

PEROXIDES-XI

Initiating Ability of the Peroxyacetates of Secondary Hydroperoxides

I. M. Nosacheva, S. G. Voronina, and A. L. Perkel’

Kuzbass State Technical University, Kemerovo, Russia

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Abstract—The kinetics of ethylbenzene oxidation in the presence of acetic anhydride, the kinetics of acetic anhydride reaction with cyclohexyl hydroperoxide, and the composition of the products of the above reactions were studied in order to evaluate the initiating abilities of 1-phenylethyl and cyclohexyl peroxyacetates generated *in situ* and to determine the directions of reactions. Anhydride additives significantly accelerated the oxidation of ethylbenzene and the degradation of cyclohexyl hydroperoxide with the predominant formation of corresponding ketones. It was found that the acceleration of ethylbenzene oxidation was due to the homolytic degradation of a peroxy ester, which results in the formation of methyl phenyl carbinol and benzaldehyde (ethylbenzene) or cyclohexanol (cyclohexyl hydroperoxide). The importance of the homolytic degradation of peroxy esters was evaluated using a mixed-initiation method (ethylbenzene) or by measuring the consumption of an inhibitor (cyclohexyl hydroperoxide).

INTRODUCTION

Secondary hydroperoxides are formed as main intermediates in the liquid-phase radical chain oxidation of saturated aliphatic, alicyclic, and some alkylaromatic hydrocarbons [1, 2]. Their subsequent transformations are usually related to unimolecular or bimolecular degradation and reactions with the participation of a substrate or oxygen-containing oxidation products [1–4]: alcohols, ketones, α -ketoalcohols, α -diketones, carboxylic acids, esters, etc. The detection of carboxylic acid anhydrides among oxidative degradation products and the substantiation of the reaction paths of their formation [4] suggest that these compounds participate not only in the formation of the esters of secondary alcohols [4, 5] but also in reactions that result in the degradation of secondary hydroperoxides [4].

Peroxy esters result from the interaction of carboxylic acid anhydrides with hydroperoxides. There are no systematic published data on the properties and initiating abilities of the peroxy esters of secondary hydroperoxides. It is well known [6, 7] that the half-lives of *n*-butyl, *sec*-butyl, and *tert*-butyl peroxyacetates at 64.6°C ($\tau_{1/2} \times 10^{-3}$, min) are 3.1, 0.9, and 280, respectively, and the first two peroxy esters do not initiate polymerization. These data indicate that the peroxy esters of secondary hydroperoxides are much less stable than those of primary and, particularly, tertiary hydroperoxides and exhibit low initiating abilities.

In this work, we studied the initiating abilities and reaction paths of 1-phenylethyl peroxyacetate and cyclohexyl peroxyacetate, which are formed in the reactions of 1-phenylethyl hydroperoxide and cyclohexyl hydroperoxide with acetic anhydride.

EXPERIMENTAL

Ethylbenzene of reagent grade was purified by treatment with concentrated sulfuric acid in accordance with a well-known procedure [8] in order to remove oxygen-containing products. After distillation in a flow of argon, a substance was obtained that contained less than 0.003 and 0.005% methyl phenyl carbinol and acetophenone, respectively, according to gas–liquid chromatography (GLC) data.

Cyclohexyl hydroperoxide was separated from commercial cyclohexane oxidation products and purified through its potassium salt [9], from which it was regenerated by bubbling CO₂. According to quantitative thin-layer chromatography (TLC) data, the concentration of cyclohexyl hydroperoxide in the purified material was no lower than $99.3 \pm 0.2\%$.

Acetic anhydride of analytical grade was purified by distillation after the preliminary conversion of acetic acid into methyl acetate with diazomethane.

Chlorobenzene of analytical grade and chemically pure *n*-octane were distilled from P₂O₅ in a flow of argon. Ionol and cumene peroxide (both of analytical grade) and chemically pure nitrobenzene were used without additional purification.

The total peroxide content of oxidized ethylbenzene was determined by colorimetry after treating the sample with a reagent containing Fe²⁺ ions and *N,N*-dimethyl-*p*-phenylenediamine [10]. The concentration of 1-phenylethyl peroxyacetate was calculated by difference between the results of the determination of 1-phenylethyl acetate in a sample reduced with triphenylphosphine and in a sample without reduction. Acetic anhydride was decomposed with a methanol–pyridine mixture (1 : 1) immediately after sampling. The con-

centration of 1-phenylethyl hydroperoxide was determined as the difference between the total concentration of peroxide compounds and the concentration of 1-phenylethyl peroxyacetate. Before GLC determination, benzoic acid was converted into a methyl ester by treatment with diazomethane. The GLC determination of the nonperoxide products of ethylbenzene oxidation was performed on a column (2000 × 3 mm) packed with 15% Carbowax 6000 on Chromaton N-AW DMCS at 140°C; nitrobenzene was used as an internal standard.

In experiments on the interaction of cyclohexyl hydroperoxide with acetic anhydride, the total concentration of peroxide compounds was determined by iodometric titration [11]. For the determination of individual peroxide compounds, a published procedure [10] was used, which is based on the TLC pre separation of analytes followed by determination with the use of *N,N*-dimethyl-*p*-phenylenediamine. The separation was performed on Silufol plates. A toluene-methanol mixture (15 : 1) was used as the mobile phase.

In the determination of nonperoxide products, acetic anhydride in an aliquot portion of the sample was decomposed with a methanol-pyridine mixture (1 : 1) and peroxide compounds were reduced with a 50% molar excess of triphenylphosphine. In this case, cyclohexyl hydroperoxide and 1-hydroxy-1-cyclohexylperoxycyclohexane were reduced to cyclohexanol, and cyclohexyl peroxyacetate was reduced to cyclohexyl acetate [11, 12]. The total concentration of cyclohexyl peroxyacetate and cyclohexyl acetate was determined on a column (3000 × 3 mm) with 5% SP-2100 silicone on Chromaton N-AW Super at 80°C; dodecane was used as an internal standard. Ionol in the same sample was determined on a column (2000 × 3 mm) with 5% OV-17 silicone on Chromaton N-AW Super at 170°C; hexadecane was used as an internal standard. The total concentration of cyclohexanone and 1-hydroxy-1-cyclohexylperoxycyclohexane, as well as the total concentration of cyclohexanol, cyclohexyl hydroperoxide, cyclohexyl acetate, and cyclohexyl peroxyacetate, was determined in samples reduced with triphenylphosphine after converting cyclohexanol into acetate with an acetic anhydride-pyridine mixture (1 : 1) at 100°C for 1 h.

Experiments on the oxidation of ethylbenzene with oxygen were performed in a manometric unit in the kinetics-controlled region of oxygen consumption. The interaction of cyclohexyl hydroperoxide with acetic anhydride was studied in a thermostated cell equipped with a gas bubbling device. In the calculations of the rates of chain radical consumption of oxygen (w_{cr}), a correction for the nonchain consumption of oxygen was made in accordance with the equation [13]

$$w_{cr} = w_{O_2} - 0.5w_i.$$

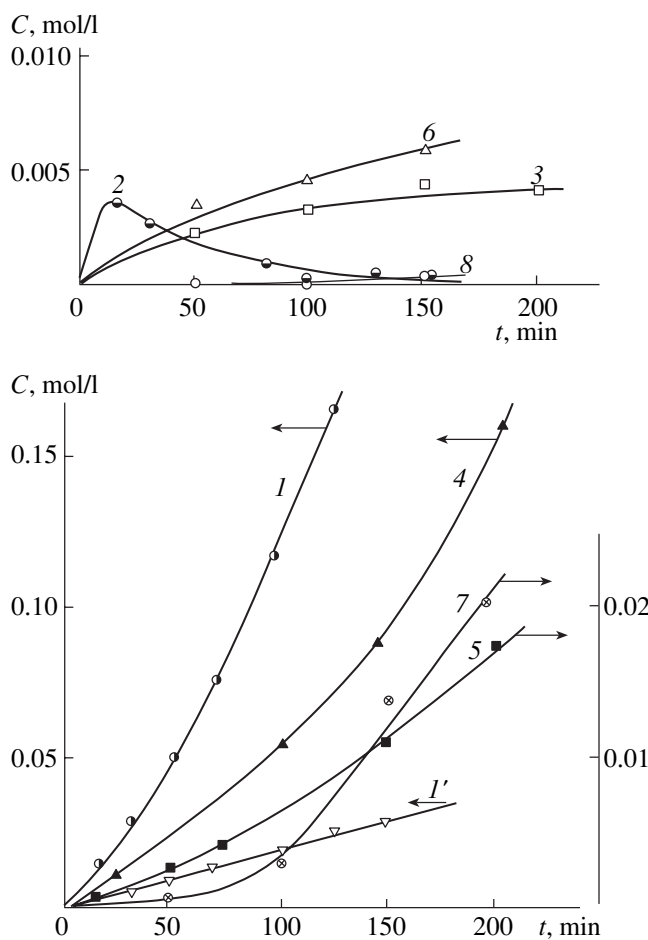


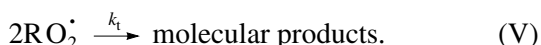
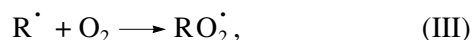
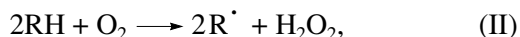
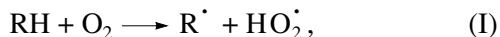
Fig. 1. Kinetics of (*I*, *I'*) oxygen consumption and the buildup of reaction products in experiments on ethylbenzene oxidation at 100°C (*I*–8) with and (*I'*) without acetic anhydride added: (2) 1-phenylethyl hydroperoxide, (3) 1-phenylethyl peroxyacetate, (4) acetophenone, (5) methyl phenyl carbinol, (6) benzaldehyde, (7) 1-phenylethyl acetate, and (8) benzoic acid.

RESULTS AND DISCUSSION

Because of the above-mentioned thermal lability of the peroxy esters of secondary hydroperoxides, they can be studied only under special conditions [6], which are difficult to compare to the conditions of hydrocarbon oxidation characterized by elevated temperatures. Therefore, to solve the problem at hand, peroxy esters were prepared *in situ* by the interaction of corresponding hydroperoxides with acetic anhydride introduced into the reaction medium.

Ethylbenzene was oxidized by oxygen at 100°C without additives and in the presence of acetic anhydride (1.1 mol/l). Figure 1 demonstrates the kinetics of oxygen consumption and of the buildup of peroxide compounds, methyl phenyl carbinol, acetophenone, 1-phenylethyl acetate, benzaldehyde, and benzoic acid.

Without acetic anhydride at 100°C, ethylbenzene was oxidized at a practically constant rate (Fig. 1). Evidently, in this case, the rate of 1-phenylethyl hydroperoxide degradation was low, and initiation was primarily performed by chain initiation reactions. In the absence of the anhydride, the chain radical oxidation occurs in accordance with the following reaction scheme:

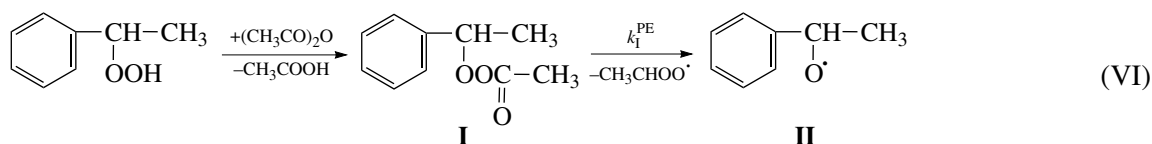


The rate of this oxidation (w_{cr}^0) is expressed by the equation

$$w_{\text{cr}}^0 = k_p(2k_t)^{-0.5}[\text{RH}](w_i^0)^{0.5}, \quad (1)$$

where k_p and k_t are the reaction-rate constants of chain propagation and termination, respectively, and w_i^0 is the rate of initiation due to chain initiation reactions.

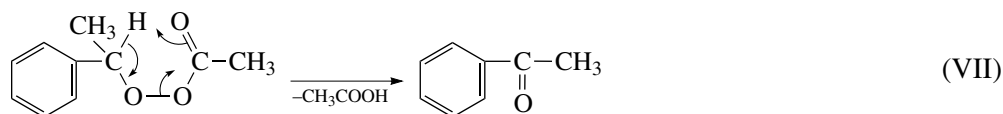
In the presence of acetic anhydride, the oxygen consumption curve exhibited a more complicated shape. It exhibited an autoaccelerated character at the initial portion and then was rectilinear (Fig. 1). The rate of ethylbenzene oxidation at the rectilinear portion was $(27.1 \pm 0.12) \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, which is higher than that in an experiment without the anhydride ($w_{\text{cr}}^0 = (3.9 \pm 0.12) \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$) by a factor of 6.9. The 1-phenylethyl hydroperoxide buildup curve (Fig. 1) exhibited a maximum, which is characteristic of intermediate products. Successively with the hydroperoxide, 1-phenylethyl peroxyacetate accumulated which was formed by the acylation of 1-phenylethyl hydroperoxide with acetic anhydride:



The hydroperoxide : peroxy ester ratio decreased with the degree of oxidation because of the autocatalysis of hydroperoxide acylation by acetic acid, which is released in the course of reaction (VI). An increase in the rate of ethylbenzene oxidation in the presence of acetic anhydride was due to an increased role of degenerate branching by the homolytic cleavage of the peroxy ester, which decomposed into radicals under reac-

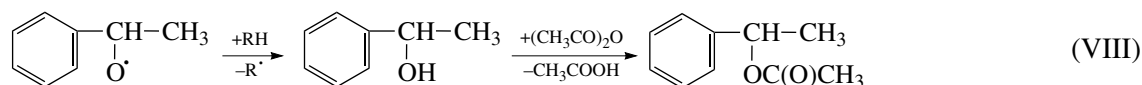
tion conditions at a higher rate than that of the parent hydroperoxide (reaction (VI)).

Acetophenone was the main product of ethylbenzene oxidation in the presence of acetic anhydride. It was formed in much greater amounts (~80%) than in the thermal oxidation of ethylbenzene at 120°C in the absence of the anhydride [2]. It is believed that the conversion of peroxy ester **I** (reaction (VI)) via a pericyclic mechanism resulted in acetophenone:

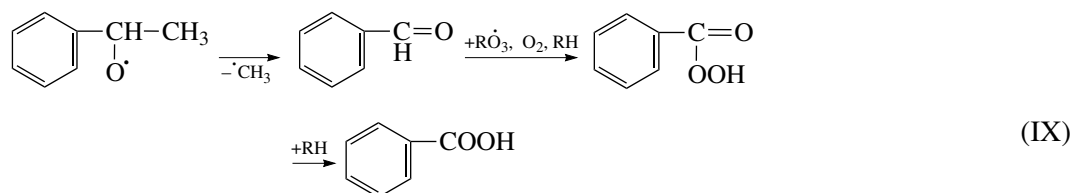


In turn, the relative yield of methyl phenyl carbinol (12.6%) in the presence of acetic anhydride (Fig. 1) was much lower than that without the anhydride [2]. It is most likely that the alcohol was

formed by the interaction of 1-phenylethyloxy radical (**II**) with the substrate, and it was partially converted into 1-phenylethyl acetate under the action of acetic anhydride (Fig. 1):



It is evident that the formation of benzaldehyde, which was then oxidized to benzoic acid, was associated with the homolytic degradation of the peroxy ester



Thus, the formation of products, the total yield of which can be related to the homolytic conversion of 1-phenylethyl peroxyacetate, was ~20%.

To evaluate the initiating ability of 1-phenylethyl peroxyacetate, the method of mixed initiation was also used. In the cumyl peroxide (CP)-initiated oxidation of ethylbenzene without additives and with acetic anhydride (AA), the rates of oxidation can be represented by Eqs. (2) and (3), respectively [12].

$$w_{\text{cr}}^{\text{CP}} = k_p(2k_t)^{-0.5}[\text{RH}]_1(w_i^0 + w_i^{\text{CP}})^{0.5}, \quad (2)$$

$$w_{\text{cr}}^{\text{AA}} = k_p(2k_t)^{-0.5}[\text{RH}]_2(w_i^0 + w_i^{\text{CP}} + w_i^{\text{PE}})^{0.5}, \quad (3)$$

where $[\text{RH}]_1$ and $[\text{RH}]_2$ are the concentrations of ethylbenzene in experiments without additives and with acetic anhydride, respectively; and w_i^{CP} and w_i^{PE} are the rates of initiation due to cumyl peroxide and the peroxy ester, respectively.

From Eqs. (2) and (3), we derived the following expression for the calculation of w_i^{PE} :

$$w_i^{\text{PE}} = \frac{(w_{\text{cr}}^{\text{AA}}[\text{RH}]_2)^2 (w_i^{\text{CP}} + w_i^0)}{(w_{\text{cr}}^{\text{CP}}[\text{RH}]_1)^2}. \quad (4)$$

To evaluate w_i^{PE} , we performed experiments on the cumyl peroxide-initiated oxidation of ethylbenzene at various initiator concentrations (Table 1).

The rates of initiation due to 1-phenylethyl peroxyacetate, which are given in Table 1, can be used for evaluating the fraction of its homolytic cleavage:

$$\frac{w_{\text{d}}^{\text{hom}}}{w_{\text{d}}^{\text{ov}}} \times 100 = \frac{w_i^{\text{PE}}}{2ew_{\text{d}}^{\text{ov}}} \times 100, \% \quad (5)$$

where $w_{\text{d}}^{\text{hom}}$ and w_{d}^{ov} are the rates of homolytic and overall degradation of 1-phenylethyl peroxyacetate, respectively; and e is the factor of radical escape from a solvent cage. For aromatic hydrocarbons, $e = 0.6$ [12].

On the assumption that 1-phenylethyl hydroperoxide, which is formed in the oxidation of ethylbenzene in the presence of acetic anhydride, almost completely decomposes through a peroxy ester, the overall rate of degradation of the peroxy ester in Eq. (5) can be replaced by the rate of chain radical oxidation:

$$\frac{w_{\text{d}}^{\text{hom}}}{w_{\text{d}}^{\text{ov}}} \times 100 = \frac{w_i^{\text{PE}}}{2ew_{\text{cr}}^{\text{AA}}} \times 100, \% \quad (6)$$

It can be seen in Table 1 that, on the average, the fraction of the homolytic transformation of 1-phenylethyl peroxyacetate calculated from Eq. (6) is 9.1%.

Table 1. Experimental data on the cumyl peroxide-initiated oxidation of ethylbenzene at 100°C with and without acetic anhydride added (rates $w \times 10^6$, mol l⁻¹ s⁻¹)

$w_i^{\text{CP}*}$	$w_{\text{cr}}^{\text{CP}}$	$\nu^{\text{CP}**}$	$w_{\text{cr}}^{\text{AA}}$	$\nu^{\text{PE}***}$	w_i^{0***}	w_i^{PE}	$\frac{w_i^{\text{PE}}}{2ew_{\text{cr}}^{\text{AA}}} \times 100, \%$
0.14	4.9 ± 0.3	26.5	15.4 ± 0.28	9.1		1.5	8.1
0.53	9.10 ± 0.23	16.0	19.0 ± 0.41	7.3	0.045	2.0	9.0
0.71	10.20 ± 0.15	13.5	21.0 ± 0.35	6.3		2.6	10.3

* Calculated from the equation $w_i^{\text{CP}} = 2ek[\text{CP}]$; $k = 6.3 \times 10^{12} \exp(-126.4 \text{ (kJ/mol)/RT})$, s⁻¹ [13]; e is the factor of radical escape from a solvent cage.

** Chain length $\nu = \frac{w_{\text{cr}}}{w_i}$.

*** Calculated from Eq. (1) with the use of the average value of parameter $k_p(2k_t)^{-0.5} = 22.2 \times 10^{-4} \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ s}^{-1/2}$ [2].

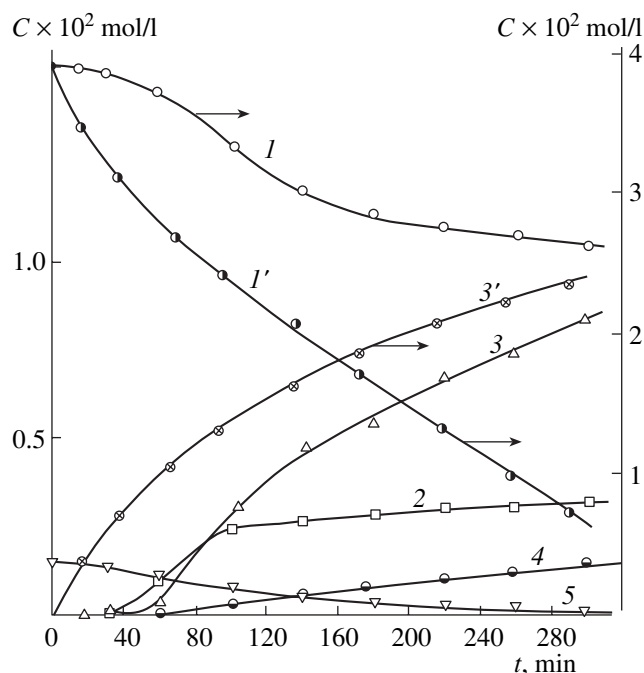


Fig. 2. Kinetics of hydroperoxide and ionol conversion and the buildup of reaction products in the reactions of cyclohexyl hydroperoxide with acetic anhydride at 70°C (1–5) without additives and (1', 3') in the presence of 0.1 M acetic acid: (1, 1') cyclohexyl hydroperoxide, (2) cyclohexyl peroxyacetate, (3, 3') cyclohexanone, (4) cyclohexanol, and (5) ionol.

To evaluate the initiating ability and the direction of reaction of cyclohexyl peroxyacetate, we studied the interaction of cyclohexyl hydroperoxide (0.039 mol/l) with acetic anhydride (0.29 mol/l) at 70°C in an *n*-octane–chlorobenzene mixture (4 : 1). To prevent hydroperoxide degradation initiated by free radicals, an inhibitor (ionol) was added to the reaction medium and oxygen was bubbled. Figure 2 demonstrates the kinetics of cyclohexyl peroxide and ionol conversions and the buildup of cyclohexyl peroxyacetate, cyclohexanone, and cyclohexanol.

Table 2. Yields of cyclohexanone and cyclohexanol and the consumption of ionol ($\Delta[\text{InH}]$) (mol % on a converted peroxy ester basis) at various cyclohexyl hydroperoxide conversions ($\Delta[\text{ROOH}]$)

$\Delta[\text{ROOH}]$, mol/l	Cyclohex- anone, mol %	Cyclohex- anol, mol %	$\Delta[\text{InH}]$, mol %
0.050	89.3	10.7	17.9
0.075	88.1	11.9	16.7
0.100	86.9	13.1	16.4
0.125	85.1	14.9	13.8
	87.4*	12.7*	16.2*

* Average value.

It can be seen in Fig. 2 that the curves of hydroperoxide conversion and the buildup of reaction products are characterized by an induction period, after which the rate of reaction noticeably increased. Evidently, this circumstance is related to the autocatalysis of the hydroperoxide reaction with acetic anhydride by acetic acid which is formed in the course of acylation, as in the case of ethylbenzene oxidation. Indeed, an induction period was not observed upon the addition of acetic acid (0.1 mol/l) to the initial mixture (Fig. 2, curves 1', 3').

Cyclohexyl peroxyacetate is the primary product of the interaction of cyclohexyl hydroperoxide with acetic anhydride. Its degradation, probably, by reactions (VII) and (VIII), results in the formation of cyclohexanone and cyclohexanol. In this case, as well as in the oxidation of ethylbenzene in the presence of the anhydride, the yield of the ketone was much higher than that of the alcohol (Fig. 2; Table 2).

Small amounts of 1-hydroxy-1-cyclohexylperoxy-cyclohexane, which was formed by the interaction of cyclohexyl hydroperoxide with cyclohexanone, and cyclohexyl acetate were also detected in the reaction mixture. Cyclohexyl acetate was accumulated in much smaller amounts than 1-phenylethyl acetate in ethylbenzene oxidation.

It can be seen in Table 2 that the formation of cyclohexanol and the consumption of ionol occurred in similar amounts. This circumstance provides support for the hypothesis on the homolytic mechanism of alcohol formation and also indicates a considerable initiating ability of cyclohexyl peracetate. The ratio between the constants of homolytic degradation (k') and overall degradation (k'') of cyclohexyl hydroperoxide at 70°C, which were calculated from Eqs. (7) and (8) [14], was equal to 0.137 and comparable with the relative value of the homolytic degradation of cyclohexyl peroxyacetate (Table 2).

$$\log k' = 11.8 - 138.9 (\text{kJ/mol}) / 2.303RT; \quad (7)$$

$$\log k'' = 10.8 - 125.9 (\text{kJ/mol}) / 2.303RT. \quad (8)$$

However, cyclohexyl peroxyacetate decomposes at a high rate under conditions when the hydroperoxide is stable.

It is also well known [14] that the ratio between ketone and alcohol yields in the decomposition of cyclohexyl hydroperoxide in *n*-hexane at 150°C is 0.31, which is much lower than the above ratio (6.9) in the decomposition of cyclohexyl peracetate.

Thus, the results of this work demonstrate that carboxylic acid anhydrides significantly accelerate the degradation of secondary hydroperoxides; moreover, they also affect the direction of reactions. Contrary to available notions [7], the resulting peroxy esters exhibit an initiating ability, although it is lower than that of the peroxy esters of tertiary hydroperoxides [7, 15]. Because the reaction of hydroperoxides with carboxylic acid anhydrides is one of the main reaction paths of

anhydride consumption [4], the degradation of the peroxy esters of secondary hydroperoxides can make a noticeable contribution to both the initiation of oxidation processes of organic compounds and the formation of carbonyl-containing products.

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