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Stability of Oligomeric α-Alkoxyhydroperoxides

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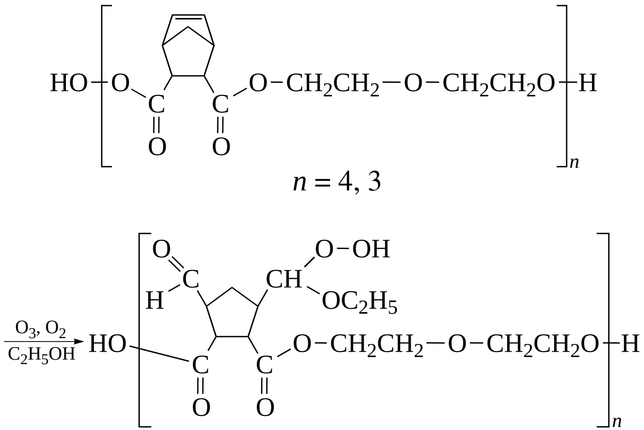
Abstract—The thermal decomposition of oligomeric α-alkoxyhydroperoxides (**I**) is described by a first-order rate law and characterized by an activation energy equal to 19.7 kJ/mol. A chain mechanism and a rate law for this reaction are proposed. The effect of amine and phenolic stabilizers on decomposition is studied, the efficiency of phenolic stabilizers is examined, and the effective rate constant of the acid-catalyzed decomposition of compounds **I** is determined.

INTRODUCTION

Compounds containing several peroxide groups in their structure attract particular attention [1] because they can be used as efficient initiators of radical polymerization [2–5]. In this case, branched polymers, which have been of increasing interest in recent years [6, 7], can be obtained.

The interaction of unsaturated compounds with ozone is a convenient method for producing substances with peroxide groups. Earlier [8], we found that the ozonolysis of oligomeric esters obtained by the polycondensation of endic anhydride with glycols allows one to obtain oligomeric alkoxyhydroperoxides in the presence of ethanol:



I $n = 4, 3$

The practical use of these oligoalkoxyhydroperoxides for initiating radical processes strongly depends on their stability.

Here, we report the results of our kinetic study of the stability of peroxide compounds **I** under various conditions.

EXPERIMENTAL

The unsaturated norbornene oligoester used in this study had an acid number of 50 mg KOH/g, which corresponds to an average molecular weight equal to 1100. The oligoester based on diethyleneglycol–endic anhydride (*endo*-bicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid anhydride) with a molar ratio of 1 : 1 was synthesized in a nitrogen atmosphere by high-temperature polycondensation in a melt at 195–200°C, as described in [9]. The synthesis was controlled by the acid number of the reaction mixture (GOST 22304-77). Chloroform (analytical grade, TU 2631-020-11291058-96) and ethanol (Extra; GOST 18300-87; 96.2% purity) were used. The structures of the synthesized oligoesters and oligomeric alkoxyhydroperoxides were found by NMR and IR spectroscopy.

Ozone was produced by passing an oxygen stream through a glow discharge zone at 6–11 kV. Its concentration ranged from 1 to 60 g/m^3 by varying the voltage at the discharge electrodes. Ozonolysis was carried out in a glass bubbling reactor by passing an ozone–oxygen mixture (0.001–0.012 m^3/h) through an oligoester solution (3 wt %) in $CHCl_3$ at –18 to 0°C in the presence of ethanol (20 wt %). Ozone was consumed completely until the solution contained compounds with double carbon–carbon bonds. The complete conversion of these compounds was judged from the appearance of ozone at the reactor outlet—ozone breakthrough detected by I_2 liberation from an aqueous KI solution. This was a criterion for the completion of reaction.

To remove dissolved ozone and oxygen, the reaction mixture was then blown with nitrogen, and the concentration of peroxide groups was determined as described in [10]. Next, the solution of oligo-α-ethoxyhydroperoxides (**I**) was kept in flat-bottom flasks closed with ground-glass stoppers (to prevent $CHCl_3$ leakage) in the cold or at room temperature depending on the chosen conditions.

THERMAL DECOMPOSITION OF OLIGO-α-ETHOXYHYDROPEROXIDES

The kinetics of the thermal decomposition of oligo-α-ethoxyhydroperoxides was studied in a $CHCl_3$ solu-

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Table 1. Rate constants of the thermal decomposition of α-ethoxyhydroperoxide groups in oligo-α-ethoxyhydroperoxides **I** at various temperatures

t, °C	$k_{eff} \times 10^7$, s^{-1}
–20	3.60
3	6.24
10	7.01
25	15.00

Note: Solvent, $CHCl_3$; the initial concentration of **I**, 6 wt %.

Table 2. Rate constants of the decomposition of oligo-α-ethoxyhydroperoxides **I** in the presence of various stabilizers at 25°C

Stabilizer	Stabilizer concentration, wt %	$k_{eff} \times 10^7$, s^{-1}
Ionol	1	5.41
	3	3.32
	5	1.74
Hydroquinone	1	1.82
	3	1.34
	5	0.74
Diaphen FP	3	11.40
	5	14.30

Note: Solvent, $CHCl_3$; the initial concentration of **I**, 6 wt %.

tion at temperatures from –20 to 25°C. The disappearance of peroxide groups is described by the first-order rate equation

$$-\frac{d[ROOH]}{dt} = k_{eff}[ROOH].$$

Table 1 presents the effective first-order reaction rate constants (k_{eff}) for the decomposition of hydroperoxides **I** at various temperatures and an initial concentration of 6 ± 0.3 wt %. The rate constants were rather low (Table 1). According to our data, the half-life of the test hydroperoxides at 25°C is longer than 5 days.

The reaction is characterized by low activation energies (E_a = 19.7 ± 4 kJ/mol) and negative activation entropies (ΔS = –420 ± 8 J K^{-1} mol^{-1}). The Arrhenius equation has the form

$$k_{eff} = 3.4 \times 10^{-3} e^{-E/RT}.$$

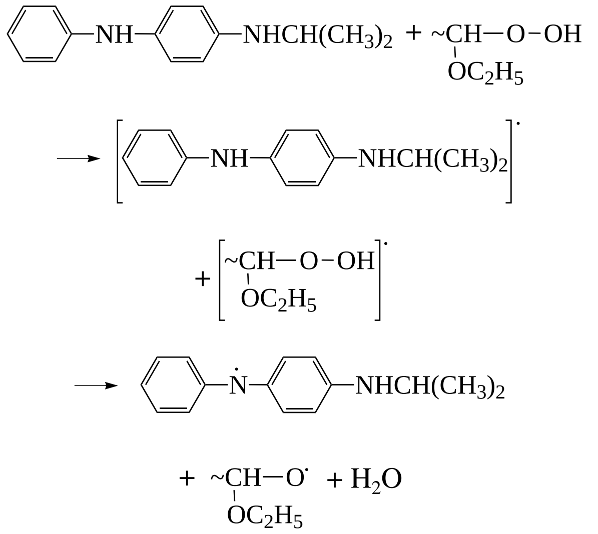
The experimental rate constants of the decomposition of hydroperoxides **I** are complex functions of the rate constants of individual steps; that is, they are effective constants. This is also true for the thermodynamic activation parameters. Therefore, a direct interpretation of these values is difficult to perform.

Then, we studied the possibility of improving the stability of the synthesized α-ethoxyhydroperoxides. Assuming that hydroperoxide decomposition occurs via a mechanism in which the initially formed radicals initiate the further decomposition of the other molecules, the transformation of active intermediate radical species into inert radicals should inhibit the decomposition of compounds **I**. Therefore, we studied the effect of phenols and aromatic amines, which are well-known stabilizers [11, 12], on the rate of decomposition of oligomeric α-ethoxyhydroperoxides.

INHIBITED DECOMPOSITION OF OLIGO-α-ETHOXYHYDROPEROXIDES

We studied the effects of 2,6-di-*tert*-butyl-4-methylphenol (Ionol), hydroquinone, and *N*-isopropyl-*N*'-phenyl-*n*-phenylenediamine (Diaphen FP) on the decomposition of oligo-α-ethoxyhydroperoxides. The amounts of these stabilizers varied from 1 to 5% of the weight of compound **I**. The inhibited decomposition of compounds **I** in the presence of these stabilizers is described by a first-order rate equation with respect to hydroperoxide groups. Table 2 presents quantitative data on the effects of stabilizers on the rate constants of decomposition.

The results obtained suggest that the use of phenolic stabilizers decreases the rate of decomposition of α-ethoxyhydroperoxide groups by more than an order of magnitude. The higher the phenol concentration, the stronger the inhibiting effect. These data confirm the fact that, indeed, compounds **I** decompose by the chain mechanism in which the reactions of primary radicals with hydroperoxide molecules play an important role. Hydroquinone exhibited a higher inhibiting activity than Ionol. The reasons for this phenomenon were discussed in detail in [13]. The influence of Diaphen FP on the decomposition of the test peroxides was somewhat surprising. The observed effect was insignificant and, moreover, the tendency for an increase in the rate of decomposition appeared with an increase in the amine concentration. Aryl and alkyl derivatives of *n*-phenylenediamine are usually more efficient radical scavengers than phenols [14, 15]. In this context, Diaphen FP would be expected to cause a stronger stabilizing effect. In our opinion, the observed inconsistency is due to the dual role of Diaphene FP in the test reactions. It really scavenges radicals, and this effect decreases the rate of the initiated decomposition of the hydroperoxide. However, the following reactions can take place:

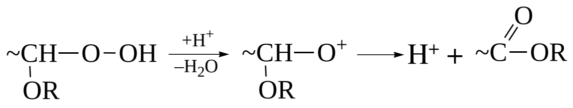


On the contrary, radical species are generated in this process. This reaction is facilitated by an increase in both the electron-donor properties of Diaphen FP and the electron-acceptor properties of the alkoxyhydroperoxide (the reaction center contains an ethoxy group with the inductive Taft constant equal to +1.366 [16]). Amines can also play such a dual role [14].

Therefore, the use of phenolic stabilizers improves the thermal stability of the test oligo-α-ethoxyhydroperoxides.

ACID-CATALYZED DECOMPOSITION OF OLIGO-α-HYDROPEROXIDES

In the synthesis of norbornene oligoesters used to produce oligo-α-ethoxyhydroperoxides, the nature of terminal groups can be purposefully changed by varying the ratio between the anhydride and the glycol. It is possible to obtain exclusively alcohol terminal groups or oligoesters with both alcohol and carboxyl terminal groups. The presence of carboxyl groups in oligoester molecules seemed undesirable because peroxide compounds are decomposed by acids [1]. It is known that the acid-catalyzed decomposition of α-alkoxyhydroperoxides is a convenient preparative method for the synthesis of esters [17, 18]:



$$\underset{\text{OR}}{\sim\text{CH}}-\text{O}-\text{OH} \xrightarrow[-\text{H}_2\text{O}]{+\text{H}^+} \underset{\text{OR}}{\sim\text{CH}}-\text{O}^+ \longrightarrow \text{H}^+ + \sim\overset{\text{O}}{\overset{/\!/}{\text{C}}}-\text{OR}$$

To elucidate how easily peroxides **I** decompose in the presence of carboxylic acids, we studied their decomposition in the presence of acetic acid. In this case, the decomposition rate is described by a first-order rate equation with respect to hydroperoxide. Assuming that the acid-catalyzed decomposition and radical degradation of compounds **I** occur independently of one another, the apparent rate constant k_Σ is the sum of the rate constants of radical defradation (k_{rad}) and acid-catalyzed decomposition (k_{ac})

$$k_\Sigma = k_{\text{rad}} + k_{\text{ac}}.$$

Using the above rate constants of radical degradation, we can determine the effective rate constant k_{ac}. Table 3 summarizes the kinetic data on the decomposition of compounds **I** in the presence of acetic acid.

Table 3. Overall (k_Σ) and effective rate constants of the acid-catalyzed decomposition (k_{ac}) of oligo-α-ethoxyhydroperoxides **I** in the presence of acetic acid

$[\text{CH}_3\text{COOH}]$, mol/l (wt %)	$k_\Sigma \times 10^7$, s^{-1}	$k_{\text{ac}} \times 10^7$, s^{-1}
0.17(1)	18.6	3.6
0.83(5)	28.8	13.8
1.67(10)	54.0	39.0

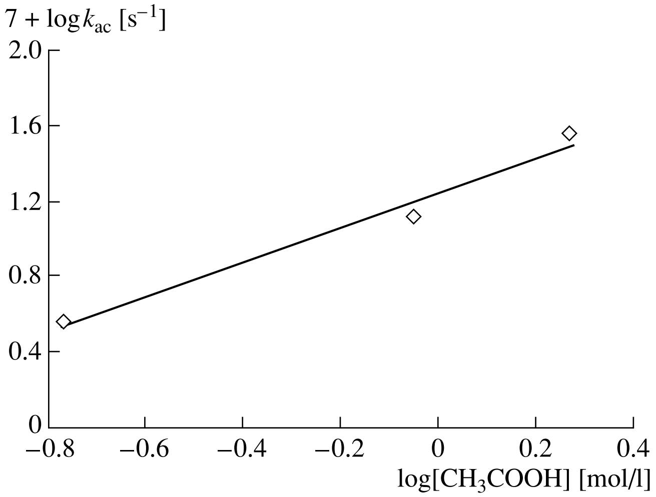
Note: Temperature, 25°C; solvent, CHCl_3; the initial concentration of **I**, 6 wt %.

The effective reaction rate constants of the acid-catalyzed decomposition of α-ethoxyhydroperoxides were low. They increased with the acetic acid concentration. This is due to the fact that the concentration of the catalyst acetic acid enters the expression for the effective rate constant. In the general case, this dependence is described by the equation

$$k_{\text{ac}} = k_{\text{ac}}^{\text{true}} [\text{CH}_3\text{COOH}]^n,$$

where $k_{\text{ac}}^{\text{true}}$ is the true rate constant of the acid-catalyzed reaction and n is the order of reaction with respect to the acid.

The order of reaction with respect to the acid and the true rate constant of the acid-catalyzed decomposition can be determined from the dependence of the logarithms of the effective rate constants of acid-catalyzed reaction on the logarithms of the acetic acid concentration (see figure). The slope of the straight line in the figure is equal to unity. Therefore, the test reaction exhibits first partial orders with respect to acetic acid and hydroperoxide groups and a second overall order. These data suggest that the acid-catalyzed decomposition of compound **I** involves the attack of the acetic acid molecule on hydroperoxide groups. The true rate constant of acid-catalyzed decomposition at 25°C determined from the figure is 20×10^{-7} l mol^{-1} s^{-1}.



Logarithm of the effective rate constant of the acid-catalyzed decomposition of oligo-α-ethoxyhydroperoxides as a function of the logarithm of the acetic acid concentration (mol/l) at 25°C (in a $CHCl_3$ solution).

Thus, we found that even such a weak acid as acetic acid catalyzes the decomposition of oligo-α-ethoxyhydroperoxides. On this basis, we concluded that the number of carboxyl groups in norbornene oligoesters should be minimized during the synthesis.

ACKNOWLEDGMENTS

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