

Initiating and Cross-Linking Ability of Organic Peroxides: Chemical Kinetic Methods for the Determination

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Abstract—This review surveys chemical kinetic methods for the quantitative determination of the initiating and cross-linking ability of organic peroxides ROOR' (peroxides, hydroperoxides, peroxyesters, diacyl peroxides, and peroxyarbonates). The conditions and limitations of the use of autoxidation, inhibitor, radical polymerization, and model cross-linking methods are analyzed. The results of the determination of the initiating and cross-linking ability of the most important organic peroxides are cited.

INTRODUCTION

Organic peroxides, which are the main source of free radicals in chemical practice, are widely used for initiating radical reactions, in particular, chain processes and polymer cross-linking [1, 2].

Thermal instability due to the presence of a weak O–O bond and a wide range of thermal decomposition times depending on the structure of peroxide provide an opportunity to use peroxides as initiators over a wide range of temperatures from 40–50 to 170–200°C. Initiation with the hydroperoxide–metal ion and diacyl peroxide–amine redox systems can be performed even at zero temperature.

It should be borne in mind that the yields of free radicals in the thermolysis of organic peroxides are lower than 100% depending on peroxide structure. This is due to the simultaneous occurrence of various rearrangements and decomposition with the formation of molecular products.

The following is required for choosing the most efficient peroxide initiators: (1) to develop standardized model procedures that give comparable characteristics in the series of both peroxides and other radical initiators; (2) to perform screening; and (3) to determine structure–initiating ability relationships for peroxides.

The detection of radicals in the pyrolysis of peroxides in a gas phase is a complicated problem. This problem is experimentally solved by the use of compounds that are radical scavengers or by freezing radical products in low-temperature traps. The problem can also be solved by calculations based on the kinetics of radical processes with known mechanisms etc. It seems impossible to measure the initiating ability of a wide variety of peroxides in a gas phase taking into account differences in thermal stability and volatility. Because peroxides are mainly used in a liquid phase, it is reasonable to perform these experiments in solutions.

The kinetics and mechanism of peroxide thermolysis in solution are highly sensitive to the properties of a medium, the presence of impurities, the initial concentration, and other factors. Thus, to evaluate radical formation in a study of homolysis in solution, it is important to provide identical conditions of decomposition. In the context of studies of the inhibitors of chain processes, various model systems were developed for evaluating the scavenging ability of inhibitors. These systems are based on the reactions of autoxidation, polymerization, etc. [3, 4].

Many quantitative studies of the homolysis of peroxides were performed under conditions that make the results obtained with different peroxides difficult to compare. The chemical kinetic methods for determining the initiating ability of peroxides and the results obtained by a number of methods under comparable conditions are considered below.

1. DETERMINATION OF THE INITIATING ABILITY OF ORGANIC PEROXIDES IN THE MODEL REACTIONS OF CUMENE AND *n*-DECANE AUTOXIDATION

The kinetics and mechanism of liquid-phase radical chain oxidation of many compounds have been studied in detail [5, 6]. The elementary constants were reliably determined, and the kinetic models of reactions were given. Therefore, this process can be used as one of the most convenient methods for determining the rate of free radical generation. For this purpose, Agabekov, Butovskaya, Antonovskii, and coauthors [7–12] developed a method for testing radical initiators. This method is based on the use of the liquid-phase oxidation of cumene and *n*-decane as model systems for low (323–353 K) and relatively high temperatures (373–403 K), respectively.

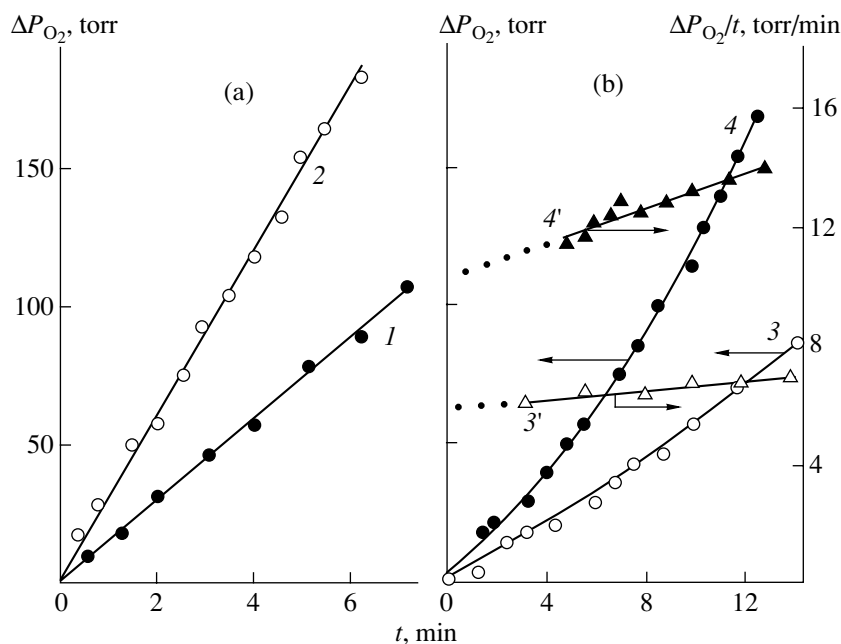
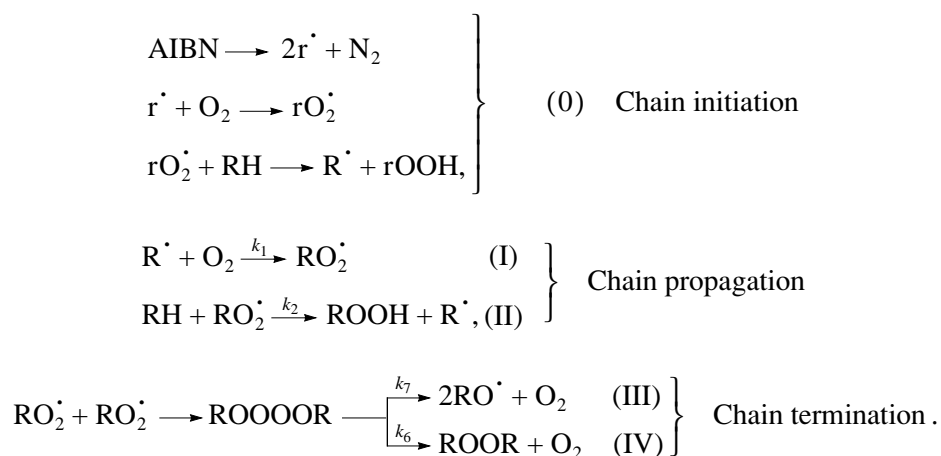


Fig. 1. Kinetic curves of oxygen consumption in the oxidation of (a) cumene ($T = 343$ K) and (b) *n*-decane ($T = 403$ K). $[AIBN] =$ (1) 1.9×10^{-3} or (2) 6.5×10^{-3} mol/l; [cumyl peroxide] = (3, 3') 1.0×10^{-3} or (4, 4') 4.9×10^{-3} mol/l.

In the oxidation of cumene and *n*-decane, 2,2'-azobisisobutyronitrile (AIBN) and cumyl peroxide, respectively, served as reference initiators for calibrating the system at regular intervals.

1.1. Cumene Oxidation

The reaction scheme of AIBN-initiated cumene oxidation at a sufficiently high partial pressure of oxygen has the form



The rate of oxidation obeys the equation

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}} [RH] \sqrt{w_i}, \quad (1)$$

where $[RH]$ is the concentration of cumene, $w_i = k_i[AIBN]$ is the rate of initiation, and k_i was calculated from published data [13, 14]. Note that under experimental conditions the time dependence of oxygen consumption was linear (Fig. 1a).

The testing of initiators implies the use of a model reaction over a wide range of initiation rates, that is, at different lengths of oxidation chains. If cumene oxidation occurs with short chains ($\nu \leq 10$), Eq. (1) should be corrected for gas absorption and evolution in the acts of chain initiation and termination. Thus, oxygen is consumed by r^{\cdot} and R^{\cdot} radicals in reactions (0) and (I) at a rate of $2w_i$. In the decomposition of AIBN, nitrogen is released at a rate of $1/2ew_i$, where e is the cage escape

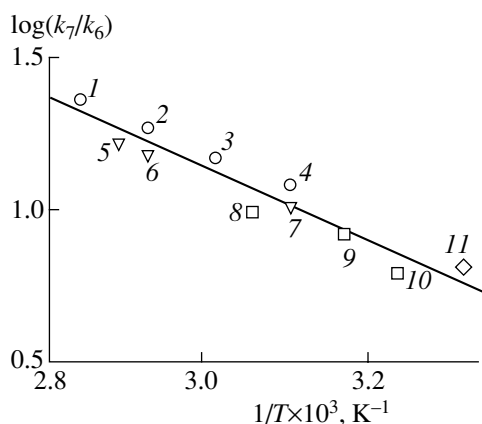


Fig. 2. Plot of $\log(k_7/k_6)$ vs. $1/T$; the values of k_7/k_6 were calculated from the (1–4) $w_{O_2}/w_i - w_i^{1/2}$ and (5–7) $w_{O_2} - [RH]$ relationships or published data from (8–10) [17] or (11) [18].

yield of radicals. Moreover, oxygen is liberated at a rate of $1/2(1 - k_7/k_6)w_i$ as a result of bimolecular reactions (III) and (IV) of ROO^\bullet radicals.

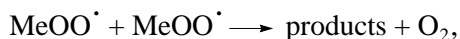
Taking into account all corrections, an expression for the experimental rate of oxygen consumption has the form

$$w_{O_2}^{\text{expt}} = \frac{k_2}{\sqrt{k_6}}[RH]\sqrt{w_i} - \alpha w_i, \quad (2)$$

where

$$\alpha = 1/2(3 - k_7/k_6 - 1/e). \quad (3)$$

At the same time, it should be borne in mind that the reaction scheme of cumene oxidation becomes more complicated under certain conditions, and the value of α is correspondingly changed. Thus, for example, Me^\bullet radicals are formed in the β cleavage of cumylperoxy radicals; the subsequent transformations of methyl radicals result in oxygen consumption and liberation [15]:



However, reactions (V) and (VI) play an important role in chain termination only at $[RH] < 100\%$ [15].

Primary peroxy radicals ($PhCHMeCH_2OO^\bullet$), which result from hydrogen atom abstraction from the methyl group of cumene, can also participate in chain termination [15]. This is evidenced by a decrease in the value of k_6 from 2×10^5 to 3.9×10^4 $l \text{ mol}^{-1} \text{ s}^{-1}$ as the hydrocarbon concentration was increased from 5 to 50 wt %, whereas k_6 remained almost unchanged with further increasing $[RH]$. Based on the analysis of prod-

ucts formed by the interaction of cumylperoxy radicals, Howard *et al.* [16] demonstrated that 2-phenyl-1-propylperoxy radicals do not participate in chain termination reactions in the course of cumene oxidation at 303 K and $P_{O_2} = 0.5\text{--}103.3$ kPa.

The contribution of primary cumylperoxide radicals to chain termination reactions in the oxidation of cumene under standardized conditions was checked by the concentration dependence of the rate of cumene oxidation. If 2-phenyl-1-propylperoxy radicals participate in chain termination reactions, the ratio of the rate of oxidation of cumene to its concentration at a constant rate of initiation will increase by a factor of 2.23 as $[RH]$ increases from 0.3 to 3.3 mol/l, and this ratio will remain unchanged with further increasing $[RH]$. It was experimentally found (with consideration for the correction αw_i) that the ratio $w_{O_2}/[RH]$ is independent of $[RH]$ over the entire range of cumene concentrations. Thus, reactions (III) and (IV) are the main chain termination reactions in the interaction of cumylperoxy radicals under standardized conditions of cumene oxidation.

The value of α is determined as the slope of a straight line on the $w_{O_2}^{\text{expt}}[I]^{-1/2} - [I]^{1/2}$ coordinates ($[I]$ is the initiator concentration) in accordance with the equation

$$\frac{w_{O_2}^{\text{expt}}}{\sqrt{w_i}} = \frac{k_2}{\sqrt{k_6}}[RH] - \alpha\sqrt{w_i}, \quad (4)$$

which was derived by rearranging Eq. (2). The value of α can also be determined from $w_{O_2}^{\text{expt}}$ as a function of $[RH]$ extrapolated to $[RH] = 0$. The values of k_7/k_6 at different temperatures were calculated from the values of α obtained from both of the functions (Table 1) using Eq. (3). In this case, both our experimental data and published values of k_7/k_6 [17–19] are adequately approximated by a straight line in the Arrhenius coordinates (Fig. 2) with the regression coefficient $\rho = 0.95$. The general expression for k_7/k_6 , which was calculated by the least-squares technique at the number of points $n = 11$, has the form

$$\log(k_7/k_6) = (4.94 \pm 0.15) - (24.35 \pm 2.90)/\theta,$$

where $\theta = 19.14T \times 10^3$ kJ/mol. Without making corrections for gas evolution and consumption in the acts of chain initiation and termination, the experimental oxidation characteristic $k_2k_6^{-1/2}$ can change with increasing rate of initiation:

$$\frac{k_2}{\sqrt{k_6}} = \frac{w_{O_2}^{\text{expt}} + \alpha w_i}{[RH]\sqrt{w_i}}.$$

Table 1. w_{O_2} , α , and $k_2k_6^{-1/2}$ in the oxidation of cumene initiated by AIBN

T, K	$w_i \times 10^8, \text{mol l}^{-1} \text{s}^{-1}$	$[RH], \text{mol/l}$	$w_{O_2} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	α			$k_2k_6^{-1/2}, (\text{l mol}^{-1} \text{s}^{-1})^{1/2}$
				1*	2*	3*	
323	7.5	3.5	2.9	4.2	5.0	4.2	3.62
323	7.5	6.8	6.6	—	—	—	—
333	9.0	6.7	8.8	5.8	7.0	—	4.55
343	10.0	6.7	14.4	7.8	9.0	7.3	6.22
348	9.6	6.6	15.1	8.8	—	8.0	7.88
348	9.7	1.7	7.7	—	—	—	—
348	9.7	1.7	3.4	—	—	—	—
353	9.0	6.6	15.8	10.2	11.0	—	8.05

Note: (1) Calculated from published data [19]; (2) found from the $w_{O_2} (w_i)^{-1/2} w_i^{-1/2}$ relationship; and (3) found from the $w_{O_2} - [RH]$ relationship.

It is evident that, at high w_i , an overestimated value of $k_2k_6^{-1/2}$ can be obtained without consideration for the value of αw_i . Indeed, Emanuel' *et al.* [3] noted that the value of $k_2k_6^{-1/2}$ at 333 K increased by a factor of ~ 1.5 as w_i decreased from 10^{-4} to $10^{-9} \text{ mol l}^{-1} \text{s}^{-1}$. In our case, the value of $k_2k_6^{-1/2}$, which was obtained taking into account αw_i , for cumene remained constant as w_i changed from 5×10^{-6} to $3 \times 10^{-8} \text{ mol l}^{-1} \text{s}^{-1}$.

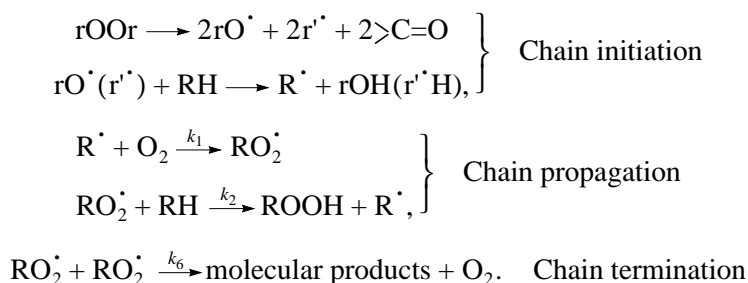
The general expression for the oxidation characteristic $k_2k_6^{-1/2}$ of cumene, which was calculated with consideration for αw_i corrections, over the temperature range 323–353 K has the form ($v = 30$ –100 units; $n = 6$; $\rho = 0.995$)

$$\log(k_2k_6^{-1/2}) = (2.24 \pm 0.22) - (29.15 \pm 1.42)/\theta.$$

Note that, with the use of various peroxides as initiators, the $r\cdot$ and $rO\cdot$ radicals formed in chain initiation reaction (0) can directly abstract a hydrogen atom from RH without the formation of $rOO\cdot$ radicals, as is the case with AIBN. Moreover, with the use of a volumetric measurement technique, highly volatile products of initiator degradation can make a certain contribution, which affects the correction factor α . In the general case, when the mechanism of initiation is unknown and oxidation chains are short, the value of α should be determined from the $w_{O_2} - [RH]$ or $w_{O_2} [I]^{-1/2} - [I]^{1/2}$ relationships.

1.2. Decane Oxidation

The oxidation of decane initiated by cumyl peroxide is described by the following reaction scheme:



The kinetic curves of oxygen consumption in the oxidation of *n*-decane initiated by cumyl peroxide (as distinct from cumene oxidation) in the temperature range 383–403 K exhibit an autoaccelerated character

(Fig. 1b). This can be explained by the fact that *n*-decyl hydroperoxide (ROOH), which is formed under experimental conditions, significantly affects the rate of *n*-decane oxidation. When a considerable amount of

Table 2. w_i , w_{O_2} , and $k_2k_6^{-1/2}$ in the oxidation of *n*-decane initiated by cumyl peroxide

T, K	$[I]_0 \times 10^3, \text{ mol/l}$	$w_i \times 10^8, \text{ mol l}^{-1} \text{ s}^{-1}$	$[RH], \text{ mol/l}$	$w_{O_2} \times 10^6, \text{ mol l}^{-1} \text{ s}^{-1}$	$k_2k_6^{-1/2} \times 10^3, (\text{mol l}^{-1} \text{ s}^{-1})^{1/2}$
383	1.01	1.01	4.37	0.62	1.45
383	2.52	2.51	4.37	0.99	"
393	1.00	3.22	4.29	2.04	2.25
393	2.50	8.05	4.29	2.75	"
393	5.00	16.10	4.29	3.78	"
403	1.01	9.51	4.20	5.21	3.75
403	2.50	23.55	4.20	7.35	"
403	4.94	46.53	4.20	10.88	"

ROOH is accumulated in the system, the rate of initiation can increase by a value of $k'_i[\text{ROOH}]$, where k'_i is the rate constant of ROOH decomposition into radicals via all conceivable reactions (O–O bond cleavage, reactions of ROOH with hydrocarbon C–H bonds, etc.). Then, the expression for the rate of oxidation has the form

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{RH}]\sqrt{w_i + k'_i[\text{ROOH}]}$$

At a point t in time,

$$\Delta P_{O_2}/t = \frac{k_2}{\sqrt{k_6}}[\text{RH}]\sqrt{w_i + b^2t},$$

where $b = 1/2k_2k_6^{-1/2}[\text{RH}]k'_i$. Hence, the rate of oxidation w_{O_2} is determined from the $\Delta P_{O_2}/t - t$ relationship (see Fig. 1b).

It was experimentally found that the rate of *n*-decane oxidation in a chlorobenzene solution is proportional to $w_i^{1/2}$ and $[\text{RH}]$, and it is described by Eq. (1).

In the calculation of $w_{O_2}^{\text{expt}}$ for the case of short chains in *n*-decane oxidation, the correction αw_i for the consumption and release of oxygen at the steps of chain initiation and termination is $1/2w_i$. Table 2 summarizes the values of w_{O_2} and $k_2k_6^{-1/2}$, and the general expression for $k_2k_6^{-1/2}$ has the form

$$\log(k_2k_6^{-1/2}) = (5.45 \pm 0.06) - (60.7 \pm 0.45)/\theta$$

at $n = 4$ and $\rho = 0.9999$.

Thus, with the use of the model reactions of initiated liquid-phase cumene and *n*-decane oxidation, the initi-

ating ability (w_i) of the test compound is found from the relation

$$\sqrt{w_i} = \frac{w_{O_2}^{\text{expt}}}{(k_2/\sqrt{k_6})[\text{RH}]}$$

In the case of long oxidation chains at $v = w_{O_2}^{\text{expt}}/w_i \geq 100$, the resulting values of w_i correspond to the true values. The minimally determined rates of initiation are $10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$.

At high initiator concentrations (or at short oxidation chains), a correction (αw_i) for gas release and consumption at the steps of chain initiation and termination to the experimentally determined rate of oxygen consumption should be made. The values of α and w_i are found, in accordance with Eq. (2), from the $w_{O_2}^{\text{expt}} - [\text{RH}]$ relation (procedure *a*) at different concentrations of the test initiator. The rate constants of initiation in unimolecular (k_i) and induced (k_{ind}) decomposition are calculated from the $w_i/[I]_0 - [I]$ relation.

The values of k_i and α are also found from the $w_{O_2}^{\text{expt}} [I]^{-1/2} - [I]^{1/2}$ plot (procedure *b*). It should be borne in mind that w_i can vary depending on $[\text{RH}]$; in this case, the values of α found by procedures *a* and *b* are not equal. Then, the rate of inhibition should be calculated for each hydrocarbon concentration using Eq. (4) and taking the values of α determined by procedure *b*.

Decane may be replaced with pentadecane [11]. In this case, $\log(k_2k_6^{-1/2}) = (5.91 \pm 0.08) - (62.64 \pm 0.54)/\theta$, where $\theta = 19.14T \times 10^{-3} \text{ kJ/mol}$.

The initiating ability of organic peroxides from different classes was determined with the use of these model oxidation systems [11]. Among these peroxides are the diperoxides ($\text{Me}_3\text{COOCMe}_2$)₂C₆H₄ (a mixture of *meta*

Table 3. Kinetic parameters of thermolysis and *n*-decane oxidation initiation for *tert*-butylperoxy derivatives **I–III**

Peroxide (initiation efficiency <i>e</i>)	<i>T</i> , K	Thermolysis of the first O–O group			
		total decomposition		initiation	
		log <i>A</i> , [s ^{−1}]	<i>E</i> , kJ/mol	log <i>A</i> , [s ^{−1}]	<i>E</i> , kJ/mol
I (0.35–0.44)	378–433	17.20	162.6	17.38	165.10
Ia (0.56)	403–433	17.32	167.20	18.24	174.43
II	393–413	–	–	17.07	166.36
III (0.59)	383–433	16.31	161.47	14.68	148.26
IIIa	403–413	–	–	14.14	150.48

and *para* isomers) (**I**), (Me₃COOCMe₂CH₂–)₂ (**II**), and (Me₃COOCMe₂–C≡)₂ (**III**) and the monoperoxides Me₃COOCMe₂C₆H₄CM₂OH (**Ia**) and Me₃COOCMe₂–C≡C–CM₂OH (**IIa**), which are formed as intermediates in oxidized *n*-decane on the thermal degradation of the above diperoxides. In the case of peroxides **II** and **III**, it was found that induced decomposition of the peroxides should be taken into account, and the measured effects should be extrapolated to zero concentrations (*C*₀) of the order of 10^{−3} mol/l. The overall rate of decomposition of compounds **II** and **III** is described by the equation $w = k_0 C_0 + k_{\text{ind}} C_0^{3/2}$ for induced decomposition, where *k*₀ is the rate constant of unimolecular degradation of the peroxide. Table 3 summarizes the kinetic parameters of the decomposition of the first peroxide group and the radical initiation of oxidation by these peroxides. The initiating ability of this group of peroxides, which was estimated from the values of *k*_i, increases in the order



A study of the initiating ability of peroxyesters in the liquid-phase oxidation reaction [9] demonstrated that both cumene oxidation at 323–363 K and *n*-decane oxidation at 373–403 K initiated by peroxyesters are described by the equation of an unbranched chain process; that is, the decomposition of cumene and *n*-decane hydroperoxides does not take place.

The rate of free radical formation on the decomposition of *tert*-butylperoxy-2-ethyl hexanoate in oxidized *n*-decane was not measured because chain oxidation was not observed even at high concentrations of the peroxide.

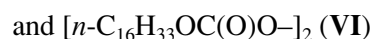
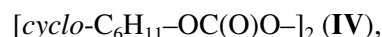
As can be seen in Table 4, induced decomposition of peroxyesters was not observed over the concentration range studied. The nonlinear dependence of the rates of oxidation of the model hydrocarbons on initiator concentration results from a change in the composition of the medium because the values of $k_2 k_6^{-1/2}$ in the oxidation of cumene and *n*-decane are independent of the concentrations of oxidized substrates in chlorobenzene

and dichlorobenzene solutions. This is also supported by data summarized in Table 5, which were obtained from different compositions of oxidized systems.

The initiating ability of diacyl peroxides in the oxidation reaction of cumene and its mixtures with chlorobenzene was evaluated. It was found that the values of *k*_i remained unchanged within the limits of studied solution compositions and peroxide concentrations of (1–5) × 10^{−3} mol/l; that is, unimolecular decomposition took place.

In the measurements of the initiating ability of diacyl peroxides, the correction factors α for gas evolution (Table 6), which were measured from the *w*_{O₂}–[RH] and *w*_{O₂} [I]^{−1/2}–[I]^{1/2} relationships, were in good agreement for all of the studied diacyl peroxides. Table 6 compares the rate constants of decomposition *k*_d, which were obtained from peroxide consumption on decomposition in cumene and from CO₂ evolution in a gasometric unit, and *k*_i estimated by the inhibitor method from the consumption of the stable nitroxyl radical tanol (>NO[•]). The results obtained by different methods are consistent with each other; in particular, this supports the reliability of the oxidation method for the evaluation of initiating ability.

Of the most thermally unstable peroxides, the peroxycarbonates



were studied [10] at concentrations lower than 2 × 10^{−3} mol/l, when their induced decomposition can be ignored.

Experiments on initiated oxidation in the mixtures of cumene with chlorobenzene at different cumene and initiator concentrations demonstrated that the polarity of the medium has no effect on *k*_i. Equal *k*_i were

Table 4. w_i and k_i for peroxyesters in the oxidation of cumene in chlorobenzene

Peroxyester	[RH], mol/l	T, K	[I] ₀ × 10 ³ , mol/l	$w_{O_2} \times 10^6$	$w_i \times 10^8$	$k_i \times 10^6$, s ⁻¹
				mol l ⁻¹ s ⁻¹		
<i>tert</i> -Butylperoxy benzoate	3.27	363	3.6	3.1	0.9	2.4
	3.27		10.7	5.0	2.4	2.2
<i>tert</i> -Butylperoxy acetate	3.27	363	4.7	4.8	2.3	4.8
	3.27		14.2	8.2	7.4	5.2
<i>tert</i> -Butylperoxy chloroacetate	3.32	353	12.2	1.6	1.0	0.8
	3.32		18.2	2.9	1.3	0.7
<i>tert</i> -Butylperoxy propionate	3.27	363	3.9	6.0	3.1	8.0
	3.27		11.6	9.5	7.8	6.7
	3.27		15.6	10.9	10.2	6.6
<i>tert</i> -Butylperoxy butyrate	3.27	363	5.5	6.7	4.7	8.5
	3.27		16.6	10.8	13.8	8.3
<i>tert</i> -Butylperoxy 2-ethylhexanoate	6.65	353	0.5	7.5	2.1	4.0
	6.65		0.8	9.1	3.1	4.1
	6.65		2.6	14.7	8.4	3.3
	6.65		5.1	20.8	17.8	3.5
Hexahydro- α -cumylperoxy propionate*	4.29	393	3.6	7.3	53.0	145.0
	4.29		7.3	10.9	114.0	155.0
	4.29		14.6	15.5	223.0	153.0

* In an *n*-decane solution.**Table 5.** Kinetic parameters of peroxyester initiation reactions in various media

Peroxyester	Medium	k_i , s ⁻¹ (333 K)	E_i , kJ/mol	log A_i , [s ⁻¹]
<i>tert</i> -Butylperoxy benzoate	cumene	1.8×10^{-8}	181.6	20.79
	cumene, chlorobenzene	1.7×10^{-8}	153.0	16.25
<i>tert</i> -Butylperoxy acetate	cumene	1.1×10^{-7}	164.8	18.77
	cumene, chlorobenzene	1.1×10^{-7}	131.6	13.67
	<i>n</i> -decane	5.0×10^{-8}	126.2	12.53
<i>tert</i> -Butylperoxy chloroacetate	cumene	3.6×10^{-8}	170.0	19.26
	cumene, chlorobenzene	3.6×10^{-8}	148.7	15.91
<i>tert</i> -Butylperoxy propionate	cumene	7.5×10^{-8}	153.4	16.97
	cumene, chlorobenzene	7.5×10^{-8}	153.4	16.97
<i>tert</i> -Butylperoxy butyrate	cumene	1.2×10^{-7}	143.5	15.62
	cumene, chlorobenzene	1.2×10^{-7}	144.4	15.67
	<i>n</i> -decane	5.2×10^{-8}	125.9	12.32
<i>tert</i> -Butylperoxy 2-ethylhexanoate	cumene	1.7×10^{-6}	153.0	18.26
	cumene, chlorobenzene	1.6×10^{-6}	136.6	15.66
Hexahydro- α -cumylperoxy propionate	<i>n</i> -decane	1.5×10^{-7}	98.2	9.28
	<i>n</i> -decane, <i>ortho</i> -C ₆ H ₄ Cl ₂	3.1×10^{-6}	81.0	7.26

obtained for compound **IV** in cumene–chlorobenzene and cumene–benzene mixtures.

The kinetic parameters of the rate constants of initiation for the test peroxy carbonates in oxidized cumene are given below (323–353 K).

Peroxy carbonate	$\log A_i, [s^{-1}]$	$E_i, \text{kJ/mol}$
IV	17.57	135.76
V	13.68	110.78
VI	14.98	120.30

phase chain reaction of *n*-decane oxidation (Table 7). The initiating activity of the Si–OOC group is lower than that of the C–OOC group in analogous peroxides primarily because of the higher thermal stability of the organosilicon peroxy group. The replacement of H by SCN in a peroxide somewhat decreases the thermal stability and, simultaneously, the initiating ability.

2. DETERMINATION OF INITIATING ABILITY IN THE RADICAL POLYMERIZATION REACTIONS OF VINYL MONOMERS

The initiating ability of organic and organoelement peroxides was studied [12] by the initiation of the liquid-

The kinetics and mechanism of radical polymerization, which is widely used, have been studied in detail.

Table 6. k_i , α , e , and k_d in the thermolysis of diacyl peroxides

T, K	$k_d \times 10^5, \text{s}^{-1}$		$k_i \times 10^5, \text{s}^{-1}$		α	e	$\log A_d, [\text{s}^{-1}]$	$E_d, \text{kJ/mol}$	$\log A_i, [\text{s}^{-1}]$	$E_i, \text{kJ/mol}$
	*	based on CO_2	based on $> \text{NO}^\bullet$	**						
Lauroyl peroxide										
333	—	—	—	1.1	19.6	—	11.46	102.9	13.96 ± 0.20	120.5 ± 2.0
343	5.9	5.9	3.8	3.8	20.6	0.3				
353	16.3	16.3	10.7	13.0	21.2	0.4				
Enanthoyl peroxide										
323	0.3	0.1	—	0.1	9.2	0.2	15.73 ± 0.20	131.7 ± 2.0	17.41 ± 0.20	143.8 ± 2.0
333	1.4	0.4	—	0.7	15.8	0.3				
343	5.6	1.4	—	2.9	19.5	0.3				
353	20.7	4.6	—	12.7	21.5	0.3				
3,5,5-Trimethylhexanoyl peroxide										
343	—	—	—	4.1	21.9	—	—	—	17.42	143.0
353	—	—	—	17.0	21.7					

* Based on the parent peroxide consumption.

** Based on the initiation of cumene oxidation.

Table 7. Kinetic parameters of the initiation of *n*-decane oxidation by peroxides containing an acetylene group or a silicon atom

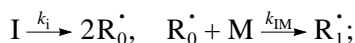
Initiator	$k_i \times 10^5, s^{-1} (413 \text{ K})$	$\log A_i, [s^{-1}]$	$E_i, \text{kJ/mol}$
$(\text{Me}_3\text{COOCMe}_2\text{--C}\equiv)_2$	4.26	14.68	148.3
$(\text{Ph}_3\text{OOCMe}_2\text{--C}\equiv)_2$	1.33	–	–
$\text{Ph}_3\text{SiOOCMe}_2\text{--C}\equiv\text{C--CMe}_2\text{OOCMe}_3$:			
group C–OO–C	2.37	14.64	152.5
group Si–OO–C	0.74	5.97	87.8
$\text{Me}_3\text{COOCMe}_2\text{--C}\equiv\text{CH}$	3.54	17.21	171.2
$\text{Me}_3\text{COOCMe}_2\text{--C}\equiv\text{C--SCN}$	2.06	16.05	163.8

Because of this, there is no question that radical polymerization, along with autoxidation, is a convenient model system for evaluating the initiating ability of peroxides. This is of paramount importance because the polymerization of vinyl monomers is the main consumer of peroxide initiators.

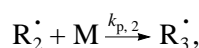
Radical polymerization is a typical unbranched chain process with quadratic termination. The kinetics of reactions of this type is based on the following three main processes [20–22]:

initiation

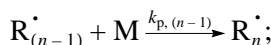
the homolysis of initiator I and reaction with monomer M



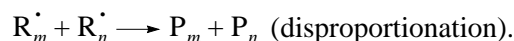
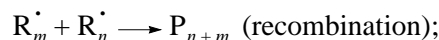
chain propagation



.....

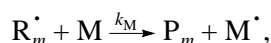


chain termination

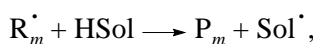


The following side reaction may occur:

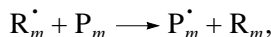
chain transfer through the monomer



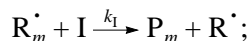
through the solvent HSol



through the polymer



and through the initiator



chain regeneration



chain termination to nonradical products



Based on the quasi-steady-state principle, simplistically assuming that the kinetics and mechanism of elementary steps are independent of the character of products at nondeep steps of polymerization, all elementary constants of chain propagation are equal ($k_{p,i} = k_{p,(i+n)}$), and the induced decomposition of an initiator

does not occur, we obtain the well-known expression for the rate of polymerization

$$w_{\text{pol}} = k_p[M]w_i^{1/2}/k_t^{1/2},$$

where k_p is the rate constant of chain propagation; k_t is the rate constant of overall chain termination; $[M]$ is the monomer concentration; and w_i is the rate of initiation, which is equal to $2ek_T[I]$ (e is the initiation efficiency, k_T is the rate constant of the thermal degradation of the initiator, and $[I]$ is the initiator concentration) on thermal initiation with a substance.

Correspondingly, the activation energy of polymerization is

$$E_{\text{pol}} = E_p - \frac{1}{2}E_t + \frac{1}{2}E_T,$$

where E_p is the activation energy of the chain propagation step.

In accordance with the equation of an unbranched chain reaction, the length of a kinetic chain is equal to the ratio of the rate propagation to the rate of initiation or to the rate of termination, which is equal to the latter under quasi-steady-state conditions.

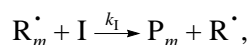
The molecular chain length or the average degree of polymerization (p) at the initial stage of polymerization (of all side processes, only chain transfer through the monomer is taken into account) is described by the equation

$$\frac{1}{p} = \frac{1}{2} \frac{k_t(1 + \lambda)}{k_p^2} \frac{w_{\text{pol}} k_M}{[M]^2 k_p},$$

where k_M is the rate constant of chain transfer through the monomer, w_{pol} is the rate of polymerization, and λ is the contribution of the disproportionation reaction to overall chain termination. With the use of this equation, the value of $k_p/k_t^{1/2}$ is found from the $1/p - w_{\text{pol}}/[M]^2$ plot (from the slope of the straight line), and k_M/k_p is found from the intercept on the axis of ordinates on extrapolation to zero conversion. The rate constants of polymerization chain termination essentially depend on the viscosity of the medium and many other factors. Therefore, in the evaluation of the initiating ability of organic peroxides by the radical polymerization method, the rate of polymerization is measured in systems and conditions precalibrated with the use of reference initiators and inhibitors; data on the average chain length of the polymer products are also used.

An enormous number of studies on the initiating ability of organic peroxides in radical polymerization processes were systematized in [1, 21, 22, etc.]. Only individual series are considered below to illustrate and characterize the behavior of some types of peroxides in polymerization processes. Peroxides are most frequently tested in the initiation of styrene and methyl methacrylate bulk polymerization with the dilatometric evaluation of the rate of polymerization.

According to O'Driscoll and White [23], in the initiation of styrene bulk polymerization with diaryl peroxides, the degradation of which in solution usually occurs with a considerable contribution from induced decomposition, compared with the simplest scheme of initiated polymerization, the following reaction of induced degradation of the peroxide (I), that is, chain transfer through the initiator, should be taken into consideration:



where R_m^\bullet is the polymer radical.

With consideration for this reaction, the rate of peroxide degradation is

$$w = k_T[I] + k_I[R_m^\bullet][I].$$

Replacing $[R_m^\bullet] = (2ek_T[I]/k_I)^{1/2}$, substituting the rate equation of initiator degradation into the main rate equation of polymerization, and integrating this equation result in the expression

$$\left(\frac{w_{\text{pol}}}{[M]}\right)_0 / \left(\frac{w_{\text{pol}}}{[M]}\right)_t = e^{k_T t} + (e^{k_T t} - 1)(k_{\text{ind}}/k_T)[I]_0^{1/2},$$

where $k_{\text{ind}} = k_I(k_T/k_I)^{1/2}$ and t is time.

The values of

$$\left(\frac{w_{\text{pol}}}{[M]}\right)_0 / \left(\frac{w_{\text{pol}}}{[M]}\right)_t$$

are taken from experiments with different $[I]_0$ for fixed points in time and plotted as a function of $[I]_0^{1/2}$. According to the above equation, the resulting straight line makes it possible to calculate k_T and k_I . The initiation efficiency (e) is calculated from the value of $\ln(w_{\text{pol}}/[M])$ extrapolated to $t = 0$.

Table 8 summarized published data [23] for a number of substituted aryl peroxides.

To determine the rate constant k_{IM} of addition of the primary radical products of initiator decomposition at the double bond of a monomer, as well as the true rate constants of other elementary reactions, the following equation proposed by Ivanchev [21] can be used:

$$\frac{1}{w_{\text{pol}}} = \frac{k_t}{k_p k_{\text{IM}} [M]^2} = \frac{k_t^{1/2}}{k_p [M] w_i^{1/2}}.$$

Plotting $1/w_{\text{pol}}$ as a function of $w_i^{-1/2}$, we found the intercept on the axis of ordinates equal to $k_t/(k_p k_{\text{IM}} [M]^2)$ and the slope of this straight line equal to $k_t^{1/2}/(k_p [M])$.

The ratio between these values is equal to $k_{\text{IM}}[M]/k_t^{1/2}$, and it can serve as a measure of the initiating activity of peroxides in a given polymerized system. Table 9 summarizes characteristics of diacyl per-

Table 8. Thermal decomposition rate constants (k_T) and initiation efficiencies (e) of substituted benzoyl peroxides $[X-C_6H_4C(O)O-]_2$ in the bulk polymerization of styrene at 90°C

X	$k_T \times 10^4, \text{s}^{-1}$	e
H	1.33	0.72
<i>para</i> -Cl	0.94	0.77
<i>meta</i> -Br	1.00	0.47
3,4-Cl ₂	1.11	0.36
<i>para</i> -NC	0.97	0.34
<i>para</i> -NO ₂	0.87	0.27

oxides as initiators of the bulk polymerization of styrene [1, 21].

Data in Table 10 illustrate the dependence of the initiating ability and the coefficient of chain transfer to the initiator (π_i) on the structure of the radical in the acid moieties of peroxyesters [24]. It can be seen that the rate constant of initiation increased with the branching at the α -carbon atom; simultaneously, E_i and e decreased. An increase in the chain length in the acid moiety somewhat increased k_i .

Data given in Table 11 characterize the initiation of polymerization by hydroperoxides, peroxides, and peroxycarbonates [1, 21].

The initiation of radical polymerization by di- and polyperoxide compounds and data on their initiating ability and the kinetics of thermolysis were considered in [21, 25]. Puzin *et al.* [26] studied the kinetics of methyl methacrylate polymerization initiated by acetylcyclohexylsulfonyl peroxide. In the temperature range 32–60°C, the rate constant of initiation is determined by the expression $\log k_i [\text{s}^{-1}] = 11.2 - 95.5/19.132 \times 10^{-3}T$. At 32°C, chain transfer to the initiator practically does not occur; however, it noticeably increased with increasing temperature of polymerization: the coefficients of chain transfer to the initiator are equal to 0.034 (40°C) and 0.10 (60°C). High rates of initiation and polymerization even at relatively low temperatures result in a decrease in the molecular weight of the polymer compared with the widely used initiators—cyclohexylperoxydicarbonate, benzoyl peroxide, and lauroyl peroxide.

3. EVALUATION OF RADICAL VULCANIZING ABILITY IN A HYDROCARBON MODEL

The main reactions of radical cross-linking of saturated polymers are the following:

the hydrogen atom abstraction from a hydrocarbon polymer chain (HP)

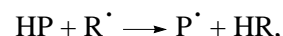


Table 9. Reaction kinetic parameters in the initiation of styrene bulk polymerization; 73.5°C, $k_t = 7.2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$

Initiator	$k_i \times 10^5, \text{ s}^{-1}$	e	$k_{\text{IM}}/k_t^{1/2} \times 10^3, \text{ l}^{1/2} (\text{mol s})^{-1/2}$	k_{IM}	$k_I \times 10^2$
				$\text{l mol}^{-1} \text{ s}^{-1}$	
Butyryl peroxide	7.50	0.60	2.9	0.35	3.1
Lauroyl peroxide	7.80	0.55	1.7	0.20	2.9
Benzoyl peroxide	3.82	0.99	1.2	0.14	0

Table 10. Kinetic parameters of the initiation of styrene bulk polymerization by *tert*-butylperoxyesters RC(O)OOCMe_3 (initial peroxyester concentration of 0.025 mol/l, 85°C)

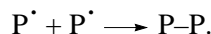
R	Thermolysis in ethylbenzene			$k_i \times 10^5, \text{ s}^{-1}$	$E_i, \text{ kJ/mol}$	π_I	Termination on primary radicals
	$k_i \times 10^5, \text{ s}^{-1}$	$E_T, \text{ kJ/mol}$	e				
Me	0.156	161.5	0.9	0.373	143.9	0.120	Not found
Me_2CH	2.050	123.8	0.7	3.08	125.5	0.200	Partial
Me_3C	58.30	122.2	0.2	28.0	100.4	—	Partial
PhCH_2	13.30	118.0	—	17.0	100.4	—	—
MeCH_2	0.193	164.0	0.9	0.394	151.0	—	—
$\text{Me}(\text{CH}_2)_3$	0.219	165.7	0.9	0.513	154.8	0.016	Not found
$\text{Me}(\text{CH}_2)_6$	0.215	165.7	0.9	0.632	153.1	0.010	Not found

Table 11. Initiation of styrene bulk polymerization by hydroperoxides, peroxides, and peroxy carbonates

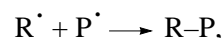
Initiator (I)	$[\text{I}]_0, \text{ mol/l}$	$T, ^\circ\text{C}$	$w_{\text{pol}} \times 10^4, \text{ mol l}^{-1} \text{ s}^{-1}$	$k_i \times 10^6, \text{ s}^{-1}$	$E_i, \text{ kJ/mol}$
$\text{Me}(\text{CH}_2)_3\text{OOH}$	0.012	90	0.83	6.18	106.7
$\text{MeCH}_2\text{CH}(\text{Me})\text{OOH}$	0.012	90	0.86	5.40	113.0
Me_3COOH	0.012	90	0.63	4.10	96.2
EtMe_2COOH	0.012	90	0.83	4.70	106.7
PhMe_2COOH	0.025	85	1.01	1.94	93.3
MePh_2COOH	0.012	85	1.97	7.35	—
$\text{Me}_3\text{COOCMe}_3$	0.010	100	0.55	0.71	166.1
$\text{EtMe}_2\text{COOCMe}_2\text{Et}$	0.010	100	140	4.60	—
$\text{PhMe}_2\text{COOCMe}_2\text{Ph}$	0.010	105	2.47	4.50	39.6
MeOC(O)OOC(O)OMe	0.025	50	1.16	17.40	—
$[\text{cyclo-C}_6\text{H}_{11}\text{—OC(O)O—}]_2$	0.025	50	1.04	14.00	—
PhOC(O)OOC(O)OPh	0.025	50	0.853	9.40	—

where R^\cdot is a radical obtained in the decomposition of the vulcanizing agent;

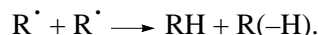
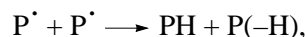
dimerization of radicals form the polymer: the main reaction of cross-link formation



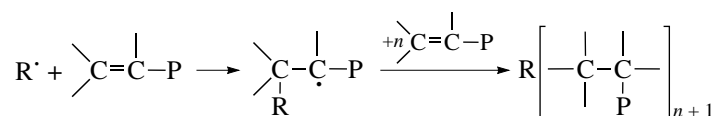
The following reactions can be side processes: recombination of low- and high-molecular radicals



disproportionation reactions with formation of an olefin and an unsaturated product without cross-linking



The cross-linking of an unsaturated polymer also involves the chain processes



The cross-linking with sulfur results in the formation of bonds like $\equiv\text{C}-(\text{S})_n-\text{C}\equiv$, which are not very strong and prone to additional transformations on heating, between polymers, whereas the cross-linking with the use of radical agents results in the formation of a network of carbon-carbon bonds. This network is responsible for good performance properties of the vulcanizate: the hardness and fracture strength are increased, the residual compression strain is decreased, and the electrical properties are improved.

The ratio of the number of cross-links formed in a polymer system to the number of decomposed molecules of a vulcanizing agent is used for the quantitative evaluation of the efficiency of the cross-linking effect of the agent. This ratio depends on both the number of radicals generated from a molecule of the vulcanizing agent and the chemical nature of the initial polymers and additives. Thus, the efficiency of polymer cross-linking under the action of cumyl peroxide (at 150–180°C) is equal to

- 8–12 for butadiene–styrene rubbers,
- 10–12 for *cis*-polybutadiene,
- 1 for natural rubber,
- 1 for polyisoprene (stereoregular),
- 0.3–0.4 for ethylene–propylene copolymers, and
- 0.3 for an ethylene–vinyl acetate copolymer (1 : 1).

Peroxide vulcanization provides an opportunity to incorporate cocuring agents with multiple bonds into the network of a cross-linked polymer; this improves the useful properties of vulcanizates.

The use of peroxides as cross-linking vulcanizing agents requires the development of laboratory procedures for testing their activity. In technical examinations performed in applied-research laboratories, the density of reticulation formed upon the vulcanization of polyethylenes, ethylene–propylene copolymers (EPCs), etc., is

evaluated from the torque after vulcanization of standardized mixtures using a Monsanto rheometer.

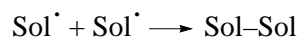
In particular, a mixture of commercial EPC with MnO and ZnO in a weight ratio of 100 : 10 : 5 was used in the comparative tests of peroxides, the results of which are considered below. A peroxide was added to the mixture in the amount that corresponded to a concentration of 0.1 g-equiv O–O groups per kilogram of the mixture. After mixing on roll mills, this mixture was allowed to stand at a given temperature, and the maximum torque (N m) was determined with the Monsanto instrument.

As well as other simplified techniques for evaluating the reticulation of polymers, this procedure significantly depends on the quality and composition of rubbers and extenders and on other conditions. This makes the standardization and comparative assessment of peroxides in terms of vulcanizing activity difficult to perform.

A model system was proposed [27–29] for quantitatively comparing the cross-linking effects of peroxides on saturated carbon-chain polymers. In this system, the thermal decomposition of a peroxide is performed in the medium of an individual low-molecular-weight hydrocarbon—*n*-heptane of isooctane (HSol). The Sol $^\cdot$ radicals result from the reaction of radicals generated from the peroxide with this hydrocarbon,



and the yield of products of the dimerization



is used as a measure of the cross-linking ability of peroxides and other radical initiators. In this case, the side reactions of disproportionation and radical combination of R^\cdot with Sol $^\cdot$ occur. As in the case of polymers, these reactions decrease the formation of Sol–Sol bridges. With the use of *n*-heptane, various heptyl radicals can be formed.

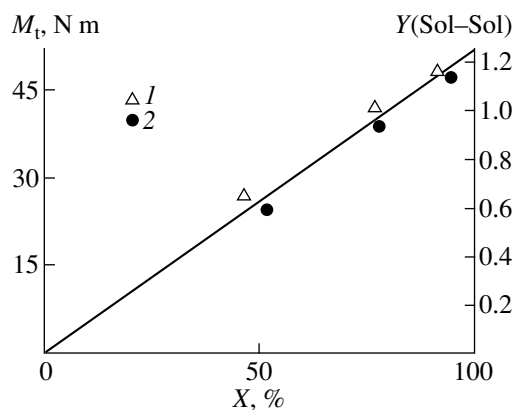


Fig. 3. (1) Torque (M_t) and (2) the yield of *n*-heptane dimers ($Y(\text{Sol-Sol})$) as functions of cumyl peroxide conversion (X) (initial concentration of 0.3 mol/l; 150°C).

The composition of diheptyls formed in this case depends on the relative reactivities of C–H bonds in *n*-heptane. The reactivities of the C–H bonds



toward methyl radicals at 55°C are equal to 0.08 : 1.00 : 1.04 : 1.04 in T (H) abstraction from carbon atoms in the 1-, 2-, 3-, and 4-positions, respectively, as determined with the use of *n*-heptane labeled with radioactive tritium (T) [30, 31].

A number of diheptyls are formed upon the decomposition of peroxides in *n*-heptane. The total yield of diheptyls, which was determined from the total area of this group of chromatographic peaks, is taken as a measure of cross-linking ability. Under comparable conditions, the yield of dimers upon decomposition in isooctane is lower than that in *n*-heptane by a factor of ~3 because the overall reactivity of C–H bonds in isooctane is lower. Therefore, the cross-linking ability of peroxides was mainly performed in an *n*-heptane medium. The procedure for determining the yield of dimers in the evaluation of the cross-linking ability of peroxides in model systems involves the thermal decomposition of the peroxide in an *n*-heptane medium in a thermo-

stated ampule followed by the chromatographic determination of the total yield of diheptyls.

Figure 3 illustrates a symbatic increase in the EPC torque (M_t) determined from curves on the Monsanto rheometer and in the yield of *n*-heptane dimers ($Y(\text{Sol-Sol})$) with the conversion (X) of cumyl peroxide. Figure 3 indicates that, over a certain range of decomposed peroxide concentrations, the torque for a standard mixture and the yield of heptane dimers (calculated in moles of dimers per mole of decomposed peroxide O–O groups) in the model system are linear functions.

As can be seen in Table 12, the yield of dimers decreased with temperature; the reaction of radical combination occurs almost without activation energy.

Simultaneously with an increase in the temperature, the cumyloxy and *tert*-butoxy radicals initially formed from these peroxides decomposed to Me^\cdot and a ketone rather than reacted with *n*-heptane. Although the reactivity of methyl radicals is higher than that of oxy radicals, the overall ratio between the rates of processes resulting in the formation of dimers and other products, in particular, disproportionation products, is responsible for a decrease in the yield of dimers.

The tests of various peroxides in the vulcanization of polymer mixtures and in model systems (Tables 13 and 14) exhibited consistent data on the cross-linking ability of the test peroxides.

A model system for the evaluation of the cross-linking ability of peroxides was used [32] in a study of the effect of the acidity of extenders on the efficiency of rubber vulcanization. The rates of decomposition of cumyl peroxide and di-(*tert*-butylperoxyisopropyl)benzene absorbed from a heptane solution increased under the action of commercial carbon additives. In this case, on the adsorption on neutral and weakly basic commercial carbon, decomposition occurred with the formation of heptane dimers in the same yield as in a hydrocarbon solution, namely, 0.40 mol per mole of decomposed O–O groups of both peroxides. Thermolysis in the presence of commercial acid carbon DG-100 resulted in the formation of dimers in an amount smaller than 0.05 mol per mole of O–O groups. In this case, phenol was the main product of cumyl peroxide decomposition; this fact additionally supported the heterolytic nonradical decomposition of the peroxide.

Table 12. Yields of heptane dimers at different temperatures

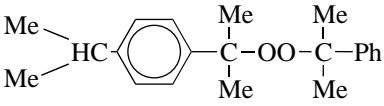
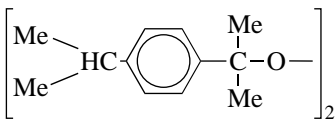
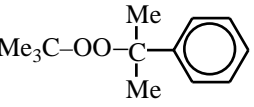
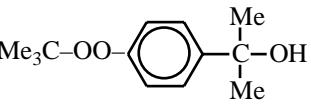
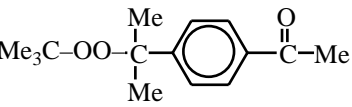
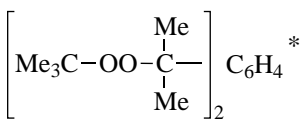
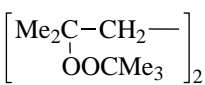
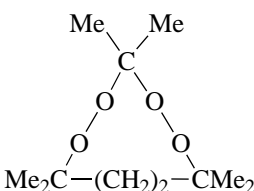
Peroxide	Yield of dimers*		
	150°C	160°C	170°C
Cumyl peroxide	0.50	0.40	0.30
Di(<i>tert</i> -butylperoxyisopropyl)benzene	0.50	0.40	0.30

* In dimer moles per mole of decomposed O–O groups of the peroxide.

4. DETERMINATION OF INITIATING ABILITY WITH THE USE OF INHIBITORS

The inhibitors of radical reactions (compounds that react with free radicals) are used for quantitative measurements of the rate of formation and the total yield of radicals in the decomposition of peroxides. In this case, compounds such as phenols, amines, molecular iodine, and stable radicals are primarily used [33, 34]. Depending on the chemical properties of inhibitors and on the structure of radicals formed upon decomposition, each inhibitor molecule reacts with different number of rad-

Table 13. Efficiency of solvent dimerization and EPC vulcanization

Peroxide	Yield of heptane dimers, ^a mol/mol	M_t , ^b N m	
		160°C	170°C
PhCMe ₂ -OO-CMe ₂ Ph	0.40	4.6	4.7
	0.25	3.8	3.8
	0.20	3.5	3.4
	0.33	4.2	4.2
	0.40	4.7	4.6
	0.38	—	—
	0.40	3.2**	—
	0.20**	2.5**	—
	0.07**	1.0**	—

Notes: The initial concentration of peroxides in *n*-heptane and EPC was 0.1 mol of O—O groups per kilogram of a mixture.

^a The yield of heptane dimers in moles per mole of decomposed O—O groups at 160°C (±10 rel %).

^b M_t is the maximum torque (±10 rel %).

* A mixture of *para* and *ortho* isomers.

** At 150°C.

Table 14. Efficiency of solvent dimerization and EPC vulcanization with di-*tert*-butylperoxy ketals $R[\text{OOC}(\text{CH}_3)_2]_2$

R	Yield of heptane dimers, mol/mol	M_t , N m
	0.27	2.9
	0.15	2.0
	0.18	2.1
	0.27	2.8
	0.15	2.0
	0.20	2.3
	0.15	2.0

Note: The initial peroxide concentration in *n*-heptane and EPC was 0.1 mol of O–O groups per kilogram of a mixture. The yield of heptane dimers in moles per mole of decomposed O–O groups at 140°C; M_t is the maximum torque at 160°C.

Table 15. Rate constant k_{inh} of the reaction of lauroyl peroxide consumption and the stoichiometry of α -naphthylamine consumption (b) in the reactions in nonane [40]

$[A] \times 10^3$, mol/l	k_{inh} , l mol ⁻¹ s ⁻¹	b
3.0	0.26	0.3
3.4	0.17	0.4
5.6	0.21	0.4
5.7	0.21	0.4
8.0	0.26	0.4

Note: Peroxide concentrations are 0.03 M; 80°C; A is α -naphthylamine.

icals (f). Stable radicals, iodine, and quinones are the most effective scavengers of alkyl radicals, whereas phenols and aromatic amines effectively scavenge oxy and peroxy radicals. Stable radicals as scavengers usually react with one radical each, and molecular inhibitors react with two radicals.

In choosing inhibitors, the possibility of direct chemical reactions of peroxides with inhibitors should be taken into account. Thus, diacyl peroxides react with amines to form both molecular and radical products, whereas they undergo heterolytic decomposition under the action of phenols, for example,

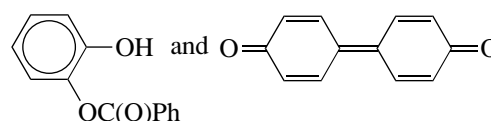
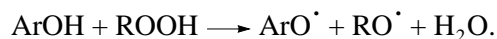


Table 15 summarizes the rate constants of the reaction of lauroyl peroxide with α -naphthylamine (A) and the stoichiometry of amine consumption (b) per mole of the peroxide. The reaction is of first order with respect to the peroxide and the amine. The presence of oxygen had no effect on the reaction rate and stoichiometry; this fact supported the nonradical mechanism of reactions.

Hydroperoxides can react with phenols either via a nonradical path or with the formation of free radicals [35] as follows:



Aromatic amines can be oxidized by hydroperoxides [36–38]. General problems of the kinetics and mechanisms of reactions that involve the inhibitors of radical processes, in particular, their use for the evaluation of initiating ability, were considered by Denisov [33, 34, 39]. The following values are measured with the use of inhibitors:

(a) the total yield of radicals on the complete consumption of a peroxide;

(b) the rate of initiation of radicals into the bulk of solution is found from the rate of inhibitor consumption.

Along with the direct evaluation of initiation efficiency, a polymerized system, as well as an autoxidation system, can be used as an indicator of the consumption of the added inhibitor. Under conditions of a small consumption of the initiator, the rate of initiation is

$$w_i = f[\text{InH}]/\tau_{\text{in}},$$

where $[\text{InH}]$ is the inhibitor concentration, f is the number of radicals scavenged by an inhibitor molecule, and τ_{in} is the induction period.

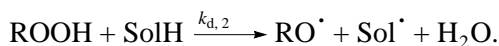
Zyat'kov *et al.* [41] used the stable nitroxyl radical tanol (its consumption was measured by the calibration method from the EPR signal intensity) for evaluating

the yield of radicals in the thermolysis of lauroyl peroxide. They found that the rate of tanol consumption at 333–353 K was independent of concentration over the range $(1-4) \times 10^{-3}$ mol/l; that is, all free radicals were scavenged by tanol; tanol was not consumed in side reactions, and it did not induce decomposition of the peroxide. In this case, the found values of k_i were consistent with those found by the autoxidation method. Thus, choosing an appropriate inhibitor, the initiating ability of peroxides can be quantitatively measured.

As an example, we consider in more detail the thermolysis of *tert*-butyl perbenzoate [42] and cumyl hydroperoxide (CHP) [36] in solution with the use of α -naphthylamine as an inhibitor, for which $f = 2$.

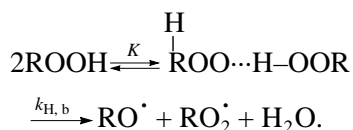
To evaluate the initiating ability of a peroxide, a series of experiments was performed at a given peroxide concentration with increasing initial concentration of the inhibitor. As a result, a number of values of the initial rate of inhibitor consumption ($w_{0, \text{inh}}$) were obtained. In this case, above a certain inhibitor concentration, $w_{0, \text{inh}}$ remained constant (Fig. 4). This constancy is indicative of the absence of a direct reaction of the inhibitor with the peroxyester. Table 16 summarizes the results of the determination of the initiating ability of the peroxyester and the efficiency of decomposition into radicals (e).

The measurement of the rate of radical formation with the use of α -naphthylamine demonstrated that $w_{0, \text{inh}}$ was a linear function of [CHP]. The first order with respect to cumene supports the conclusion that the hydroperoxide undergoes decomposition by the bimolecular reaction



The rate constant of this bimolecular reaction is $k_{d,2} = 5 \times 10^7 \exp(-109/RT)$, where the activation energy is expressed in kJ/mol.

In the thermolysis of cumyl hydroperoxide in chlorobenzene in the absence of compounds with active hydrogen, the decomposition occurs by the bimolecular reaction involving the intermediate formation of an associate:



In accordance with this reaction scheme, over a wide concentration range,

$$w_i = k_{d,1}[\text{ROOH}]_\Sigma + k_{H,b}[\text{ROOH}]_{H,b},$$

where $k_{d,1}$ is the rate constant of unimolecular decomposition of the hydroperoxide, $k_{H,b}$ is the rate constant of decomposition of hydrogen-bonded dimers, $[\text{ROOH}]_\Sigma$ and $[\text{ROOH}]_{H,b}$ are the total peroxide concentration and the concentration of peroxides hydrogen-bonded as dimers. At low total concentrations,

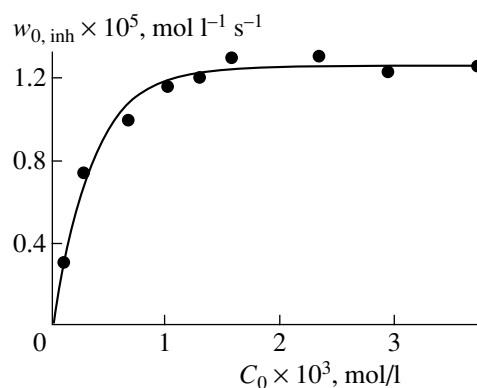


Fig. 4. Initial rate of α -naphthylamine consumption as a function of initial concentration. $T = 110^\circ\text{C}$; solvent, *n*-undecane. The initial concentration of *tert*-butylperoxy benzoate was 0.038 mol/l.

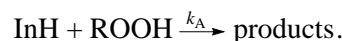
$$[\text{ROOH}]_{H,b} \sim 2K[\text{ROOH}]_\Sigma^2,$$

$$w_i/[\text{ROOH}]_\Sigma \approx k_{d,1} + 2Kk_{H,b}[\text{ROOH}]_\Sigma,$$

and at high concentrations, when $[\text{ROOH}]_{H,b} \approx [\text{ROOH}]_\Sigma$,

$$w_i/[\text{ROOH}]_\Sigma \approx k_{d,1} + k_{H,b} = \text{const.}$$

The proposed scheme was tested by the thermolysis of cumyl hydroperoxide in *n*-heptane. It was found in an *n*-heptane medium that, along with direct thermolysis, cumyl hydroperoxide was simultaneously consumed in the reaction with the amine:



To take into account this side reaction, the measurements were performed with several amine concentrations at a constant $[\text{CHP}]_0$; in this case, the rate of thermal initiation was found by the extrapolation

$$w_i = 2\lim_{[\text{InH}]_0 \rightarrow 0} w_{\text{InH}} \quad (5)$$

As can be seen in Table 17, the $w_i/[\text{ROOH}]_\Sigma$ ratio initially increased with the total cumyl hydroperoxide concentration $[\text{ROOH}]_\Sigma$, reflecting the formation of $\text{ROOH}\cdots\text{ROOH}$ associates, and then remained constant at $[\text{ROOH}]_\Sigma$ higher than 0.7 mol/l, when all cumyl hydroperoxide molecules occurred as dimeric associates.

To study the effect of oxidation products on the thermolysis of hydroperoxides, the amount of radicals formed in the decomposition of cumyl hydroperoxide in the presence of benzoic acid was measured [43]. The radical decomposition of cumyl hydroperoxide linearly increased with benzoic acid concentration. Because at a constant concentration of a carboxylic acid the rate of radical formation is a linear function of $[\text{ROOH}]$, consequently, the formal rate equation for initiation in this system is

$$w_i = k_i[\text{ROOH}][\text{R}'\text{C}(\text{O})\text{OH}].$$

Table 16. Initiating ability of *tert*-butylperoxy benzoate on thermal decomposition in *n*-nonane (α -naphthylamine inhibitor)

$T, ^\circ\text{C}$	$C_0, \text{mol/l}$	$w_{0,d} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	$w_{0,\text{inh}} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	e
130	0.0097	4.03	2.98	0.77
	0.0096	3.98	3.00	0.79
	0.0096	3.98	3.10	0.81
110	0.0380	1.63	1.27	0.81
	0.0380	1.63	1.30	0.83
	0.0380	1.63	1.21	0.77
90	0.1900	0.85	0.67	0.82
	0.1900	0.85	0.67	0.82
	0.1900	0.85	0.62	0.76

Note: C_0 is the peroxyester concentration; $w_{0,d}$ is the initial rate of peroxyester decomposition; and $w_{0,\text{inh}}$ is the initial rate of inhibitor consumption.

Table 17. Thermal decomposition of cumyl hydroperoxide into radicals (α -naphthylamine as an inhibitor (InH); heptane as a solvent)

$[\text{ROOH}]_\Sigma, \text{mol/l}$	$[\text{InH}], \text{mol/l}$	$w_{0,\text{inh}} \times 10^8, \text{mol l}^{-1} \text{s}^{-1}$	$k_A \times 10^4, \text{l mol}^{-1} \text{s}^{-1}$	$w_i \times 10^8, \text{mol l}^{-1} \text{s}^{-1}$	$w_i / [\text{ROOH}]_\Sigma \times 10^8, \text{s}^{-1}$
0.175	0.50	0.085	0.55	0.08	0.46
0.175	1.00	0.135	"	"	"
0.350	0.97	0.690	0.80	0.64	1.80
0.350	2.50	1.100	"	"	"
0.700	2.50	3.700	1.01	3.20	4.60
0.700	5.00	5.500	"	"	"
0.875	2.50	5.700	1.30	4.60	5.20
1.050	1.25	5.000	1.41	5.30	5.00
1.050	2.50	7.000	"	"	"
1.050	5.00	10.700	"	"	"
1.400	2.50	9.100	1.43	6.60	4.70
1.750	1.25	8.200	1.45	8.40	4.80
1.750	2.50	11.600	"	"	"
1.750	5.00	18.000	"	"	"

Table 18 summarizes data on the efficiencies of homolysis of ROOR' peroxides obtained with the use of α -naphthylamine [44]. The efficiency of radical escape (e) depends on temperature only slightly and equals 0.36–0.88, depending on the structure of the peroxide.

Table 19 summarizes analogous data for a number of peroxyesters. As a rule, the efficiency of radical escape in peroxides of the same type increases with decreasing activity of the formed radicals. In peroxyes-

ters, an increase in the stability of the radical formed in the decarboxylation of a carboxy radical is favorable for the simultaneous rupture of two bonds with the formation of CO_2 : $\text{R}\cdots|\text{CO}_2|\cdots\text{OCMe}_3$, which also increases the efficiency of radical escape.

Because substituents can only affect the reactivity of the radical residue of the acid moiety of a peroxyester, the differences observed in the values of e should be completely attributed to differences in the reactivity of

Table 18. Initiating ability of peroxides on thermal decomposition (α -naphthylamine as an inhibitor; *n*-nonane as a solvent)

Peroxide	$T, ^\circ\text{C}$	$C_0, \text{mol/l}$	$w_{0, \text{inh}} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	$w_{0, \text{d}} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	e
Di- <i>tert</i> -butyl peroxide	110	0.1490	0.177	0.392	0.45
	130	0.00943	6.780	8.800	0.39*
1,1-Di- <i>tert</i> -butylperoxycyclohexane	110	0.0277	2.030	2.590	0.37*
	90	0.0554	0.336	0.473	0.36*
<i>tert</i> -Butyl <i>tert</i> -amyl peroxide	130	0.0220	0.537	1.045	0.52
	110	0.0417	0.173	0.337	0.51
<i>tert</i> -Butyl pinyl peroxide	130	0.0161	0.600	0.723	0.83
	110	0.0645	0.420	0.477	0.88
<i>tert</i> -Butyl cumyl peroxide	130	0.0179	0.403	0.650	0.62
	110	0.1100	0.271	0.443	0.61
Dicumyl peroxide	120	0.0296	0.337	0.675	0.50
	110	0.0809	0.332	0.684	0.49
Cumyl 1,1-diphenylethyl peroxide	130	0.0109	0.835	1.330	0.63
	110	0.0219	0.263	0.385	0.68

* Calculated on a ruptured O–O bond basis.

Table 19. Initiating ability of $\text{RC}(\text{O})\text{OOCMe}_3$ peroxyesters on the thermal decomposition in *n*-undecane

R	$T, ^\circ\text{C}$	$C_0, \text{mol/l}$	$w_{0, \text{d}} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	$w_{0, \text{inh}} \times 10^6, \text{mol l}^{-1} \text{s}^{-1}$	e
<i>ortho</i> -Cl-C ₆ H ₄ -	120	0.0098	1.57	1.73	0.95
	110	0.0330	1.84	2.05	0.94
	90	0.0990	0.56	0.62	0.94
<i>meta</i> -Cl-C ₆ H ₄ -	120	0.0084	0.58	0.89	0.68
	110	0.0340	0.79	1.22	0.67
	90	0.1630	0.42	0.63	0.70
<i>para</i> -Cl-C ₆ H ₄ -	120	0.0086	0.50	0.95	0.55
	110	0.3400	0.61	1.12	0.57
	90	0.1700	0.20	0.35	0.60
2,4-Cl ₂ -C ₆ H ₄ -	120	0.0099	1.44	1.50	1.0
	110	0.0280	1.43	1.52	0.98
	90	0.1700	0.86	0.88	1.0
<i>para</i> -NO ₂ -C ₆ H ₄ -	120	0.0140	0.90	0.94	1.0
	110	0.0320	0.71	0.78	0.95
<i>ortho</i> -Me-C ₆ H ₄ -	120	0.0088	1.46	2.22	0.70
	110	0.0350	1.95	3.0	0.73
<i>meta</i> -Me-C ₆ H ₄ -	110	0.0350	1.05	1.76	0.62
<i>para</i> -Me-C ₆ H ₄ -	120	0.0350	0.98	1.68	0.61
	110	0.0160	1.83	3.56	0.54
Me-	110	0.0550	1.82	3.85	0.49
	90	0.2600	0.87	1.76	0.51
	120	0.0098	1.67	2.78	0.63
Me(CH ₂) ₄ -	110	0.0390	1.89	2.98	0.66
	90	0.2000	0.75	1.29	0.61

this radical. The presence of *ortho* substituents, which cause steric hindrances for recombination, increases the efficiency of decomposition into radicals. The *para*-NO₂ substituent, which exhibits a strong negative conjugation effect, decreases electron density at the reaction site (free valence) of the formed radical and, correspondingly, increases *e* to almost unity. The fact that the efficiency of chlorine-substituted peroxy benzoates is lower than that of peroxy benzoate, although the reverse would be expected based on the sign of the inductive effect (*-I* effect), is indicative of the dual nature of Cl, which exhibits a conjugation effect opposite in sign to the inductive effect (*+C* effect). Experimental data indicate that the *+C* conjugation effect is stronger than the *-I* inductive effect, which is opposite in sign, of Cl on the stability of radicals.

Methyl substituents at *meta* and *para* positions somewhat decreased the efficiency of decomposition of aromatic peroxyesters. In the case of the decomposition of aliphatic peroxyesters, the efficiency of radical escape is very low because an aliphatic substituent has no stabilizing effect on the radical formed.

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