1

MECHANISMS OF DECOMPOSITION OF INITIATORS

1.1 INTRODUCTION

A lot of organic molecules, dealing with technique, technological processes, and organic synthesis, are stable at moderate (~300–400 K) and elevated (>400 K) temperatures. Atoms of these compounds are connected by sufficiently strong chemical bonds with bond dissociation energy (BDE) ~350–500 kJ mol^{-1}. Radical initiators are molecules bearing one or several weak bonds with BDE ~100–200 kJ mol^{-1}. When the temperature of the reaction is sufficiently high, the initiator decomposes with homolysis of the weakest bond and produces free radicals. These free radicals initiate a chain or nonchain free radical reaction.

What are the factors that influence the BDE of any chemical bond? First, there are atoms forming the bond. Here are a few examples of the types of bonds in various compounds:[1,2]

Compound	CH_4	Et	$MeNH_2$	MeOH	MeI	MeOOMe
Bond	C−H	C−C	C−N	C−O	C−I	O−O
D (kJ mol^{-1})	440	378	358	388	240	161

The following bonds have sufficiently low values of BDE:

Compound	MeOOMe	MeONO	$HONO_2$	Me_3CNO_2	MeNO	$PrN_2CH_2CH{=}CH_2$
Bond	O−O	O−N	O−N	C−N	C−N	N−C
D (kJ mol^{-1})	157	175	207	245	167	141

Organometallic compounds have weak metal–carbon bonds:[2]

Compound	$SnMe_4$	$SbMe_5$	$HgMe_2$	$PbMe_4$	$BiMe_4$	$TiMe_4$
Bond	Sn–C	Sb–C	Hg–C	Pb–C	Bi–C	Ti–C
D ($kJ\,mol^{-1}$)	294	255	255	239	218	167

Atoms surrounding the atom with the bond being split also influence the BDE. Here are a few examples:[2–4]

Peroxide[3]	MeOOMe	EtOOEt	$(Me_3CO)_2$	$(MeC(O)O)_2$	$(PhC(O)O)_2$
D_{O-O} ($kJ\,mol^{-1}$)	158.1	153.1	166.5	131.2	124.4

Hydrazine[2]	H_2NNH_2	H_2NNHMe	H_2NNMe_2	H_2NNHPh	$Ph_2N{-}NPh_2$
D_{N-N} ($kJ\,mol^{-1}$)	275.3	268.2	246.9	218.8	125.0

Polysulfide[4]	EtSSEt	PhSSPh	EtS-SSH	PhS-SSH	EtSS–SSEt
D_{S-S} ($kJ\,mol^{-1}$)	285.0	223.0	213.0	182.0	142.0

A π-bond in the α-position has a strong influence on the dissociating bond. This influence is clearly seen for several alkylaromatic hydrocarbons:[1,3]

Hydrocarbon	Et–Et	$Et{-}CH_2Ph$	$PhPr_2C{-}CPr_2Ph$	$Ph_2MeC{-}CMePh_2$
D_{C-C} ($kJ\,mol^{-1}$)	364	318	150.6	125.5

This dependence is the result of stabilization of the formed radical due to the interaction of an unpaired electron with π-electrons of the benzene ring.

Different mechanisms of free radicals formation as a result of initiator decomposition are known. Most initiators decompose with dissociation of the weakest bond, for example,

$$R^1O{-}OR^2 \rightarrow R^1O^\bullet + R^2O^\bullet$$

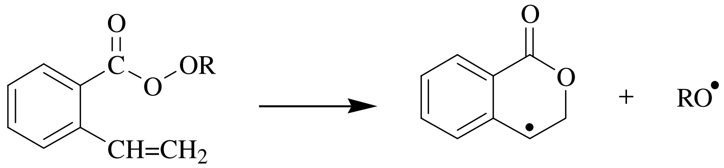
Initiators that decompose with simultaneous dissociation of two or more bonds are known, for example,[5,6]

$$R{-}N{=}N{-}R \rightarrow R^\bullet + N_2 + R^\bullet$$

$$RC(O)O{-}OR^1 \rightarrow R^\bullet + CO_2 + R^1O^\bullet$$

This decay is known as concerted fragmentation (see Section 1.3).

Some ortho-substituted benzoyl peroxides decompose with formation of unstable intermediates. These intermediates are the result of formation of an additional bond between the oxygen atom of the benzoyloxy radical and ortho substituent, for example,[5,6]



This decay was called anchimerically assisted peroxide cleavage (see Section 1.4).

The decomposition of initiators very often proceeds homolytically with dissociation of the molecule to free radicals only. However, there are compounds that decay simultaneously to free radicals and molecular products. For example, peresters decay to free radicals with dissociation on the O−O bond and their isomerization to aryloxyester proceeds in parallel:[6]

$$\mathrm{PhMe_2COOC(O)Ph \rightarrow PhMe_2CO^{\bullet} + PhC(O)O^{\bullet}}$$

$$\mathrm{PhMe_2COOC(O)Ph \rightarrow PhOCMe_2OC(O)Ph}$$

Free radicals formed from the initiator react with the reactant or recombine. Free radicals formed from the initiator or reactant also can react with the initiator.[6] If this reaction proceeds intensely, the initiator is decomposed by free radicals, and this decreases its effectiveness as an initiator (see Section 1.5).

1.2 NONCONCERTED UNIMOLECULAR DECOMPOSITION

Before decomposition, a molecule of the initiator (I) should be activated. Its activation is the result of collisions of the initiator molecule with other molecules M in the gas or liquid phase. The energized molecule may undergo deenergization by collision with a normal molecule, or it may undergo a unimolecular reaction to form products. These three processes are quite distinct and the situation may be represented as:

$$\mathrm{I + M \rightarrow I^* + M}$$

$$\mathrm{I^* + M \rightarrow I + M^*}$$

$$\mathrm{I^* \rightarrow I^{\#} \rightarrow R_1^{\bullet} + R_2^{\bullet}}$$

where I^* is the activated molecule and $I^{\#}$ is the activated complex. The activated molecule I^* passes through the top of the activation barrier. The energized molecule I^* has acquired all the energy it needs to become the activated molecule $I^{\#}$. The full description of the activation process and reaction is given by the Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular reactions.[7−12] This theory describes the dependence of the rate constant for unimolecular decay of molecules on gas pressure. When the pressure is growing, the rate constant of decomposition $k_d \to k_\infty$, and

$$k_\infty = k^\# e^{-E/RT} \quad (1.1)$$

where $k^\#$ is the rate constant of $I^\#$ decay. The expression for initiator decay in solution, where the frequency of molecular collisions is extremely great, is the same. According to transition state theory, the rate constant of unimolecular reactions at high pressure is the following:[11]

$$k_d = k_\infty = e\frac{RT}{Lh}e^{\Delta S^\#/R}e^{-E/RT} \quad (1.2)$$

When a polyatomic molecule, for example, peroxide ROOR, decomposes to two free radicals RO•, the following changes in the energy distribution are observed:[13]

1. One stretching vibration along the O—O bond disappears,
2. One inner rotation of the O—O bond disappears,
3. Two C—O—O angles vibrations disappear.

As a result, the activation entropy of unimolecular decomposition $\Delta S^\# > 0$ and the preexponential factor $[A = eRT(Lh)^{-1}\exp(\Delta S^\#/R)]$ is sufficiently higher than $eRT(Lh)^{-1} \approx 10^{13}$ s^{-1}. For many unimolecular reactions $\Delta S^\# \approx 20\text{–}80$ J mol^{-1} K^{-1}.[13]

Due to the elongation of the dissociating bond (e.g. O—O in peroxide), the volume of the transition state $I^\# > I$. As a result, the difference in the volumes $V(I^\#) - V(I) = \Delta V^\#$ is positive. The study of decomposition of initiators with one bond dissociation under pressure gives evidence that $\Delta V^\#$ is positive and helps us to evaluate $\Delta V^\#$ according to the following dependence of k on pressure p:[3,14]

$$\ln k = \ln k_0 - \frac{\Delta V^\#}{RT}\frac{p}{1+bp} \quad (1.3)$$

where $k_0 = k$ at $p = 0$ and $b = 9.2 \times 10^{-9}$ Pa^{-1}. The value of $\Delta V^\#$ depends on the pressure p:

$$\Delta V^{\neq} = \Delta V_0^{\neq}(1+bp)^{-2} \quad (1.4)$$

1.3 CONCERTED FRAGMENTATION OF INITIATORS

Peroxides have the weak O—O bond and usually decompose with dissociation of this bond. The rate constants of this decomposition of ROOR into RO• radicals demonstrates a low successibility of the BDE of the O—O bond to the structure of the R fragment (see Chapter 4). Bartlett and Hiat[15] studied the decay of many peresters and found that rate constants of their decomposition covered a range $>10^5$ s^{-1}. The following mechanism of decomposition was proposed:[5]

$$RC(O)OOR^1 \rightarrow R^\bullet + CO_2 + R^1O^\bullet$$

parallel with a simple dissociation of one O—O bond. This decay of the molecule to fragments was named concerted fragmentation. The energy needed for the activation of the molecule is concentrated simultaneously on the two bonds: R—C(O) and O—O. Among other products, CO_2 is formed as the result of perester fragmentation. The formation of the π bond of formed carbon dioxide partially compensates for the energy of dissociation of the C—C and O—O bonds of perester. The decay of perester into four fragments is known:[16]

$$Me_3COOCMe_2C(O)OOCMe_3 \rightarrow 2Me_3CO^\bullet + MeCOMe + CO_2$$

The following peculiarities characterize the concerted fragmentation in comparison to the decay of a molecule with dissociation of one bond:[5,6]

Decay with Dissociation of One Bond	**Concerted Fragmentation**
1. Activation energy is equal to the dissociation energy of the weakest bond. ($E \approx D \approx 140{-}160$ kJ mol^{-1} for peresters.)	Activation energy of decay is sufficiently lower than the BDE of the weakest bond. ($E \approx 90{-}125$ kJ mol^{-1}for peresters.)
2. Entropy of activation $\Delta S^{\#} > 0$, $\Delta S^{\neq} \approx 20{-}80$ J mol^{-1} K^{-1} for peroxide decomposition.	Entropy of activation is low; for perester decomposition, $\Delta S^{\neq} \approx -10{-}10$ J mol^{-1} K^{-1}.
3. The dissociation of one bond leads to an increase in the volume of the molecule; $\Delta V^{\#} \approx 10 \pm 3$ cm^3 mol^{-1} (see Table 1.1).	Concerted decomposition occurs through the compact transition state and $\Delta V^{\#}$ is close to zero; $\Delta V^{\neq} \approx -5{-}5$ cm^3 mol^{-1} (see Table 1.1).
4. Rate constant of decay of symmetric RN=NR and nonsymmetric RN=NR^1 molecules are close due to a low difference in BDE of the R—N bonds in these two molecules (see Chapter 4).	The rate constants of decay of RN=NR and RN=NR^1 azo compounds are very different due to their simultaneous dissociation (see Chapter 4).

The model for interacting oscillators was developed to describe the concerted decomposition of a molecule.[33] The decomposing molecule is treated as a collection of oscillators. The reaction of concerted decomposition is described as the transition of the system of oscillators from the thermal vibration with amplitude

TABLE 1.1 Values of $\Delta V^{\#}$ of Unimolecular Nonconcerted and Concerted Decomposition of Initiators (Eq. 1.3)

Initiator	Solvent	T (K)	$\Delta V^{\#}$ ($cm^3\ mol^{-1}$)	Reference
Dissociation of One Bond				
$Me_3COOCMe_3$	Benzene	393	12.6	17
$Me_3COOCMe_3$	Carbon tetrachloride	393	13.3	17
$Me_3COOCMe_3$	Cyclohexane	393	6.7	17
$Me_3COOCMe_3$	Toluene	393	5.4	17
$Me_3COOCMe_3$	Heptane	398	13.4	18
$Me_3COOCMe_3$	Heptane	428	9.8	18
$PhC(O)OOC(O)Ph$	Carbon tetrachloride	333	9.6	19
$PhC(O)OOC(O)Ph$	Carbon tetrachloride	343	8.6	19
$PhC(O)OOC(O)Ph$	Styrene	303	10	20
$PhC(O)OOC(O)Ph$	Allyl acetate	353	4.7	21
$PhC(O)OOC(O)Ph$	Acetophenone	353	4.8	21
$CH_3C(O)OOCMe_3$	Acetophenone	403	5.0	22
$PhC(O)OOCMe_3$	Cumene	352.6	10.2	23
$PhC(O)OOCMe_3$	Chlorobenzene	352.6	12.7	23
$PhC(O)OOCMe_3$	Chlorobenzene	403	8.0	22
(E)-$EtCH{=}CPrC(O)OOCMe_3$	Cumene	373	6.8	24
(Z)-$EtCH{=}CPrC(O)OOCMe_3$	Cumene	373	9.0	24
Ph_3CCHPh_2	Toluene	343	13.1	25
Simultaneous Dissociation of Two Bonds				
$[Me_2CHC(O)O]_2$	Isooctane	323	−5.1	26
$PhCH_2C(O)OOCMe_3$	Cumene	352.6	1.0	27
$PhCH_2C(O)OOCMe_3$	Cumene	243.6	0.4	28
$PhCH_2C(O)OOCMe_3$	Cumene	403	1.7	22
$PhCH_2C(O)OOCMe_3$	Chlorobenzene	352.6	1.5	27
3-$ClC_6H_4CH_2C(O)OOCMe_3$	Cumene	352.6	1.6	28
4-$ClC_6H_4CH_2C(O)OOCMe_3$	Cumene	352.6	1.2	28
4-$MeC_6H_4CH_2C(O)OOCMe_3$	Cumene	352.6	0.2	28
4-$MeOC_6H_4CH_2C(O)OOCMe_3$	Cumene	333	0.2	28
4-$MeOC_6H_4CH_2C(O)OOCMe_3$	Cumene	403	3.1	22
$[MeOC(O)(CH_2)_3C(O)O]_2$	Benzene	343	0.0	29
$[MeOC(O)(CH_2)_3C(O)O]_2$	Toluene	343	0.0	29
$Me_2CHC(O)OOCMe_3$	Different solvents	403	1.6	30
$Me_2CHC(O)OOCMe_3$	Cumene	338	0.3÷1.9	30
$Me_2CHC(O)OOCMe_3$	Cumene	338	1.6÷3.2	30
cyclo-$C_6H_{11}C(O)OOCMe_3$	Cumene	352.6	1.6÷3.9	23
$(CN)Me_2CN{=}NCMe_2(CN)$	Toluene	335.5	3.8	31
$(CN)Me_2CN{=}NCMe_2(CN)$	Toluene	335.3	3.4÷2.5	32
$PhMe_2CN{=}NCMe_2Ph$	Cumene	328	5.0	24
$PhMe_2CN{=}NCMe_2Ph$	Chlorobenzene	328	4.3	24
$[4$-$CH_3C_6H_4CMe_2]_2N_2$	Cumene	328	4.6	24
$Me_3CON{=}NOCMe_3$	Octane	328	4.3	25

d to the vibration with critical amplitude d^*. If n bonds participate in concerted decomposition and the activated energy is equal to E_n the rate constant of concerted decomposition k_n depends on n and E_n according to Eq. (1.5):

$$k_n = A_0 \frac{n}{2n-1}\left(\frac{nRT}{\pi E_n}\right)^{n-1/2} \exp\frac{-E_n}{RT} \tag{1.5}$$

where $A_0 = A$ at $n = 1$. When $n = 2$,

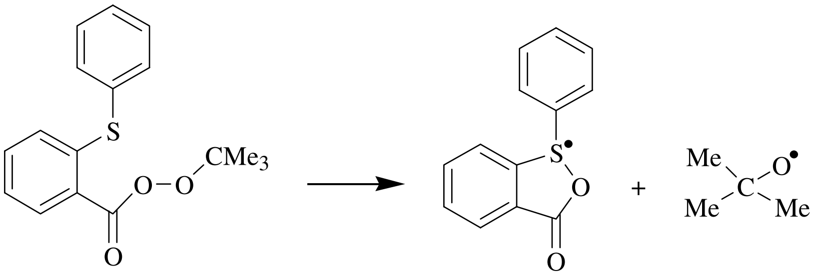
$$k_2 = A_0\sqrt{\frac{2RT}{\pi E_2}} \exp\frac{-E_2}{RT} \tag{1.6}$$

1.4 ANCHIMERICALLY ASSISTED DECOMPOSITION OF PEROXIDES

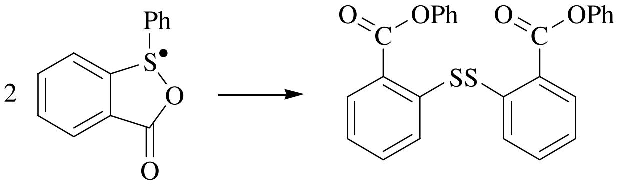
There is experimental evidence that some ortho substituents in 1,1-dimethylethylbenzoyl peresters strongly accelerate the decomposition of peresters.[5] Ortho substituents in 1,1-dimethylethylbenzoyl peresters and values illustrating the ratio of rate constants k_d(ortho substituted)/k_d(H) at 333 K are written below:[5]

o-CH=CHPh$_2$	o-SCH$_3$	o-SPh
67	140.000	250.000

We see a very strong influence of the ortho substituent containing sulfur. The following mechanism was proposed:[5]



Accelerating action of ortho substituents with p- or π-electrons is due to the formation of an intermediate bond of the type O$^\bullet\cdots$S or O$^\bullet\cdots$C=C in the transition state.



Disulfide was found to be the main product (yield 52.5%) of this perester decomposition. This bond formation compensates (partially) for the activation energy for dissociation of the O—O bond in perester. The empirical peculiarities of anchimeric assistance decomposition are the following:

1. Activation energy of this decomposition is lower than the BDE for the O—O bond, and the rate constant is much higher than the typical k_d for compounds of this class.
2. Solvent changes the rate constants of this decomposition dramatically.
3. Products of the recombination of radical pairs in the cage differ from the parent compounds.

1.5 DECAY OF INITIATORS TO FREE RADICALS AND MOLECULAR PRODUCTS

Peroxides split easily into free radicals because they have a weak O—O bond. In addition to homolytic reactions, peroxides can participate in heterolytic reactions as well, for example, they can undergo hydrolysis under the catalytic action of acids. Both reactions, homolytic and heterolytic, can occur simultaneously. For example, perbenzoates decompose to free radicals and simultaneously isomerize to esters.[34] The kinetic characteristics of both reactions are given in Table 1.1. It is seen that the para substituent slightly influences the rate constants of the homolytic splitting of the perester. The rate constant of heterolytic isomerization, by contrast, strongly depends on the nature of the para substituent. Polar solvent accelerates the heterolytic isomerization. Reaction of isomerization was proposed to proceed through the cyclic transition state.[35]

Parallel reactions of homolytic splitting and heterolytic isomerization was evidence for triphenylcumylperoxylsilane (anisole, $T = 433–463$ K):[34]

$$Ph_3SiOOCMe_2Ph \rightarrow Ph_3SiO^\bullet + PhMe_2CO^\bullet \qquad (k_d)$$

$$Ph_3SiOOCMe_2Ph \rightarrow PhOSiPh_2OCMe_2Ph \qquad (k_{is})$$

The rate constants k_d and k_{is} were estimated and found to be the $\log[k_d(s^{-1})] = 15.5 - 167/RT$ and $\log[k_{is}(s^{-1})] = 8.2 - 104/RT$, $\Delta S^\#_d = 39.7$ J mol^{-1} K^{-1} and $\Delta S^\#_{is} = -39.7$ J mol^{-1} K^{-1}. It is seen that $E_d > E_{is}$, however, $\Delta S^\#_d > 0$

and $\Delta S^{\#}_{\mathrm{is}} < 0$. The cyclic transition state was assumed for the isomerization reaction.[34] Isomerization of this kind was not observed in the case of aliphatic silane peroxides. Polyarylperoxysilanes take part in isomerization of this type:[35]

$$\mathrm{Ph_2Si(OOCMe_3)_2 \rightarrow Ph(PhO)Si(OOCMe_3)(OCMe_3)}$$

Alkylperoxyphosphates undergo heterolytic isomerization simultaneously with homolytic splitting:[36]

$$\mathrm{Me_3COOP(O)Et_2 \rightarrow MeOMe_2COP(O)Et_2} \qquad (k_{\mathrm{is}})$$

$$\mathrm{Me_3COOP(O)Et_2 \rightarrow Me_3CO^{\bullet} + Et_2P(O)O^{\bullet}} \qquad (k_{\mathrm{d}})$$

The rate constants of these reactions were found to be very close: $k_{\mathrm{d}} = 2.0 \times 10^{-5}\ \mathrm{s^{-1}}$ and $k_{\mathrm{is}} = 2.2 \times 10^{-5}\ \mathrm{s^{-1}}$ (n-nonane, 403 K). Competition between homolytic and heterolytic reactions influences the effectiveness of initiation. When the heterolytic isomerization of initiator occurs, its effectiveness on initiation is $e = k_{\mathrm{i}}\ (2k_{\mathrm{d}} + 2k_{\mathrm{is}})^{-1}$. It can be increased by changing the solvent and temperature.

TABLE 1.2 Kinetic Parameters of Heterolytic Isomerization and Homolytic Decomposition of Peresters[a]

Para Substituent	Conditions	$k \times 10^4$ ($\mathrm{s^{-1}}$)	E ($\mathrm{kJ\,mol^{-1}}$)	$\log(A)$ ($\mathrm{s^{-1}}$)
		$p\text{-}\mathrm{XC_6H_4Me_2COOC(O)Ph \rightarrow}$ $p\text{-}\mathrm{XC_6H_4OCMe_2OC(O)Ph}$ (373 K)		
H	313–393 K	5.8	115	12.94
Cl		1.92	121	13.28
Br	Chlorobenzene	2.68	119	13.19
$\mathrm{NO_2}$		0.0945	129	14.09
		$p\text{-}\mathrm{XC_6H_4C(O)OOCMe_2Ph \rightarrow}$ $p\text{-}\mathrm{XC_6H_4C(O)OC(OPh)Me_2}$ (298 K)		
$\mathrm{NO_2}$	283–323 K	282	84	13.15
Br		70	87	14.05
H	Methanol	26	90	14.14
$\mathrm{CH_3}$		19	83	12.80
		$p\text{-}\mathrm{XC_6H_4C(O)OOCMe_3 \rightarrow}$ $p\text{-}\mathrm{XC_6H_4C(O)O^{\bullet} + Me_3CO^{\bullet}}$ (383 K)		
H	373–403 K	0.28	156	16.85
$\mathrm{CH_3}$		0.32	151	16.11
Cl	Phenoxybenzene	0.16	164	17.66
$\mathrm{NO_2}$		0.16	172	18.22

[a] See Refs. 34 and 35.

1.6 CHAIN DECOMPOSITION OF INITIATORS

Initiators are introduced into the reactant, as a rule, in very small amounts. Initiators produce free radicals and most react with reactant or solvent, or recombine with other free radicals. Radicals formed from the initiator or reactant react only negligibly with the initiator. However, we know systems (initiator-reactant) where free radicals induce the chain decomposition of initiators.[6,37,38] Bartlett and Nozaki were the first to recognize the induced decomposition of benzoyl peroxide in different solvents.[39,40] They found that the empirical rate constant of benzoyl peroxide decomposition increases with an increase in the peroxide concentration in a solution. The dependence of the rate of peroxide decomposition on its concentration was found to be

$$v = k_d[\mathrm{PhC(O)OOC(O)Ph}] + k_{ind}[\mathrm{PhC(O)OOC(O)Ph}]^{3/2} \tag{1.7}$$

This dependence is the result of common proceeding of homolytic decay of peroxide with the rate constant k_d and chain decomposition of peroxide due to reactions with the radical formed from the solvent RH according to the following kinetic scheme:

$$\begin{aligned}
\mathrm{PhC(O)OOC(O)Ph} &\rightarrow [\mathrm{PhCO_2^{\bullet} + PhCO_2^{\bullet}}] \rightarrow 2\mathrm{PhCO_2^{\bullet}} && (k_i)\\
[\mathrm{PhCO_2^{\bullet} + PhCO_2^{\bullet}}] &\rightarrow [\mathrm{PhCO_2^{\bullet} + Ph^{\bullet}}] + \mathrm{CO_2} &&\\
[\mathrm{PhCO_2^{\bullet} + Ph^{\bullet}}] &\rightarrow \mathrm{PhCO_2^{\bullet} + Ph^{\bullet}} &&\\
[\mathrm{PhCO_2^{\bullet} + Ph^{\bullet}}] &\rightarrow \mathrm{PhC(O)OPh} &&\\
\mathrm{PhCO_2^{\bullet} + RH} &\rightarrow \mathrm{PhCOOH + R^{\bullet}} &&\\
\mathrm{Ph^{\bullet} + RH} &\rightarrow \mathrm{PhH + R^{\bullet}} &&\\
\mathrm{R^{\bullet} + PhC(O)OOC(O)Ph} &\rightarrow \mathrm{PhC(O)OR + PhCO_2^{\bullet}} && (k_p)\\
\mathrm{R^{\bullet} + R^{\bullet}} &\rightarrow \mathrm{RR \text{ or } RH + R'H} && (2k_t)
\end{aligned}$$

Empirical $k_{ind} = k_i^{1/2}k_p(2k_t)^{-1/2}$ and $k_i = 2ek_d$. The chain length depends on the ratio $k_p(2k_t)^{-1/2}$: the faster the reaction of the radical $\mathrm{R^{\bullet}}$ with peroxide, the longer the chain length. Intensive chain decay of peroxide was observed at a sufficiently high peroxide concentration. For example, $k_d = 6.36 \times 10^{-5}$ s^{-1} and $k_{ind} = 3.35 \times 10^{-4}$ (L/mol)$^{1/2}$ s^{-1} for dibenzoyl peroxide decomposition in cyclohexane at 353 K;[39,40] and $k_d[\mathrm{I}] = k_{ind}[\mathrm{I}]^{3/2}$ at $[\mathrm{PhC(O)OOC(O)Ph}] = 3.6 \times 10^{-2}$ s^{-1}. When peroxide is used as an initiator of the free radical polymerization reaction of the macroradical with peroxide, the molecular weight of the forming polymer is lower.[41] For the rate constants of these reactions, see Chapter 18.

The very intensive chain decomposition of benzoyl peroxide was found in alcoholic solutions.[39,42,43] This is the result of the very high reductive activity of ketyl radicals formed from alcohol. They cause the chain decomposition of peroxide by the following mechanism:

$$\mathrm{PhC(O)OOC(O)Ph} \rightarrow 2e\mathrm{PhCO_2}^{\bullet} \qquad (k_d)$$

$$\mathrm{PhCO_2}^{\bullet} + \mathrm{R^1R^2CHOH} \rightarrow \mathrm{PhCOOH} + \mathrm{R_1R_2C^{\bullet}OH}$$

$$\mathrm{R^1R^2C^{\bullet}OH} + \mathrm{PhC(O)OOC(O)Ph} \rightarrow \mathrm{R^1R^2C(O)} + \mathrm{PhCOOH} + \mathrm{PhCO_2}^{\bullet} \quad (k_p)$$

$$2\mathrm{R^1R^2C^{\bullet}OH} \rightarrow \mathrm{R^1R^2C(O)} + \mathrm{R^1R^2CHOH} \qquad (2k_t)$$

The kinetics of peroxide decomposition are described by Eq. (1.7). However, the values of $k_{\mathrm{ind}} = k_p k_i^{1/2}\ (2k_t)^{-1/2}$ are sufficiently higher. For the rate constants k_p and $2k_t$, see Chapters 18 and 20.

An exotic chain mechanism was found for the 1,1-dimethylethyl hydroperoxide chain decomposition. This hydroperoxide decomposes at elevated temperatures (370 K and higher). Introduction of initiator (I) into the solution with this hydroperoxide induces its decay with the rate $\nu = \mathrm{const} \times [\mathrm{I}]$. The initiators used were found to decompose more rapidly with the hydroperoxide. The following chain mechanism was proved:[44–46]

$$\mathrm{I} \rightarrow \mathrm{r}^{\bullet} \qquad (k_i)$$

$$\mathrm{r}^{\bullet} + \mathrm{ROOH} \rightarrow \mathrm{rH} + \mathrm{RO_2}^{\bullet}$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RO_2}^{\bullet} \rightarrow 2\mathrm{RO}^{\bullet} + \mathrm{O_2} \qquad (k_p)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RO_2}^{\bullet} \rightarrow \mathrm{ROOR} + \mathrm{O_2} \qquad (k_t)$$

The peculiarity of this mechanism is the unusual reaction of chain propagation, namely, $2\mathrm{RO_2}^{\bullet} \rightarrow 2\mathrm{RO}^{\bullet} + \mathrm{O_2}$. As a result, the rate of chain propagation is independent of the reactant (ROOH) concentration. The ratio $k_p/k_t = 4.1 \times 10^4 \exp(-22/RT)$ for 1,1-dimethylethylperoxyl in a benzene solution.[47]

Secondary hydroperoxides are easily attacked at the α-C−H bond. As a result, peroxide $\mathrm{R^1OOH}$ can react by its O−O bond with the alkyl radical formed from the solvent RH:

$$\mathrm{R^1OOH} + \mathrm{R}^{\bullet} \rightarrow \mathrm{R^1O}^{\bullet} + \mathrm{ROH} \qquad (k_{p1})$$

and its α-C−H bond:

$$\mathrm{R^1R^2CHOOH} + \mathrm{R}^{\bullet} \rightarrow \mathrm{RH} + \mathrm{R^1R^2C(O)} + \mathrm{HO}^{\bullet} \qquad (k_{p2})$$

The kinetics of hydroperoxide decomposition obeys Eq. (1.8):[6]

$$\ln\frac{[\mathrm{ROOH}]_0}{[\mathrm{ROOH}]} + \ln\frac{[\mathrm{ROOH}]^{1/2} + k_d/(k_{p1}+k_{p2})}{[\mathrm{ROOH}]_0^{1/2} + k_d/(k_{p1}+k_{p2})} = k_d t \qquad (1.8)$$

For the values of rate constants, see Chapters 4 and 18.

Chain decomposition of secondary hydroperoxides proceeds in an oxidized reactant ($R^1R^2CH_2$) in the reaction with peroxyl radicals:[6]

$$R^1R^2CHOOH + RO_2^{\bullet} \rightarrow ROOH + HO^{\bullet} + R^1R^2C(O) \qquad (k_{p2})$$

This reaction plays an important role in the liquid-phase oxidation of hydrocarbons.[48]

REFERENCES

1. W. Tsang, in *Energetics of Free Radicals*, A. Greenberg and J. Liebman (Eds.), Blackie Academic and Professional, New York, 1996, p. 22.
2. *Handbook of Chemistry and Physics*, D. R. Lide (Ed.), CRC Press, Boca Raton, FL, 1991–1992.
3. E. T. Denisov, *Liquid-Phase Reaction Rate Constants*, IFI/Plenum, New York, 1974.
4. C. Chatgilialoglu and M. Guerra, in *The Chemistry of Sulfur-Containing Functional Groups*, S. Patia and Z. Rappoport (Eds.), Wiley, Chichester (1993).
5. T. Koenig, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 113.
6. E. T. Denisov, *Mechanisms of homolytics decomposition of molecules in the liquid phase, in Itogi Nauki i Tekhniki, Ser. Kinetika i Kataliz* (Russian), VINITI, Moscow, 1981.
7. P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions*, John Wiley & Sons, Inc., London, 1972.
8. W. Forst, *Theory of Unimolecular Reactions*, Academic, New York, 1973.
9. V. N. Kondratiev and E. E. Nikitin, *Gas-Phase Reactions*, Springer-Valley, Berlin, 1981.
10. H. O. Pritchard, *The Quantum Theory of Unimolecular Reactions*, Cambridge University Press, 1984.
11. K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987.
12. R. P. Wayne, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1969, Vol. 2, p. 189.
13. S. Benson, *Thermochemical Kinetics*, John Wiley & Sons, Inc., New York, 1968.
14. M. G. Gonikberg, *Chemical Equilibrium and Reaction Rate under High Pressures* (Russian), Khimiya, Moscow, 1969.
15. P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.* **80**, 1398 (1958).
16. W. H. Richardson and W. C. Koskinen, *J. Org. Chem.* **41**, 3182 (1976).
17. C. Walling and G. Metzger. *J. Am. Chem. Soc.* **81**, 5365 (1959).
18. A. S. Okunevich, S. A. Samoilov, and V. N. Monastyrskiy, *Zh. Fiz. Khim.* **43**, 2265 (1969).
19. A. E. Nicholson and R. G. W. Norrish. *Discuss Faraday Soc.* **22**, 97 (1956).
20. A. E. Nicholson and R. G. W. Norrish. *Discuss Faraday Soc.* **22**, 104 (1956).
21. C. Walling and J. Pellon, *J. Am. Chem. Soc.* **79**, 4782, 4786 (1957).
22. J. Owens and T. Koenig, *J. Org. Chem.* **39**, 3153 (1974).

23. R. C. Neuman and J. V. Behar. *J. Am. Chem. Soc.* **91**, 6024 (1969).
24. R. C. Neuman and G. D. Holmes. *J. Am. Chem. Soc.* **93**, 4242 (1971).
25. R. C. Neuman and R. J. Bussey. *J. Am. Chem. Soc.* **92**, 2440 (1970).
26. R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *J. Am. Chem. Soc.* **87**, 3928 (1965).
27. R. C. Neuman and J. V. Behar, *J. Am. Chem. Soc.* **89**, 4549 (1967).
28. R. C. Neuman and J. V. Behar, *J. Org. Chem.* **36**, 654 (1971).
29. V. M. Zhulin, E. K. Starostin, S. I. Moryasheva, and G. I. Nikishin, *Izv. AN SSSR, Ser. Khim.* 1237 (1979).
30. R. C. Neuman and R. P. Pankratz, *J. Am. Chem. Soc.* **95**, 8372 (1973).
31. A. H. Ewald and R. G. W. Norrish, *Discuss Faraday Soc.* **22**, 138 (1956).
32. M. Ya. Botnikov, V. M. Zhulin, L. G. Bubnova, and G. A. Stashina, *Izv. AN SSSR, Ser. Khim.* 229 (1977).
33. I. V. Aleksandrov, *Teor. Experim. Khimiya*, **12**, 299 (1976).
34. V. A. Yablokov, *Isomerisation of Organic and Elementorganic Peroxides of IV Group Elements*, Doctor Diss. Thesis (Russian), Leningrad Technological Institute, Leningrad, 1976.
35. Yu. A. Aleksandrov, *Liquid-Phase Autooxidation of Elementorganic Compounds* (Russian), Nauka, Moscow, 1978.
36. V. P. Maslennikov, *Organic Peroxides of Elements of II-V Groups of Periodic System*, Doctor Diss. Thesis (Russian), Moscow State University, Moscow, 1976.
37. K. U. Ingold and B. P. Roberts, *Free-Radical Substitution Reaction*, Wiley-Interscience, New York, 1971.
38. M. L. Poutsma, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 113.
39. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 1686 (1946).
40. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 2377 (1946).
41. G. C. Eastmond, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976 Vol. 14A, p. 1.
42. P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.* **69**, 2299 (1947).
43. P. D. Bartlett and W. E. Vaughan, *J. Phys. Chem.* **51**, 942 (1947).
44. J. A. Howard, *Adv. Free Radical Chem.* **4**, 49 (1972).
45. T. Mill and D. G. Hendry, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 1.
46. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **47**, 3797 (1969).
47. J. R. Thomas, *J. Am. Chem. Soc.* **87**, 3935 (1965).
48. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.