 \text{ L/mol} \cdot \text{cm}$). In each case an average over the results of five measurements was calculated; the deviation from the average value did not exceed 15%. The initial concentration of hydroperoxides in the oxidized PP was 0.05 mol/kg.

During exposure to NO-containing atmosphere the room-temperature ESR spectra of the sam-

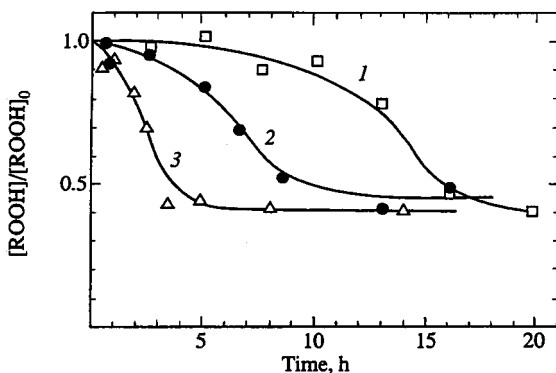


Figure 1 Decomposition of PP hydroperoxides for various NO pressures: 1—30 Torr, 2—60 Torr, 3—77 Torr.

ples were measured (without removal of nitric oxide from ampoules) with RA-100 spectrometer operated at low microwave power (<0.3 mW). ESR spectra of liquid samples were measured at HF modulation amplitude of 0.27 mT on the initial stage of reaction and 0.03 mT when the signals increased.

The g -factor values and hyperfine coupling constants in ESR spectra were determined using Mn^{+2} in MgO as a reference. The values estimated in this way within the measurement error (± 0.05 mT for splitting and ± 0.0003 for g -factor) did not differ from the appropriate quantities estimated from ESR spectra of the same samples recorded on radiospectrometers with simultaneous measurements of resonance frequency and intensity of constant magnetic field.

RESULTS AND DISCUSSION

The kinetic curves of PP hydroperoxide consumption at 25°C and a number of concentrations of nitric oxide in gas phase are presented in Figure 1. As is seen from the figure, the hydroperoxide consumption rate is initially low and then sharply increases. The low-rate stage of the process (we shall denote it as an induction period) decreases, and the maximum rate of ROOH decomposition increases with the growth of the NO concentration.

Decomposition of PP hydroperoxide in the NO atmosphere is accompanied by the formation of free radicals in polymer. Figure 2 shows the ESR spectra of these radicals. The ESR spectrum of samples in the presence of nitric oxide exhibits a signal typical of dialkyl nitroxide radicals in the

solid state representing an anisotropic triplet with $g_{\parallel} = 2.0024 \pm 0.0003$ and $A_{\parallel}^{\text{N}} = 3.1 \pm 0.1$ mT [Fig. 2(a)]. Upon pumping out NO from the ampoule the ESR spectrum displays an additional signal due to acylalkyl nitroxide radicals ($g_{\parallel} = 2.0026 \pm 0.0003$, $A_{\parallel}^{\text{N}} = 2.1 \pm 0.1$ mT) [Fig. 2(b)]. This signal is not observed in nonevacuated specimens because acylalkyl nitroxide radicals form nonparamagnetic complexes with NO molecules.⁹ The fraction of acylalkyl nitroxide radicals increases with duration of a sample exposure to the NO atmosphere and amounts to about 30% after 100 h and above at the pressure of 230 Torr. No nitroxide radicals were found in control PP samples free of hydroperoxides—including both the unoxidized PP and the oxidized polymer with hydroperoxides decomposed by heating in vacuum at 130°C for 16 h. These results indicate that free nitroxide radicals are formed during the decomposition of PP hydroperoxide in the NO-containing atmosphere rather than upon interaction of NO with some other products of polymer oxidation.

Figure 3 shows a series of kinetic curves representing accumulation of nitroxide radicals at various concentrations of nitric oxide. Similar to hydroperoxide decomposition, the accumulation of nitroxide radicals exhibits the sharp dependence of induction period on nitric oxide concentration and decreasing of maximum rate of the process with diminishing of NO pressure. The limiting concentrations of radicals differ only slightly and amount to about 2.2×10^{-4} mol/kg. The end of the induction period for the nitroxide radicals accumulation approximately corresponds to the time of attaining the maximum rate of hydroperoxide decomposition [Fig. 4(a)].

It was found that induction periods of hydroperoxide decomposition and of nitroxide macroradicals accumulation depend greatly on the experiment conditions. For example, prolonged

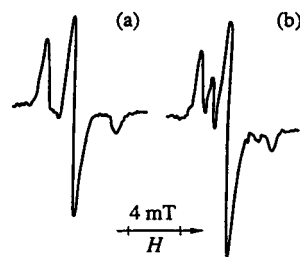


Figure 2 ESR spectra of nitroxide macroradicals, formed in oxidized PP after NO exposure: (a) in the presence of NO; (b) the same sample after evacuation.

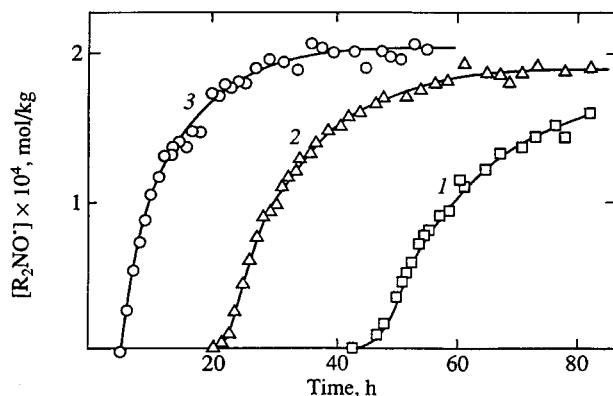


Figure 3 Accumulation of nitroxide radicals in oxidized PP for various NO pressures: 1—15 Torr, 2—32 Torr, 3—116 Torr.

(for several days) preliminary evacuation of system employed to fill the ampoules with nitric oxide resulted in a marked increasing of the induction periods. This period increased even more when the careful evacuation of the system was followed by slow admission of NO into ampoules with oxidized PP through the U-shaped trap cooled to -95°C or the layer of askarite. In this connection each curve of hydroperoxide decomposition presented in Figures 1 and 4 was obtained in experimental series with the same conditions of the preliminary sample treatment and filling ampoules with NO.

Note that the accumulation of radicals is detected with a much greater degree of reliability compared to that achieved for the hydroperoxide decomposition. This is related, in particular, to the fact that the entire curve of radical accumulation was measured on one sample, while each of the points on the curve of the hydroperoxide consumption corresponds to the separate sample. Because of this, the dependence of the kinetic parameters of reaction on the NO concentration is more pronounced for radical accumulation. However, it must be kept in mind that nitroxide radicals are not the primary products of hydroperoxide decomposition.

The results described above lead to the conclusion that the induction periods of hydroperoxide decomposition and nitroxide radicals accumulation are controlled by the trace amounts of impurities (probably of higher nitrogen oxides or substances capable of producing these oxides in the course of interaction with nitric oxide). To verify this assumption we studied the kinetics of PP hydroperoxide decomposition and nitroxide radi-

cal accumulation in an atmosphere of NO (60 Torr) with 0.1% admixture of NO_2 . As Figure 4(b) shows, the presence of NO_2 leads to the disappearance of the induction period on the curve of hydroperoxide decomposition, and a significant decrease of the induction period of the nitroxide radicals accumulation. No nitroxide radicals were found to form under similar conditions in the case when hydroperoxide decomposition was induced by pure NO_2 . The added amount of NO_2 could decompose less than 10% of the initial PP hydroperoxides if used alone. Apparently, the impurities introduced into the system together with NO and affecting the induction period serve as a "seed" in the autoaccelerated process. The maximum rates of hydroperoxide decomposition and nitroxide radical accumulation depend mainly on the gas-phase concentration of nitric oxide, which determines the formation of a product responsible for the accelerated decomposition of hydroperoxides. Note that the catalytic effect of trace concentrations of NO_2 was observed in some other reactions of nitric oxide.^{10,11}

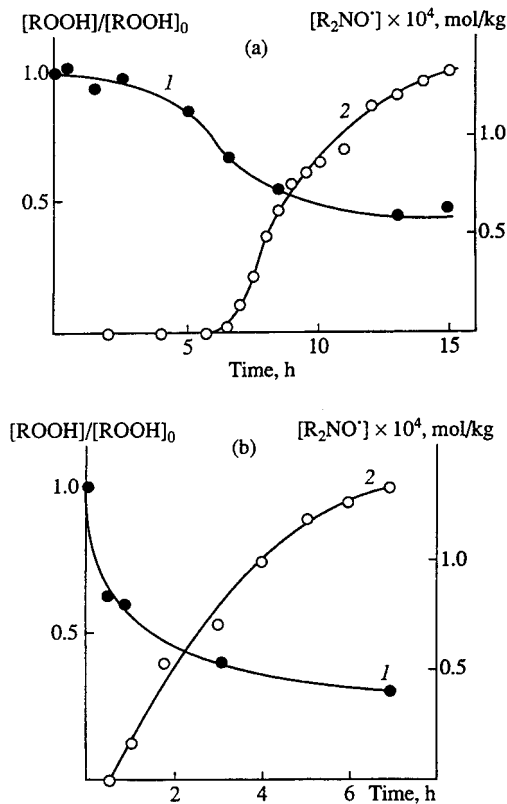


Figure 4 Kinetics of PP hydroperoxide decomposition (1) and nitroxide radical accumulation (2): (a) in NO atmosphere (60 Torr); (b) in the mixture of nitrogen oxides (60 Torr of NO and 0,06 Torr of NO_2).

Table I Parameters of ESR Spectra of Nitrogen-Containing Radicals

Type of Radical	Spectrum Structure	<i>g</i> -Value	a_N , mT	a_H mT
di- <i>sec</i> -Alkylnitroxide	3×3	2.0057	1.54	0.38 (2H)
<i>sec</i> , <i>tert</i> -Dialkylnitroxide	3×2	2.0057	1.51	0.25 (1H)
di- <i>tert</i> -Alkylnitroxide	3	2.0056	1.50	
<i>sec</i> -Alkylacylnitroxide	3×2	2.0070	0.70	0.12 (1H)
Primary alkylacylnitroxide	3×3	2.0075	0.67	0.12 (2H)
Iminoxyl	3	2.0049	2.8	
Iminoxyl	3	2.0048	3.1	

Autoaccelerated character of ROOH and NO interaction may be due not only to the peculiarities of chemical process but also physical reasons: restricted diffusion or polychronic kinetics of reactions in solids.¹²

To clear up the real nature of acceleration in this process the liquid system decane + cumyl hydroperoxide + NO was studied. The rapid hydroperoxide consumption after the induction period and a bad reproducibility of data obtained on various samples prevented achieving the reliable kinetics of hydroperoxide consumption. For this reason the main conclusions concerning reaction mechanism were based on analysis of kinetic regularities of the nitrogen-containing radical accumulation. In these experiments the concentration of reagents was varied over a wide range. The curve of radical accumulation in the liquid system is similar to that in the solid PP. For a long time no free radicals are registered at all (the induction period), then the rapid "explosion-like" increase of radical concentration follows. Parameters of ESR spectra of nitrogen-containing radicals registered on different stages of process are presented in Table I.

Right after the induction period dialkylnitroxide radicals predominate. ESR spectrum of the specimen on the initial stage of radical accumulation is presented in Figure 5(a).

Acylalkylnitroxide radicals $r-C(=O)-N(-O^{\bullet})-CHr_1r_2$ are the most stable ones. Their contribution in respect to the total amount of radicals is rather small at the initial stage of radical accumulation, but when the radical concentration increases rapidly, these radicals are the only detectable paramagnetic particles [Fig. 5(b)].

In several experiments besides dialkyl and acylalkyl nitroxide radicals, ESR spectra attributed to iminoxyl radicals were registered for a short time (see the table above).

Formation and interconversion of different types of nitrogen-containing radicals is a very complicated process, and consideration of its particular mechanism goes out of scope of this communication.

The observed ESR spectra represented a superposition of signals from various types of radicals, and we succeeded in distinguishing at any stage of radical accumulation the individual components of acylalkylnitroxide radicals only.

Figure 6 shows a series of kinetics of acylalkylnitroxide $r-C(=O)-N(-O^{\bullet})-CHr_1r_2$ radicals

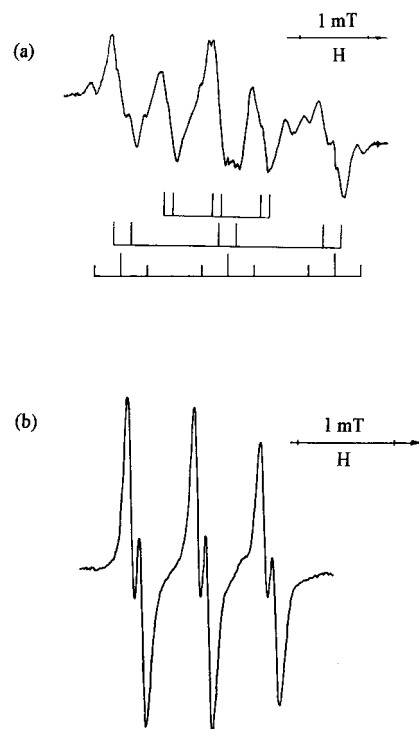


Figure 5 ESR spectra of nitroxide radicals, formed in the course of cumyl hydroperoxide decomposition in decane in the presence of NO: (a) at the initial part of the accumulation curve; (b) at the high-rate stage of radical accumulation.

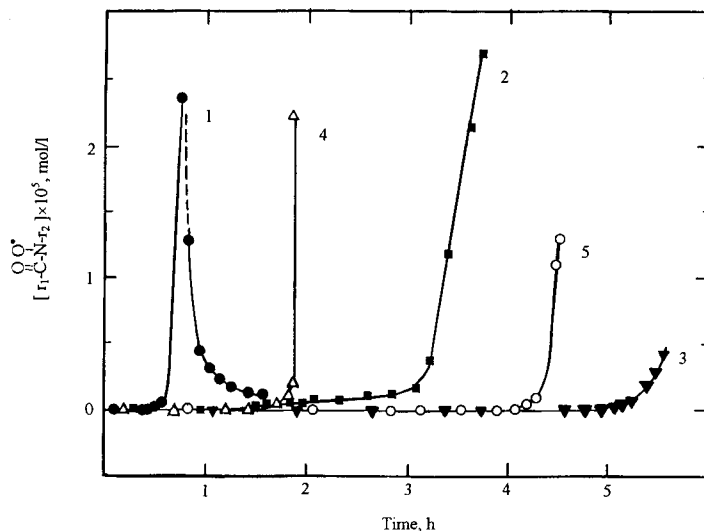


Figure 6 Kinetics of $r\text{-C(=O)-N(O}\cdot\text{)-CHr}_1\text{r}_2$ radical accumulation at different ROOH concentrations and NO pressures: 1—0.04 mol/L, 600 Torr; 2—0.04 mol/L, 150 Torr; 3—0.04 mol/L, 80 Torr; 4—0.2 mol/L, 150 Torr; 5—0.01 mol/L, 600 Torr.

accumulation at various concentrations of ROOH and NO. From this figure one can see that a decrease of concentration both in hydroperoxide and in nitric oxide leads to an increase of the induction period. The process may exhibit such kinetic regularities only in the case if the reaction rate is determined by hydroperoxide decomposition followed by the fast free radical transformations (see the scheme of the process below). It should be noted, that in contrast to the process in the solid PP, in the liquid system the chemical conversions of nitroxide radicals are not diffusion controlled, so the stage of rapid accumulation of free radicals is followed by sharp diminishing of their concentration according to quadratic kinetic equation.

Thus, data received for liquid system show that autoaccelerated kinetics of PP hydroperoxide decomposition in NO atmosphere is not related to the specificity of a solid phase, and has a common character. These data lead to the conclusion that hydroperoxide decomposition is an autoaccelerated process in liquid like in solid phases. The induction period of the process is determined by a trace amount of admixtures, NO_2 in particular; and increasing of reaction rate is related to accumulation of some product capable to decompose hydroperoxides effectively.

In the general case, the autoaccelerated kinetics is characteristic of both the autocatalytic processes and the degenerate-branched chain reactions. Neither our results nor data available in

the literature are sufficient to judge between the hydroperoxide decomposition catalyzed by the final stable products and the reaction with degenerate chain branching. It cannot be excluded, however, that some kind of mixed mechanism may be operative in systems studied. In any case, the process must involve (a) the stages of initiation, (b) accumulation of products, responsible for accelerated hydroperoxide decomposition in reactions with NO, and (c) free radical reactions leading to the formation of nitroxide radicals.

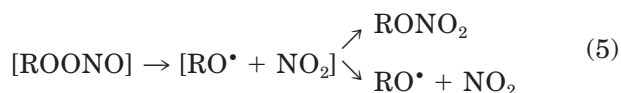
As was noted above, the act of initiation of hydroperoxide decomposition by NO was believed earlier to be represented either by reaction (1) yielding alkoxy radicals and nitrous acid^{1,3} or reaction (2) of NO-induced abstraction of hydrogen atom from hydroperoxide group.² There is little likelihood that reaction (2) takes place at 25°C because of its high endothermicity. Reaction (1) is exothermic, but it yields mainly nitrites and alcohols, the last-mentioned converting to nitrites in the presence of NO.³ However, it was stated in ref. 3 that reaction of PP hydroperoxide decomposition in NO-contained atmosphere produces predominantly macromolecular nitrates.

The above-mentioned dependence of induction periods on the degree of nitric oxide purity leads us to suggestion that the most important role in the initiation act is played by reactions of a trace amount of higher nitrogen oxides with ROOH. We consider that in investigated systems the interac-

tion of hydroperoxide with nitrogen oxides more probably occur through the reaction

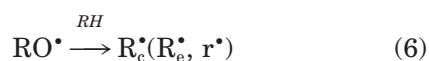


Thermally unstable peroxyxynitrites formed in reaction (4) transform with high rate in a following way:



In solution 58% of cumylperoxyxynitrite converts in a "cage" to nitrate (reaction 5) and 42% of $\text{RO}\cdot$ escape from the "cage" and form alcohol in a reaction with solvent or decompose to give acetophenone.⁴ In solids, recombination of radicals in the "cage" must be highly efficient so the main product of macromolecular peroxyxynitrite conversion is nitrate.²

Alkoxy radicals of PP generated in reactions (1) and (5) can decompose or enter into a substitution reaction with neighboring macromolecules to form chain $\text{R}_c\cdot$ and end alkyl macroradicals $\text{R}_e\cdot$ and low-molecular alkyl radicals $r\cdot$. The appearance of radicals $r\cdot$ in the reaction of PP hydroperoxides with nitric oxide was verified in ref. 1:



The reaction of alkyl radicals with NO must lead to the formation of macromolecular and low-molecular nitrosocompounds:

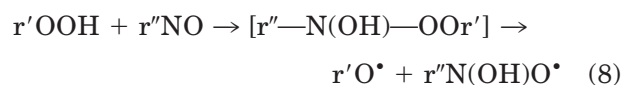


The increase in the rate of hydroperoxide decomposition with time can be related to reactions of such nitrosocompounds.

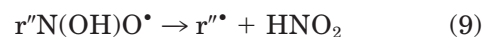
There are two possible variants of these processes.

Variant 1

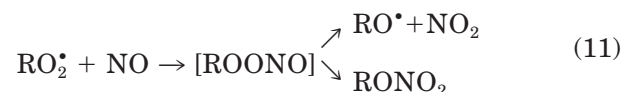
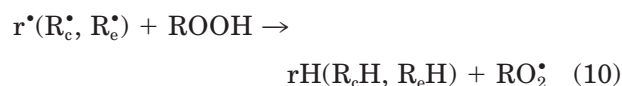
As was shown in ref. 13, the interaction of nitrosocompounds with hydroperoxides in the liquid phase results in intensive decomposition of the latter into free radicals.



Alkoxyalkyl nitroxide radicals have low stability and can decompose, in particular, according to the reaction



Reactions of alkyl radicals formed in the system may lead to the stimulated hydroperoxide decomposition:¹⁴

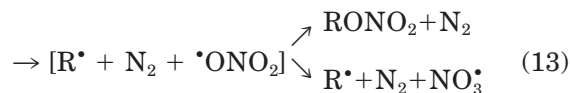


Thus, the set of reactions (6)–(11) may essentially lead to degenerate chain branching. Moreover, nitrous acid formed in reactions (4) and (9) can increase the initiation rate through the reaction



Variant II

Another process that may account, in principle, for the increased rate of hydroperoxide decomposition is disproportionation of nitric oxide to N_2 and NO_3 , which proceeds with the participation of nitrosocompounds and promotes accumulation of nitrogen dioxide in the system:¹¹



Reactions (13) and (14) can lead to increasing NO_2 concentration in the system that will result in acceleration of reaction (4). The alkyl radicals formed in reaction of disproportionation can disappear in the "cage" (reaction 13), with formation of nitrates.

Both variants proposed above consider nitroso-compounds to play the key role in acts of autoacceleration. The presence of nitroso-compounds in the system studied is confirmed by synthesis of nitroxide radicals.

The set of reactions presented above suggests that trace amounts of NO_2 introduced together with NO into the system may act as a catalytic "seed" for the hydroperoxide decomposition. However, the same effect can be caused by some other (not NO_2) compounds, such as HNO_3 , which can give rise to NO_2 synthesis in slow reaction with NO on the wall of the reaction vessel: $2\text{HNO}_3 + \text{NO} \rightarrow \text{H}_2\text{O} + 3\text{NO}_2$ [10]).

According to the first variant of the scheme, the hydroperoxide decomposition by nitric oxide is, as a fact, a chain reaction with a degenerated branching; the second variant considers the process to be autocatalytic. Irrespective of the particular mechanism of the PP hydroperoxide decomposition by nitric oxide at 25°C , we have unambiguously established that this process has an autoaccelerated character and proceeds with participation of free radicals.

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