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Thermolysis of organic peroxides in solution

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Contents

I.	Introduction	939
II.	Alkyl and aralkyl peroxides	940
III.	Hydroperoxides	941
IV.	Dioxiranes	943
V.	1,2-Dioxetanes	947
VI.	Trioxides	948
VII.	Hydrotrioxides	950
VIII.	Acyl peroxides	951
IX.	Sulfonyl peroxides	957
X.	Peroxide derivatives of carbonyl compounds	958
XI.	Conclusion	961

Abstract. The results of investigations on the kinetics and mechanisms of thermolysis of the main classes of organic peroxides in solution are generalised. The relationship between the kinetics and mechanism of thermolysis and the peroxide structure is analysed. The main attention is given to the decomposition reactions of peroxides that are not confined to mere homolysis of the O—O bond and the factors responsible for the abnormalities in the thermolysis mechanism. The thermolysis mechanisms of trioxides, dioxiranes and peroxides are considered in detail. The bibliography includes 210 references.

I. Introduction

Organic peroxides are the main sources of free radicals in chemical practice. They are widely used for initiating radical (including chain) processes and crosslinking of polymers.[1,2]

The low thermal stability of peroxides due to the presence of a weak O—O bond and the strong dependence of the decomposition time on their structures allow their wide use as initiators in a broad range of temperatures, from ~ 40 to ~ 200 °C. Redox systems of the type 'hydroperoxide – metal ion' and 'diacyl peroxide – amine' enable initiation even at 0 °C.

The present review is the first attempt to generalise the published data on the thermolysis of virtually all classes of organic peroxides in solution. Some previous publications were intentionally included in the review in order to present the problem in a complete and comprehensive way.

Thermal decomposition of peroxides in solution follows both homolytic (with cleavage of one or two bonds simultaneously) and non-radical routes. The kinetics and mechanism of thermolysis depend on the structures of peroxides and the modes of their interactions with the solvent. The latter is especially important for hydroperoxides, which easily form hydrogen bonds.

The kinetics and mechanisms of reactions occurring in solutions were discussed in several monographs and reviews.[1–3] Special attention was given to motion and collisions of the reacting species in liquid media and effects of their direct interactions with solvent molecules. As a result of such interactions, the original species and the transition states become surrounded by a structurised shell consisting of solvent molecules, which changes their electronic structures and, as a consequence, their reactivities.

There are few papers devoted to the analysis of a relationship between the structure of peroxides and the mechanism of their thermolysis in the gas phase (see Ref. 4 and references cited therein), whereas thermolysis in solution has been studied for virtually all synthesised organic peroxides. This circumstance permits one to compare structural features of these compounds and to establish differences between them.

It is noteworthy that the mechanism of homolysis is not always sensitive to specific characteristics of the medium, since this process is not accompanied by any significant redistribution of charges in the molecules of the starting peroxides. However, if there is a competition between ordinary homolysis and other thermolysis routes, including non-radical rearrangements and, especially, heterolytic transformations, changes in solvent properties may have a crucial effect on the mechanism of the thermolysis.

Intermolecular contacts and reactions occurring in the solvent cage affect essentially the kinetics, mechanism and, as a consequence, composition of reaction products.[1,2] Thermal decomposition of organic peroxides has previously been considered in several monographs.[5–10] The effect of pressure on the kinetics and mechanisms of thermolysis (including $\Delta V^{\neq}$) depends on the mode of the interaction of the reactants with the solvent, the viscosity of the solvent and the processes occurring in the solvent cage.[11]

The idea of N N Semenov on the competition between bimolecular homolytic reactions and monomolecular reactions simultaneously generating a highly stable product was confirmed by the calculations of Denisov[12,13] based on the use of a semiempirical parabolic model. Such a decomposition route also takes place in the thermolysis of peroxides.

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In the limiting step, thermolysis of peroxides usually involves initial cleavage of the weakest O—O bond. However, depending on the structures of the reactants and the reaction conditions, there may be some deviations from the 'simple' mechanism. The main attention in this review is given to the abnormalities of the mechanisms of thermal decomposition of peroxides, particularly of non-trivial mechanisms with complex rearrangement of the bonds.

II. Alkyl and aralkyl peroxides

As a rule, the passage from gas-phase decomposition to thermolysis in solution does not result in any changes in the reaction mechanism. Thus rate constants for high-pressure decomposition of di-*tert*-butyl peroxide in cyclopropane[14] in vapour (124–160 °C) and in the liquid phase (100–124 °C) represent a common straight line with a preexponential parameter $\log A = 15.52 \pm 0.23$ (s^{-1}) and $E = 156.9 \pm 0.4$ kJ mol^{-1} in the $\log k_1 - 1/T$ coordinates. The values around the critical point of cyclopropane phase transition also fall on this straight line.

The decomposition kinetics of a series of alkyl and aralkyl peroxides in the gas phase and in hydrocarbon solvents were compared.[15] The correlation dependence for these compounds [$\log A = 1.883E - 1.0$ (A in s^{-1}, E in kJ mol^{-1})] was shown to correspond to the isokinetic temperature of 483 K. The activation energies for the decomposition of the symmetrical peroxides ROOR increase in the following order: Et < $PhMe_2C$ < Me ≈ Pr^n < Bu^t ≈ $EtMe_2C$.

The main decomposition route for the peroxides R^1OOR^2 includes homolysis of the O—O bond:

$$R^1OOR^2 \longrightarrow R^1O^{\bullet} + R^2O^{\bullet}.$$

The oxy radicals thus formed undergo either further recombination in the solvent cage with subsequent regeneration of the original peroxide, or reaction with the surrounding solvent molecules (HSol):

$$R^1O^{\bullet} + HSol \longrightarrow R^1OH + Sol^{\bullet},$$

or monomolecular decomposition to form a ketone and a radical of lower molecular mass (β-decomposition):

$$R^1O^{\bullet} \longrightarrow \diagdown C{=}O + (R^3)^{\bullet}.$$

The radicals thus generated are eventually replaced by the radicals derived from the solvent

$$(R^3)^{\bullet} + HSol \longrightarrow Sol^{\bullet} + R^3H,$$

which are then recombined into dimers

$$2\,Sol^{\bullet} \longrightarrow Sol-Sol,$$

or undergo disproportionation to give an alkene and a stable saturated molecule.

As a rule, electronic effects of substituents only slightly affect the rate of thermal decomposition of alkyl peroxides. Thus the coefficient ρ^* in the Taft equation for the electron-withdrawing groups of tertiary peroxides is −0.13 (150 °C, chlorobenzene),[16] whereas that for *tert*-butyl peroxybenzoates is 0.38 (120 °C, CCl_4).[17] A very strong effect of electron-donor groups ($\rho^* = -11.0$) and a small effect of electron-withdrawing groups ($\rho^* = -0.13$) were observed in the decomposition of dialkyl peroxides.[18,19] However, such a discrepancy in the ρ^* values can be attributed to the fact that steric effects have not been taken into consideration.[20]

The thermolysis of allyl *tert*-butyl peroxide in toluene,[21] in addition to ordinary homolysis of the O—O bond, is accompanied by two types of induced decomposition:

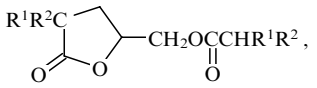
(1) abstraction of H$^{\bullet}$

$$Bu^tO^{\bullet} + CH_2{=}CH-CH_2OOBu^t \longrightarrow$$
$$\longrightarrow Bu^tOH + CH_2{=}CH-C^{\bullet}HOOBu^t,$$
$$CH_2{=}CH-C^{\bullet}HOOBu^t \longrightarrow Bu^tO^{\bullet} + CH_2{=}CHCHO,$$

(2) addition

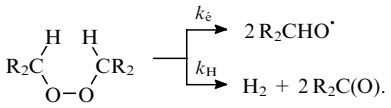
$$PhCH_2^{\bullet} + CH_2{=}CH-CH_2OOBu^t \longrightarrow$$
$$\longrightarrow Bu^tO^{\bullet} + PhCH_2CH_2\underset{\diagdown\,O\,\diagup}{CH}-CH_2.$$

The presence of an allyl group in a peroxide offers diverse possibilities for their synthetic use in the thermolysis in solution. Thus the thermolysis of allyl *tert*-butyl peroxide in the presence of carboxylic acids ($R^1R^2CHCOOH$) gives rise to lactones (yield 20%–50%)



which represent recyclisation products of the expected epoxy acids.[22]

The presence of α-C—H bonds in peroxides brings about a competition between homolysis of the O—O bond and concerted cyclic formation of molecular hydrogen:



These reactions were studied in detail;[21,23,24] the yields of H_2 for different peroxides are listed in Table 1.

Table 1. The formation of H_2 in the thermolysis of the peroxides ROOR in solution.

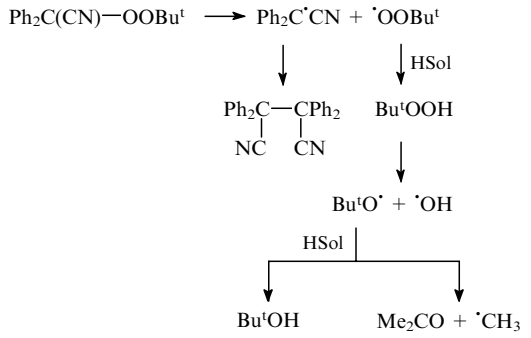
R	Solvent	Yield of H_2 (%)[a]	$10^5 k_H$ /s^{-1} (see[b])	E_H /kJ mol^{-1}
Temperature 130 °C				
EtMeCH	toluene	22	1.35	134
Ph_2CH	"	95	19.3	117
Temperature 140 °C				
Me_2CH	toluene	7.5	5.0 (62.6)	134
	propan-2-ol	8.4	28.5 (310.5)	–
	methanol	30.5	67.2 (152.6)	72
	water	41.5	296.0 (419.0)	–

[a] Upon complete decomposition of the peroxide; [b] the rate constant for the homolysis is given in parentheses ($10^5 k_r$ /s^{-1}).

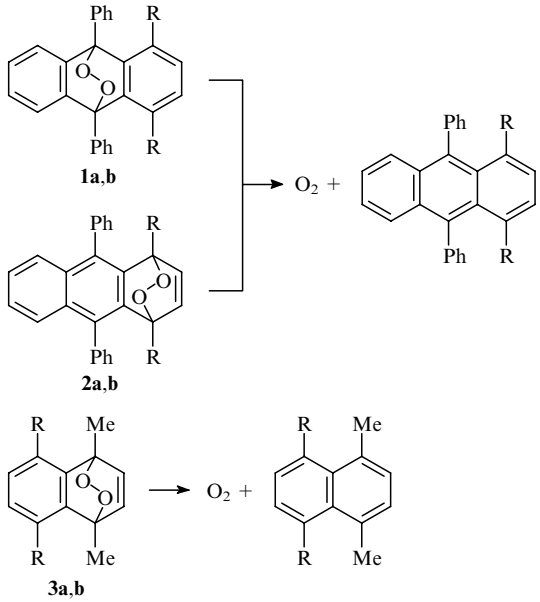
With an increase in the solvent polarity, the rate constant for hydrogen formation increases much faster than the homolysis rate constant. The yield of H_2 in the pyrolysis of diisopropyl peroxide in the gas phase is insignificant, which confirms the polarity of the transition state of the concerted cyclic reaction.

The presence of a double bond and other substituents favouring stabilisation of a carbon-centred radical formed in the α-position with respect to the peroxy group favours decomposition of peroxides at the C—O bond instead of the O—O bond.

tert-Butyl diphenylcyanomethyl peroxide undergoes decomposition in boiling cumene[25] to give acetone and *tert*-butyl alcohol in low yields (5% and 16%, respectively); tetraphenylsuccinonitrile is formed as the main product.



Endoperoxides of anthracene and its derivatives are readily decomposed into the original aromatic compounds and oxygen. Thus the thermolysis of 9,10- (**1**) and 1,4-anthracene endoperoxides (**2**) and 1,4-naphthalene endoperoxides **3** affords the original arenes and oxygen in yields exceeding 95%.[26,27]



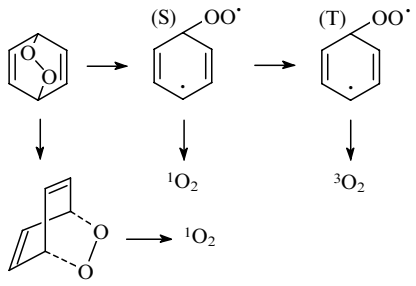
R = H (**a**), Me (**b**).

Part of the oxygen is formed in the singlet state ($^1O_2$) (Table 2). As can be seen, the yield of $^1O_2$ decreases with an increase in the preexponential factor A (positive activation entropy $\Delta S^{\neq}$); for low values of A, the yield of $^1O_2$ is virtually quantitative. It is of note that the biradical mechanism of oxygen formation provides low yields of $^1O_2$ due to S,T conversion, whereas the concerted mechanism with simultaneous bond cleavage ensures a quantitative yield of $^1O_2$:

Table 2. Activation parameters and the yield of $^1O_2$ in the thermolysis of endoperoxides.

Peroxide	T /°C	$10^6 k$ /s^{-1}	E_a /kJ mol^{-1}	log A	Yield of $^1O_2$ (%)
1a	60.2 [a]	0.45	138	15.4	32
	66.2 [b]	1.70	133	14.9	35
1b	60.2 [a]	0.44	135	14.9	52
	66.2 [b]	1.74	126	13.7	73
2a	73.2 [a]	0.43	127	13.0	92
	15.1 [b]	2.09	103	13.0	95
3a	12 [b]	5.30	103	13.7	76
3b	24.8 [b]	2.10	110	13.8	69

[a] In 1,4-dioxane; [b] in chlorobenzene.



The high exothermicity of O_2 formation and the drop in $^1O_2$ yields with an increase in temperature point to the predominance of the biradical mechanism. The enrichment of triplet oxygen generated from endoperoxide **1a** with the isotope ^{17}O was observed in a strong magnetic field,[27] which is the result of ultrafine interactions within the biradical and provides additional evidence in favour of the biradical mechanism.

Studies of the thermolysis of β-hydroxyperoxides [28–30] characterised by relatively high solubility in water revealed that their decomposition, similar to the decomposition of other peroxides R^1OOR^2, begins with the cleavage of the O—O bond. In the case of acyl derivatives and in the presence of water, thermolysis is accompanied by simultaneous hydrolysis of the ester bond.

III. Hydroperoxides

Thermolysis of hydroperoxides, which form homo- and heteroassociates in solution, is more complex than in the gas phase.[31,32]

According to Denisov,[31] bimolecular decomposition of the type

$$ROOH + HX \longrightarrow RO^{\bullet} + HOH + X^{\bullet},$$

occurs much faster than monomolecular decomposition, since the stability of the newly formed H—OH bond (483 kJ mol^{-1}) usually exceeds that of the H—X bond cleaved. The role of HX can be played by saturated hydrocarbons, alkenes, amines, alcohols and other compounds.[33]

In the case of thermolysis involving association of two hydroperoxides

$$ROOH\cdots\underset{\displaystyle H}{\underset{|}{O}}-OR \longrightarrow RO^{\bullet} + H_2O + ROO^{\bullet},$$

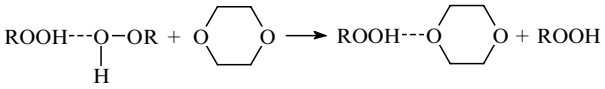
the activation energies of their decomposition in the complexes formed are the lower the higher is the enthalpy of the hydrogen bond.

According to X-ray diffraction data,[34] the hydroperoxide homoassociates $R-O^{(1)}-O^{(2)}-H$ can have different structures depending on the structure of the radical R. Thus *tert*-butyl hydroperoxide molecules form a hydrogen bond including the $O^{(1)}$ atom, whereas 1,1-diphenyl hydroperoxides form a hydrogen bond including the $O^{(2)}$ atom. Because of steric hindrance, triphenylmethyl hydroperoxide forms a hydrogen bond with the π-electrons of the benzene ring of the second hydroperoxide molecule rather than with oxygen atoms. Obviously, the difference in the structures of the associates determines the mechanism of their thermolysis.

The dependence of specific rates of the decomposition of 1-methylcyclohexyl hydroperoxide and the consumption of the inhibitor on the initial concentration of the starting compound [35] suggests that homoassociation of hydroperoxides increases their reactivities up to a certain threshold level. Further aggregation of the hydroperoxide into a polymolecular associate does not lead to any further decrease in its thermal stability.

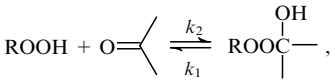
The addition of compounds that form stable associates with hydroperoxides results in dissociation of homoassociates with subsequent monomolecular decomposition (with respect to the hydroperoxide). Thus the addition of dioxane decreases the rate of

initiation of hydroperoxide decomposition in comparison with the initial solution.[36]

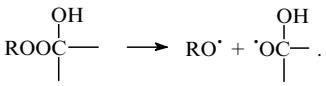


The formation of hydroperoxide associates with electrophiles in solution favours the homolysis of the O—O bond: the stronger the electron shift in this bond, the more intense the homolysis.

At low concentrations of hydroperoxides in solution, their decomposition occurs predominantly by a monomolecular mechanism; with an increase in the hydroperoxide concentration, the bimolecular mechanism becomes predominant. The effect of addition of alcohols on the rate of hydroperoxide thermolysis is concentration-dependent. For example, the addition of cyclohexanol to a solution of cyclohexyl hydroperoxide in chlorobenzene [5, 37] results in the increase in the reaction rate to a maximum at a definite concentration of the alcohol and then to its decrease. The inhibition observed at higher concentrations of the alcohol is attributed to the formation of ternary complexes ROOH · 2 ROH which dissociate into radicals more slowly. The presence of carbonyl compounds along with associates in the reaction mixture results in the formation of 1-hydroperoxides

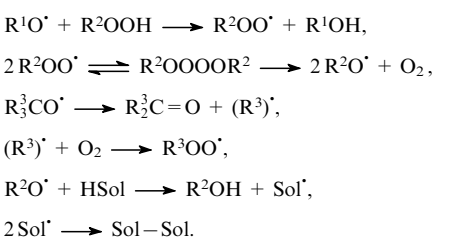


which are less thermostable than the original hydroperoxides [38] and undergo decomposition by the reaction:



The kinetic and thermodynamic parameters of reactions of cycloalkyl hydroperoxides with cyclohexanone in cyclohexane (the initial concentrations of the hydroperoxide and the ketone are equal to 0.02–0.05 mol litre^{-1}) (see Ref. 39) are listed in Table 3. Special mention should be made of the inertness of higher cyclic ketones in this reaction. Similar inactivity of higher cyclic ketones due to steric hindrance in the transition from the planar sp^2-configuration to the sp^3-configuration is observed in the addition of HCN to the corresponding ketones. The reversible formation of 1-hydroxyperoxides is catalysed by carboxylic acids. The data listed in Table 4 point to an increase in the rates of thermal decomposition of hydroperoxides upon addition of a ketone.

Of special note are reactions of hydroperoxides with the radicals formed upon thermolysis; these are accompanied by induced decomposition of hydroperoxides and their chain decomposition. This occurs in parallel with a series of secondary reactions:



The reaction of secondary hydroperoxides with the radicals ROO$^\bullet$ is accompanied by further destruction of hydroperoxides:

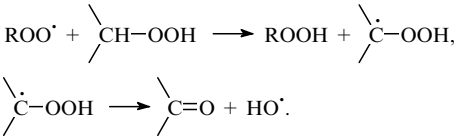


Table 3. Kinetic parameters of the reactions of hydroperoxides ROOH with cyclohexanone at 25 °C.

R	$10^3 k_2$ /litre mol^{-1} s^{-1}	$K = k_2/k_1$ /litre mol^{-1}	E_a /kJ mol^{-1}	$Q = E_1 - E_2$ /kJ mol^{-1}
Cyclohexyl [a]	1.0	8.0	21.2	39.4
Cyclooctyl	1.0	7.0	25.5	41.9

[a] The reaction with cyclooctanone and cyclododecanone does not take place.

Table 4. Increase in the rate of the thermal decomposition of octyl hydroperoxide at 110 °C upon addition of cyclohexanone.

Reaction time /h	Decomposition (%)	
	without additives	with cyclohexanone
2	1.5	14.2
4	5.9	30.0
6	11.1	40.1

Note. For octyl hydroperoxide, c_0 = 0.06 mol litre^{-1}, for cyclohexanone c_0 = 0.33 mol litre^{-1}

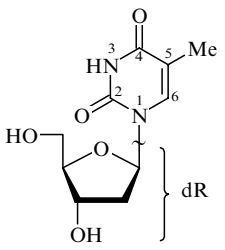
The introduction of free radical scavengers suppresses induced decomposition of peroxides and permits one to estimate the contribution of the peroxide thermolysis proper (see also Refs 5 and 31). The kinetic characteristics of the reactions of the radicals RO$^\bullet$ and ROO$^\bullet$ with hydroperoxides are listed in Table 5 (data from Refs 40–47).

In biological objects, hydroperoxides exist in an aqueous medium. It is noteworthy that the transition from a hydrocarbon to an aqueous medium is accompanied by a significant decrease in the activation energy and an increase in the rate of hydroperoxide thermolysis. The corresponding parameters for *tert*-butyl hydroperoxide are as follows:[6]

Solvent	Initial concentration /mol litre^{-1}	Decomposition rate constant /s^{-1} (T /°C)	E_a /kJ mol^{-1}
n-Hydrocarbon	0.17	0.9×10^{-5} (150)	163
Water	0.05	0.14×10^{-5} (130)	126

The effect of pH on the decomposition kinetics of this hydroperoxide in water was studied.[48]

Hydroperoxides are formed upon free-radical oxidation of DNA, which plays a crucial role in mutagenesis induced by ionising radiation. Thus the oxidation of 2′-deoxythymidine yields eight diastereomers of 5(6)-hydroxy-6(5)-hydroperoxy-5,6-dihydro-2′-deoxythymidine (**4a**–**d**, **5a**–**d**) and 5-(hydroperoxymethyl)-2′-deoxyuridine (**6**). The thermolysis of thymidine hydroperoxides in aqueous solutions was studied by Wagner *et al*.[49]

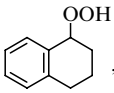


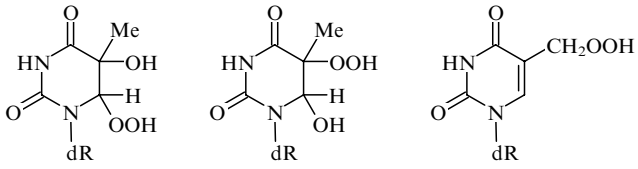
2′-deoxythymidine

Table 5. Kinetic parameters ($\log k$) of the reactions of peroxyl and alkoxyl radicals ROO$^{\bullet}$ and RO$^{\bullet}$ with hydroperoxides.

R in ROO$^{\bullet}$	Hydroperoxide	T /°C	$\log k$	R in ROO$^{\bullet}$	Hydroperoxide	T /°C	$\log k$
cyclo-C_6H_{11}	cyclo-$C_6H_{11}OOH$	75	1.25	$PhMe_2C$	$PhMe_2COOH$	30	7.95
		21	0.20	$EtMe_2C$	$EtMe_2COOH$	30	7.95
cyclo-C_6H_{11}	cyclo-$C_6H_{11}OOH$	75	1.08	1-Me-cyclo-C_6H_{10}	1-Me-cyclo-$C_6H_{10}OOH$	30	7.60
Bu^t	Et(Me)CHOOH	21	2.68	Bu^t	cyclo-$C_6H_{11}OOH$	30	8.45
Bu^t	see [a]	30	2.75	Bu^t	1-Me-cyclo-$C_6H_{10}OOH$	30	8.18
		75	3.17	Bu^t	Bu^tOOH	30	8.40
$PhMe_2C$	see [a]	30	2.78	Pr^i	Pr^iOOH	30	7.70
See [b]	$PhMe_2COOH$	30	3.40				

Note. The reactions of cyclo-$C_6H_{11}OO^{\bullet}$ with hydroperoxides are related to the $S_N2(C-H)$ type; the reactions of other radicals are of the type $S_N2(OO-H)$.

[a] Hydroperoxide , [b] R .



4a–d **5a–d** **6**

trans-(5*R*,6*R*) (**a**), *trans*-(5*S*,6*S*) (**b**), *cis*-(5*S*,6*R*) (**c**), *cis*-(5*R*,6*S*) (**d**).

The thermolysis of thymidine hydroperoxides in highly purified water occurs in accordance with the following schemes (see Table 6):

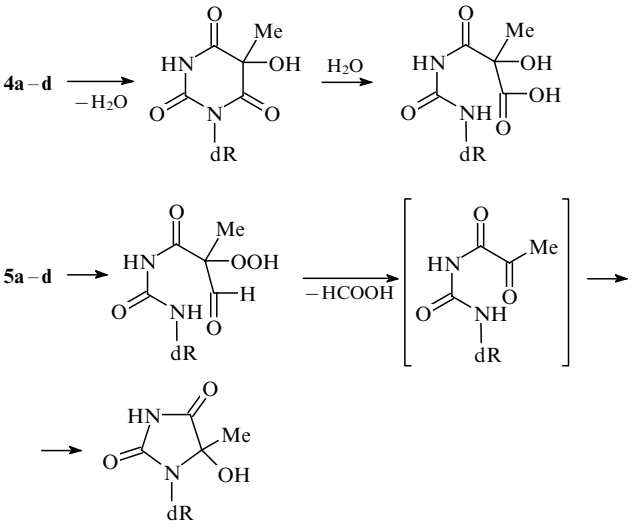


Table 6. Kinetic parameters of the thermal decomposition of thymidine hydroperoxides in aqueous solutions.

Hydroperoxide	$10^5 k_1$ /s^{-1} (37 °C)	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J mol^{-1} K^{-1}
4a	19	103	9.6
4b	12	105	15.4
4c	1.9	96	−31
4d	1.9	96	−31
5a	2.3	121	52
5b	2.0	125	64
5c	1.2	119	41
5d	0.56	147	125

As can be seen, the decomposition of the hydroperoxides **4a–d** involves dehydration of secondary hydroperoxide groups and subsequent hydrolysis, whereas the thermolysis of compounds **5a–d** involves tautomeric conversion of the hydroperoxide into an aldehyde and recyclisation.

IV. Dioxiranes

A series of novel oxidants, *viz*., dioxiranes, possessing a unique combination of properties (high regio- and stereoselectivity of oxidation, high reactivity and mild reaction conditions) have been introduced into laboratory practice since the mid-1980's. The majority of investigations into the chemical properties of dioxiranes were carried out with dimethyldioxirane (**7b**, DMDO) and methyl(trifluoromethyl)dioxirane (**7c**) as examples.



7

$R^1 = R^2 = H$ (**a**), Me (**b**); R^1 = Me, $R^2 = CF_3$ (**c**).

Thermal stability studies have shown that highly reactive dioxiranes react simultaneously by several routes. This accounts for discrepancies in results obtained by different authors. According to some authors,[50, 51] the half-life ($\tau_{1/2}$) of dioxirane **7b** at room temperature is 7 h or 26 days, respectively. According to other authors,[50, 52, 53] the decomposition of dioxiranes **7b** and **7c** cannot be described by first- or second-order kinetic equations, since the corresponding kinetic curves display a distinct induction period. However, at low concentrations of the dioxirane **7b** ($< 3 \times 10^{-2}$ mol litre^{-1}, see Refs 51 and 53) the rate of its thermolysis obeys the first-order kinetic law. Oxygen, which suppresses the decomposition of DMDO, has a pronounced effect on the composition of the reaction products.[53]

The thermolysis of the dioxirane **7b** in acetone [54, 55] occurs by three main routes, *viz*., isomerisation (i), radical (r) and molecular (m) routes (Scheme 1).

The composition of the thermolysis products of DMDO depends on the presence of oxygen in the solution as well as on the presence and number of C–H bonds in the solvent molecule. The ratio of the main reaction products also depends on temperature (Table 7). If the decomposition is carried out in the presence of oxygen at 10 °C, methyl acetate is virtually the only reaction product. Its proportion in the total yield of the reaction products diminishes to 59%, if the reaction is carried out at 50 °C. Under these conditions, acetol (1-hydroxypropan-2-one) (39%) and acetic acid (2%) are formed in addition to methyl acetate. Quite a different situation is observed in the decomposition of DMDO in the absence of oxygen (the latter is removed by purging the

Scheme 1

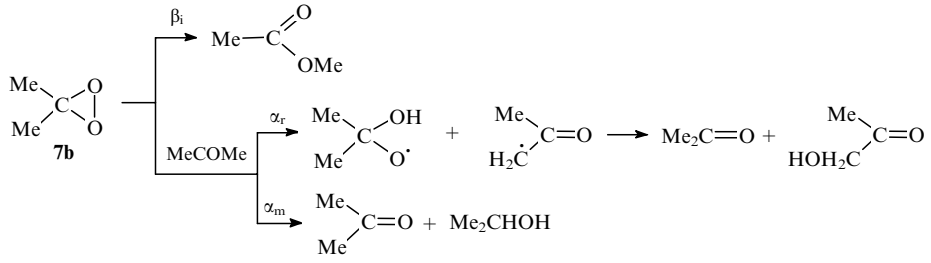


Table 7. Yields of the thermal decomposition products of dimethyldioxirane.

Atmosphere	T /°C	MeCOMe ‖ O	MeCCH$_2$OH ‖ O	MeCOCH$_2$CMe ‖ O ‖ O	MeCOH ‖ O
O_2	10	0.98	0.02	–	–
O_2	50	0.59	0.39	–	0.02
O_2 [a]	50	1.00	–	–	–
Ar	41	traces	traces	1	traces

[a] CCl_4 was used as a solvent; in other cases, acetone was used.

solution of DMDO with argon). Acetol acetate MeC(O)OCH$_2$.C(O)Me is the main thermolysis product at 41 °C; methyl acetate and acetol were found in insignificant amounts. The decomposition rate of dimethyldioxirane decreases in CCl_4. The reason is the absence of C–H bonds in the solvent molecule; therefore, the isomerisation of DMDO into methyl acetate is the main pathway of its consumption.

The presence of dissolved oxygen is critical for the stability of dioxirane solutions. When oxygen is present in the solution, the rate of DMDO thermolysis is relatively small and obeys the first-order kinetic law with respect to dioxirane (Fig. 1). Removal of oxygen by purging the solution with argon or by chemical binding sharply increases the rate of DMDO consumption (see Fig. 1, curve *3*); the reaction order is intermediate between the first and the second with respect to dioxirane. The reason for the sharp increase in the reaction rate is intense radical-chain induced

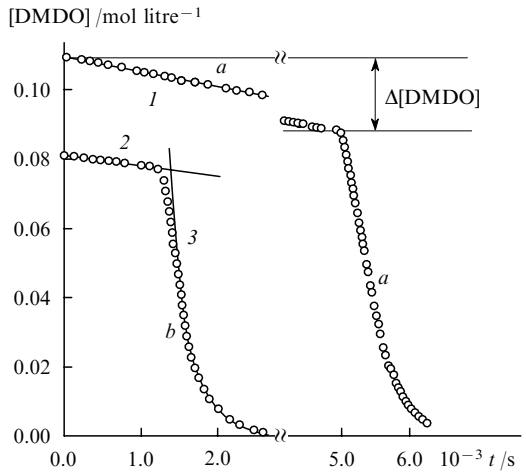
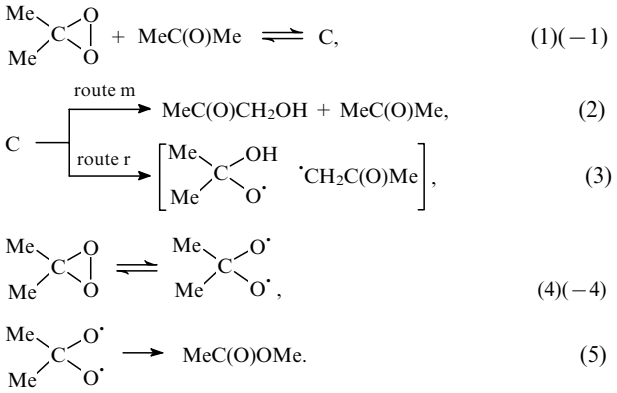
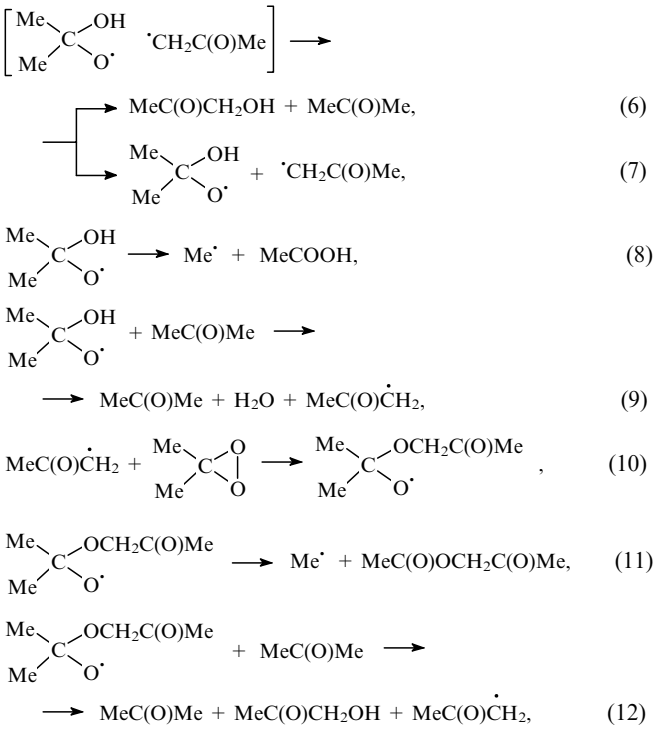


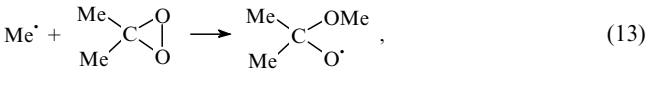
Figure 1. Typical kinetic curves for the consumption of dimethyldioxirane. Conditions: acetone, 50 °C, preliminary purging of the solution with oxygen (*a*) or argon (*b*). The solid lines designate the results of treatment of the kinetic curves using a first-order (curves *1* and *2*) or a mixed (first + second)-order equation (curve *3*).

decomposition of the peroxide in the absence of O_2. The thermolysis of DMDO proceeds in accordance with the following scheme (C is a complex):[54, 55]

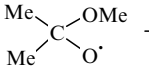


Further transformations of radical intermediates are apparent: the alkyl radicals react with oxygen and induce the decomposition of dioxirane **7b** in the absence of oxygen [reactions (10)–(13)] and undergo decay in the recombination [reactions (16)–(18)]. Oxygen-centred radicals undergo β-cleavage [reactions (8), (11), (14)] or abstract the hydrogen atom from the acetone molecule [reactions (9), (12), (15)].

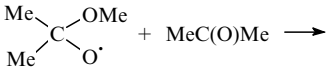




(13)



(14)



(15)

$$MeC(O)\dot{C}H_2 + MeC(O)\dot{C}H_2 \longrightarrow MeC(O)CH_2CH_2C(O)Me, \quad (16)$$

$$MeC(O)\dot{C}H_2 + Me^{\bullet} \longrightarrow MeC(O)CH_2Me, \quad (17)$$

$$Me^{\bullet} + {}^{\bullet}Me \longrightarrow MeMe. \quad (18)$$

The induced decomposition of dioxirane under the action of the methyl radical [reaction (13), $k_{13} \approx 10^5 - 10^6$ litre mol^{-1} s^{-1}][56–58] competes with the abstraction of hydrogen from the acetone molecule with the rate constant of 2.7×10^3 litre mol^{-1} s^{-1} (see Ref. 59)

$$Me^{\bullet} + MeC(O)Me \longrightarrow CH_4 + MeC(O)\dot{C}H_2. \quad (19)$$

In the absence of oxygen, the chain decomposition of dioxirane **7b** occurs with the involvement of $Me^{\bullet}$ and $MeC(O)\dot{C}H_2$ radicals. In the presence of oxygen, the induced decomposition of compound **7b** is suppressed, while the chain termination involves the peroxy radicals.

$$MeC(O)CH_2^{\bullet} \text{ (or } Me^{\bullet}) + O_2 \longrightarrow MeC(O)CH_2OO^{\bullet} \text{ (or } MeOO^{\bullet}), \quad (20)$$

$$ROO^{\bullet} + ROO^{\bullet} \longrightarrow \text{alcohol} + \text{ketone} + O_2. \quad (21)$$

Under these conditions, the thermolysis of DMDO is described by equations (1)–(9), (20), (21). A kinetic analysis of the decomposition reaction gave the following expression for the reaction rate:

$$W_{\mathbf{7b}} = \{(\alpha_m + \alpha_r)\, k_1[MeC(O)Me] + \beta_i k_4\}\,[\mathbf{7b}] = k_{eff}[\mathbf{7b}], \quad (22)$$

where α_m and α_r are the contributions of the molecular and radical routes during the conversion of the complex C: $\alpha_m = k_2/A$, $\alpha_r = k_3/A$, where $A = k_{-1} + k_2 + k_3$; $\beta_i = k_5/(k_{-4} + k_5)$. Indeed, thermal decomposition of DMDO in acetone solutions saturated with oxygen obeys the kinetic law for first-order reactions with respect to dioxirane. The effective thermal decomposition rate constant, k_{eff}, does not depend on the concentration of dioxirane. At 50 °C:

$$k_{eff} = 1.8 \times 10^{-5} + 1.5 \times 10^{-6}[MeC(O)Me]\ s^{-1}.$$

The activation parameters, *i.e.*, the preexponential factor $\log A$ and the energy of activation E_a, for the overall decomposition of DMDO in acetone are described by the expression:

$$\log k_{eff} = (10.2 \pm 0.6) - \frac{(90.4 \pm 3.8)}{\theta},$$

where $\theta = 2.3\,RT$ kJ mol^{-1}. As mentioned above, the thermolysis of DMDO in carbon tetrachloride occurs at a slower rate, since in this case the thermal decomposition occurs by only one route, *viz.*, isomerisation of dioxirane into methyl acetate. The temperature dependence of the rate constant $k_i = \beta_i k_4$ in CCl_4 appears as:

$$\log k_{eff} = \log k_i = (7.1 \pm 0.3) - \frac{(75.3 \pm 2.1)}{\theta}.$$

The activation parameters of the isomerisation of the dioxirane **7b** into methyl acetate are consistent with the results of quantum-chemical calculations of a high basis set.[60] The energy diagram for the isomerisation of DMDO and the simplest dioxirane **7a** on a standard enthalpy of formation scale is shown in Fig. 2. The difference between experimental and calculated values of E_a seems to be related to the effect of the solvent. The limiting step of isomerisation, *viz.*, the formation of a biradical, requires the opening of the dioxirane ring in order to minimise the repulsion of lone electron pairs coplanar with the ring. The opening of the ring associated with the reduction of the bond angle between the substituents at the carbon atom is more difficult for substituents with larger size, which explains the increase in E_a in the homolysis of the dioxirane **7b** in comparison with compound **7a**. Indeed, the dioxirane **7a** is thermally much less stable than **7b**. Contrariwise, sterically hindered bis(mesityl)dioxirane forms stable crystals even at room temperature.[61]

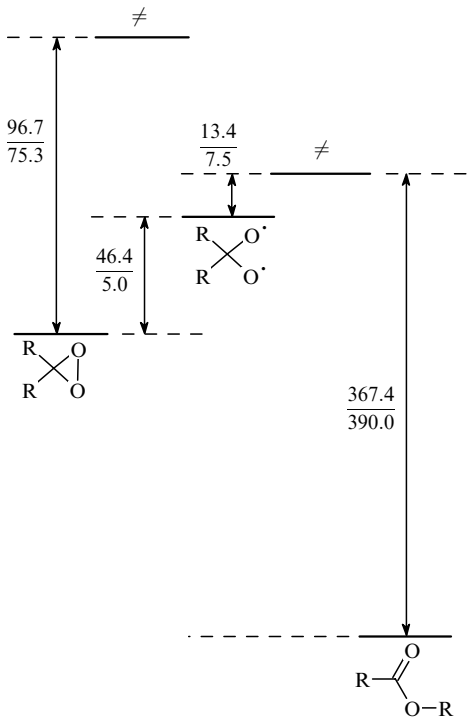


Figure 2. The energy diagram of isomerisation of dioxirane **7a** (R = H, $\Delta H_f^\circ = -1.3$ kJ mol^{-1}) and dimethyldioxirane **7b** (R = Me, $\Delta H_f^\circ = -105.9$ kJ mol^{-1}) into formic acid and methyl acetate, respectively. (The corresponding values for compounds **7b** and **7a** (in kJ mol^{-1}) are given in the numerator and the denominator, respectively). The sign ≠ designates the transition state.

The O–O bond homolysis product (biradical) decomposes through migration of H or Me resulting in the formation of the corresponding acid or its ester. This process is characterised by low activation energy, *e.g.*, for the biradical $^{\bullet}OCMe_2O^{\bullet}$ it is 13.4 kJ mol^{-1}. The decomposition of the biradical (or DMDO) into CO_2 and ethane requires much energy; therefore, this reaction cannot compete with the rearrangement into an ester.[60] Indeed, vacuum flash-pyrolysis of the dioxirane **7c** gives quantitative yields of methyl trifluoroacetate (> 98%).[62] The photolysis and thermolysis of dioxiranes in solutions are complicated by the decomposition of the peroxide induced by free radicals.

While analysing the ratio of the radical (r) and molecular (m) routes of dioxirane decomposition, one should bear in mind that dioxiranes react with many organic compounds at a very fast rate ($k_m \gg k_r$). In this case, we deal with a manifestation of a high oxidative activity of dioxirane with respect to the other reactant rather than with its thermolysis. The problems related to the products, kinetics and mechanisms of oxidation of various organic compounds by dioxiranes are documented.[63–68] In the presence of compounds with non-activated C–H bonds, the radical route of dioxirane oxidation becomes more pronounced.

As mentioned above, complete removal (purging or chemical binding) of O_2 shifts the reaction towards radical-chain decom-

position of DMDO. This includes chain initiation [reactions (1)–(9)], propagation [reactions (10)–(15), (19)] and termination [reactions (16)–(18)]. It was found [55] that cross recombination is the most plausible step in the chain termination (17). In this case, the kinetic analysis of DMDO decomposition gives the following expression for the rate of consumption of the dioxirane **7b**:

$$W_{\mathbf{7b}} = k^{(1)}[\mathbf{7b}] + k^{(2)}[\mathbf{7b}]^2, \quad (23)$$

where $k^{(1)}$ and $k^{(2)}$ are complex combinations of kinetic constants and acetone concentration. The first component of Eqn (23) reflects the consumption of compound **7b** in the reaction with the acetonyl radical, while the second one describes the contribution of reaction (13) to the total rate of DMDO decomposition. This differential equation is readily transformed into an analytical expression which appears as:[57, 66]

$$\ln\frac{(k^{(1)} + k^{(2)}[\mathbf{7b}])[\mathbf{7b}]_0}{(k^{(1)} + k^{(2)}[\mathbf{7b}]_0)[\mathbf{7b}]} = k^{(1)}t. \quad (24)$$

Equation (24) effectively describes the kinetic curves of consumption of the dioxirane **7b** under conditions of induced decomposition.

Thus the role of oxygen in the thermolysis of DMDO consists of the inhibition of free-radical induced decomposition of the peroxide by route r. The calculation of the ratio of the amount of dissolved oxygen to the dioxirane **7b** decomposed in the induction step can be used for determining the contribution of the radical route of thermal decomposition of DMDO to the overall process. The ratio of decomposition reactions by routes r and m was studied [55] in the reactions of DMDO with acetone and some aliphatic hydrocarbons (Table 8). These data suggest that the reaction of DMDO with aliphatic hydrocarbons is indeed a radical reaction; it is not excluded that it proceeds exclusively by a homolytic mechanism ($k_3 \gg k_2$), whereas the efficiency of initiation is decreased due to intracage recombination [reaction (6)].

The known contribution of the radical route of the reaction of dioxirane **7b** containing a C–H bond and the kinetic parameters of the overall reaction allow one to determine the rate constants k_r and k_m as well as the corresponding activation parameters. The data for the reactions of DMDO with acetone and 2,2,4-trimethylpentane are given below.

Reagent	Reaction route	
	radical	molecular
Acetone	$\log k_r = 11.9 - 112.1/\theta$	$\log k_m = 9.5 - 96.2/\theta$
2,2,4-Trimethylpentane	$\log k_r = 11.1 - 91.2/\theta$	$\log k_m = 4.0 - 51.5/\theta$

The preexponential factors of the rate constants for the radical reaction of the dioxirane **7b** with acetone and 2,2,4-trimethylpentane are similar (with allowance for the statistic correction for six C–H bonds of acetone). The difference in the activation energies for these reactions (21 kJ mol^{-1}) reflects the difference in the strengths of the C–H bonds of acetone and 2,2,4-trimethylpentane subjected to the attack.

The values of partial rate constants for the reaction of DMDO with RH were calculated from the effective rate constant for the consumption of dioxirane in the oxidation of hydrocarbons (RH) and acetone:[55, 57, 58, 69]

$$k^{H} = \frac{k_{eff}}{n[RH]} = \frac{(\alpha_r + \alpha_m)k_1}{n},$$

where n is the number of equivalent C–H bonds attacked by dioxirane. The results of calculations of k^H are listed in Table 9. Although the ratio of reaction routes for the reaction **7b** + RH changes in the series of compounds under study, the calculated values of partial rate constants can be used to determine the relative reactivities of the substrates RH. The changes in k^H demonstrate the following regularities (Table 9):

1. Dioxirane is a pronounced regioselective oxidant. The primary C–H bond is attacked 10^4 times less actively than the tertiary bond. Probably, the true value of the k_{tert}/k_{pri} ratio is somewhat smaller, since the reactivity of acetone is decreased due to deactivation of the α-C–H bonds by the carbonyl group.

2. The activity of tertiary C–H bonds changes in the following order: aliphatic (1.0) < 'aromatic' (H–CAlk$_2$Ar) (2.0) < cage (4.0). Weakening of the C–H bond strength and retention of the radical reaction mechanism result in an increase in k^H on going from 2-methylbutane to cumene. The presence of carbocation-stabilising fragments in the molecule RH increases the contribution of the molecular route and the reactivity of the C–H bond (2-methylbutane and adamantane).

The ratio of radical and molecular routes is quantitatively characterised by the $[O_2]/\Delta[\mathbf{7b}]$ ratio. The conditions influencing the ratio of these two routes are as follows:

— the contribution of the radical mechanism increases with temperature (see Table 8);

— the energy of homolytic dissociation of the C–H bond depends on the nature of the substrate to be oxidised: an increase in energy diminishes the contribution of the radical route. The energy of homolytic dissociation of tertiary C–H bonds is lower than that of secondary bonds.

The ratio of molecular and radical routes of reactions of peroxide oxidants with substrates to be oxidised has been repeatedly discussed in the literature. It is well known that the more pronounced the electrophilic properties of the peroxide (the affinity of the oxidant for the electron can be used as a measure of activity) and the electron-donor properties of the compound to be oxidised, the lower the temperature and the more polar the

Table 8. Ratio of the molecular and radical routes in the reactions of dimethyldioxirane with organic compounds.

Substrate	$[RH]_0$ /mol litre^{-1}	$[\mathbf{7b}]_0$ /mol litre^{-1}	T /°C	$[O_2]/\Delta[\mathbf{7b}]$
Acetone	13.6	0.108	50	0.20
	13.6	0.096	56	0.23
2,2,4-Trimethylpentane	0.61	0.061	41	0.68
	0.83	0.083	41	0.76
	0.99	0.079	41	0.73
	1.1	0.078	41	0.76
	1.2	0.075	41	0.71
	1.7	0.070	25	0.57
n-Octane	0.84	0.077	41	0.51
	1.2	0.071	41	0.53
Cyclohexane	1.7	0.078	41	0.66
2-Methylbutane	0.52–4.6	0.019–0.071	25	0.50

Table 9. Partial rate constants for the reaction of dimethyldioxirane with organic compounds (RH) at 25 °C.

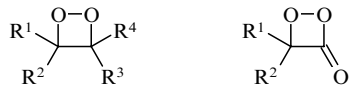
RH	[RH] /mol litre^{-1}	$\log k_{eff}$ (s^{-1})	k_{eff} /s^{-1}	k^H /litre mol^{-1} s^{-1}
Acetone	13.7	$10.2 - 90.4/\theta$	2.3×10^{-6}	2.8×10^{-8}
2-Methylbutane	1.0	–	2.1×10^{-4}	2.1×10^{-4}
Adamantane [a]	–	$7.94 - 59.4/\theta$	3.4×10^{-3}	8.4×10^{-4}
Cumene	4.0	$6.4 - 52.3/\theta$	1.7×10^{-3}	4.2×10^{-4}

[a] Temperature dependence of a bimolecular rate constant.

solvent, the higher the probability of the molecular route of the oxidation. A similar situation is observed in the chemistry of dioxiranes. From a synthetic point of view, it is more reasonable to select conditions favouring the nonradical mechanism, *viz.*, low temperature, the use of dioxiranes possessing stronger oxidising properties (*e.g.*, **7c**) and compounds to be oxidised with activated C–H bonds that can effectively stabilise the positive charge on the C atom generated upon partial transfer of the electron density to dioxirane.

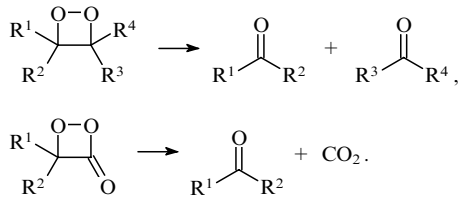
V. 1,2-Dioxetanes

Luminescence appearing upon formation of an electron-excited product is the main characteristic feature of the thermolysis of 1,2-dioxetanes (**A**) and their keto derivatives (α-peroxy lactones, **B**) (see Refs 70–74 and the references cited therein).



A **B**

The excitation of the product is due to the fact that the difference between the enthalpy of activation $\Delta H^{\neq}$ of thermolysis and the standard enthalpy of the same reaction ΔH° exceeds the energy of the electron-excited state E^*, *i.e.*, $\Delta H^{\neq} - \Delta H^{\circ} \geqslant E^*$. The main routes of the thermolysis of 1,2-dioxetanes (**A**) and α-peroxy lactones (**B**) are as follows:



The schemes illustrating the ratios of energies in the individual steps of the thermolysis of some typical representatives of dioxetanes and α-peroxy lactones are shown in Fig. 3.[72]

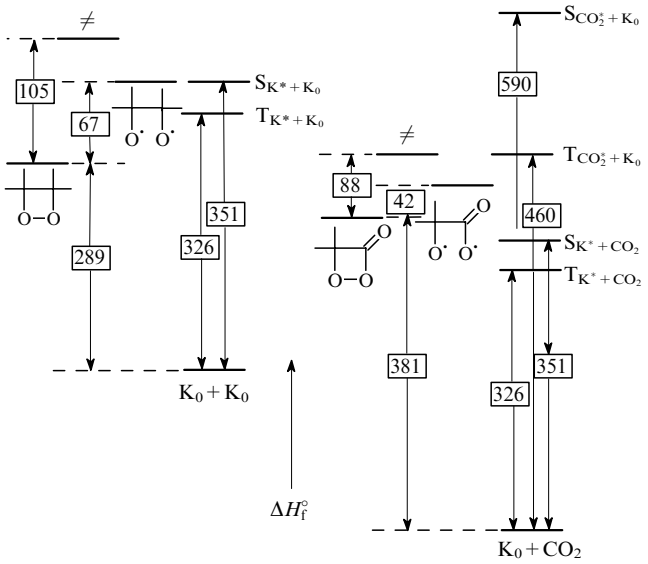
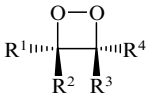
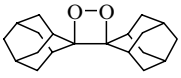
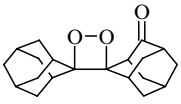
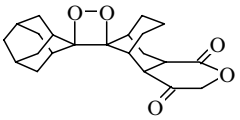


Figure 3. Diagram of the enthalpies of formation of reaction products (ΔH_f° /kJ mol^{-1}) in the thermolysis of tetramethyl-1,2-dioxetane and dimethyl-1,2-dioxetanone.
Product states: singlet S_K, triplet T_K, excited K* and ground K_0. The figures designate the energy of the transition from one state to another.

The values of ΔH° for different compounds lie in the range from −250 to −380 kJ mol^{-1}, while $\Delta H^{\neq}$ varies from 85 to 140 kJ mol^{-1}, which enables the occupation of triplet ($E_T^* = 250-330$ kJ mol^{-1}) and singlet [$E_S^* = E_T^* + (20-63)$ kJ mol^{-1}] states. A comparison of 1,2-dioxetanes and α-peroxy lactones has shown that the decomposition of the latter is much more exothermic. This is not surprising, however, since the incorporation of an sp^2-hybridised carbon atom into a strained four-membered 1,2-dioxetane ring increases the exothermic character of the ring opening. The decomposition of α-peroxy lactones yields electron-excited CO_2 molecules; the energies of their excited triplet and singlet states are very high. The kinetic characteristics of the

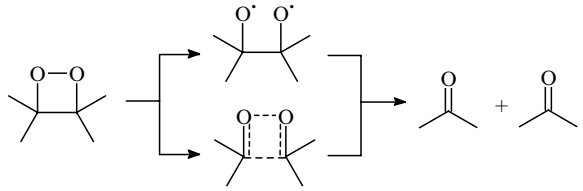
Table 10. Kinetic parameters and yields of the excited states (T*, triplet; S*, singlet) in the thermolysis of dioxetanes in solution.

Compound	R^1	R^2	R^3	R^4	Solvent	E_a /kJ mol^{-1}	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J mol^{-1} K^{-1}	Yield (%)	
									T*	S*
	Me	Me	Me	Me	toluene	116	104	−11.7	35	0.25
	Me	Me	Me	Me	*o*-xylene	115	–	–	–	–
	Me	Me	Me	Me	benzene (liquid)	117	–	–	–	–
	Me	Me	Me	Me	benzene (solid)	116	–	–	–	–
	Me	Me	Me	H	toluene	109	98	−19.7	25	0.1
	Me	H	H	Me	"	103	94	−21.3	7.8	0.018
	Me	Me	H	H	"	104	90	−31.8	12	0.018
	Me	H	Me	H	"	101	90	−30.9	13	0.019
	Me	H	H	H	"	95	90	−23.4	4.3	0.003
	H	H	H	H	"	95	79	−52.7	0.24	0.0003
					acetonitrile	151	145	20.1	17.3	1.8
					xylene	166	141	12.1	15	2
						139	136	−0.84	3.8	0.43
						153	148	−2.1	1.1	0.07

thermolysis of some dioxetanes in solution are listed in Table 10.[75–78]

The kinetic parameters of the thermolysis of tetramethyldioxetane in various solvents are very similar. The conservation of the activation energy in the decomposition of tetramethyldioxetane in benzene solutions and solid benzene templates at low temperatures is of note.[75] The activation energy of the thermolysis of unsubstituted dioxetane in the gas phase is equal to 91 ± 5 kJ mol^{-1}, *i.e.*, it is 4 kJ mol^{-1} less than that for toluene. Thus, the energy of molecular thermolysis does not virtually depend on the phase state of the medium in the absence of a direct interaction with the solvent molecules. The stability of dioxetanes of the diadamantylidene series with respect to decomposition is especially high: E_a reaches 153 kJ mol^{-1}. The data listed in Table 10 and other published data suggest that the yields of excited singlet states are many times smaller than those of triplet states, *i.e.*, spin-forbidden processes occur much more intensely than spin-allowed ones. The yields of excited triplets usually increase with an increase in the stability of the starting peroxide.

Two main mechanisms for the thermal decomposition of dioxetanes have been proposed: formation of a biradical and concerted redistribution of the bonds.



The effect of substituents on the chemical kinetics of thermolysis and thermochemical and quantum-chemical calculations confirm the biradical mechanism of thermolysis.[73, 74, 77] The enthalpies of formation, the geometry of the central fragment, the torsion angle O–C–C–O and the strain energies in the ring were calculated for a large series of substituted dioxetanes and intermediate biradicals on the basis of a biradical model using the molecular mechanics method (MM2).[79] Together with the thermochemical calculations the use of the Benson additive group contribution method has made it possible to obtain efficient correlation equations relating the Arrhenius and free activation energies with the values of angle strain energies in the starting dioxetane and in the biradical. A relatively high predictive capacity of these correlation equations provides additional evidence in favour of the biradical mechanism.

VI. Trioxides

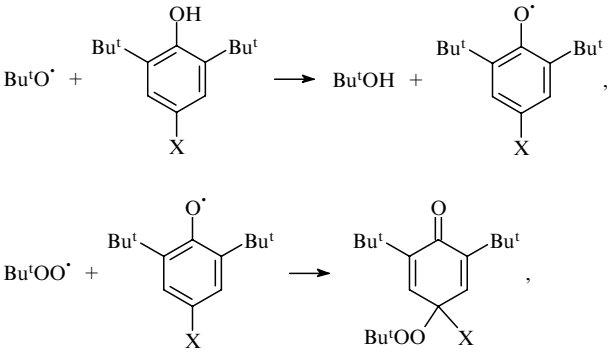
Compounds containing three or more neighbouring oxygen atoms are considerably less thermostable than peroxides (RO–OR).[80]

Thermal decomposition, which proceeds exclusively by a homolytic mechanism, is the most typical reaction of dialkyl trioxides. Their decomposition yields alkoxy (RO$^{\bullet}$) and peroxy (ROO$^{\bullet}$) radicals which determine all subsequent reactions and reaction products. Direct evidence for the formation of peroxy radicals in the decomposition of di-*tert*-butyl trioxide was obtained by ESR (see, *e.g.*, Ref. 81). The *tert*-butoxy radical was identified from the signal of its adduct with a spin trap (2-methyl-2-nitrosopropane).[82] Indirect evidence for the generation of Bu^{t}O$^{\bullet}$ radicals also follows from a significant increase in the concentration of the radical Bu^{t}OO$^{\bullet}$ after addition of *tert*-butyl hydroperoxide to a solution of Bu^{t}OOOBu^t in CH_2Cl_2 :

$$Bu^tO^{\bullet} + Bu^tOOH \longrightarrow Bu^tOH + Bu^tOO^{\bullet}.$$

The decomposition of Bu^{t}OOOBu^t in the presence of free radical scavengers (sterically hindered phenols) occurs without evolution of oxygen, but is accompanied by yellow colouration of the solution due to the formation of quinolide peroxide.[81, 83]

$$Bu^tOOOBu^t \longrightarrow Bu^tO^{\bullet} + Bu^tOO^{\bullet},$$



X = Me, Bu^t.

The kinetics of radical decomposition of di-*tert*-butyl trioxide in $CFCl_3$ and CH_2Cl_2 (–20 to 7 °C) was followed [84] by monitoring ionol (2,6-di-*tert*-butyl-4-methylphenol) consumption. The following activation parameters were established:

$CFCl_3$	$\log A = 14.8 \pm 1.2$ (s^{-1})	$E_a = 90.4 \pm 5.9$ kJ mol^{-1},
CH_2Cl_2	$\log A = 14.1 \pm 1.6$ (s^{-1})	$E_a = 84.1 \pm 7.9$ kJ mol^{-1}.

The probability (e) of the exit of radicals into the solution in the decomposition of di-*tert*-butyl trioxide does not virtually depend on temperature and constitutes $(90 \pm 10)\%$.[84]

Under certain conditions, the decomposition of ROOOR is accompanied by chemiluminescence (CL) in the visible (350–650 nm) and IR (1000–1300 nm) regions of the spectrum.[85] Excited carbonyl compounds (*e.g.*, singlet-excited phosgene in the case of CH_2Cl_2) emit in the visible region, while singlet oxygen $^1\Delta_gO_2$ emits in the IR region. CL emitters are formed upon recombination of peroxy radicals generated in the decomposition of di-*tert*-butyl trioxide with subsequent involvement of the solvent in the radical-chain reaction.[86]

$$Bu^tOOOBu^t \longrightarrow Bu^tO^{\bullet} + Bu^tOO^{\bullet},$$

$$Bu^tO^{\bullet} + CH_2Cl_2 \longrightarrow Bu^tOH + {}^{\bullet}CHCl_2,$$

$${}^{\bullet}CHCl_2 + O_2 \longrightarrow Cl_2CHOO^{\bullet},$$

$$Cl_2CHOO^{\bullet} + Bu^tOO^{\bullet} \rightleftharpoons Cl_2CHOOOOBu^t \longrightarrow$$

$$\longrightarrow Cl_2C{=}O + Bu^tOH + O_2.$$

The energy of the last reaction (~ 375 kJ mol^{-1}) is sufficient to generate phosgene or oxygen in the excited states (the excitation energies are equal to ~ 290 and 94 kJ mol^{-1}, respectively).[87] The chemiluminescence method was used to determine the excitation yields of singlet oxygen upon decomposition of di-*tert*-butyl trioxide in CH_2Cl_2.[87] At –5.5 °C, this yield is 22% (as calculated per original trioxide) and diminishes slightly with an increase in temperature (18% at 5.0 °C). The termination of the kinetic chains in the decomposition of di-*tert*-butyl trioxide in CH_2Cl_2 occurs predominantly as cross recombination of peroxy radicals.[86]

The quenching of the chemiluminescence in both visible and IR regions of the spectrum obeys first-order kinetics and is characterised by similar rate constants. The activation parameters of the thermal decomposition of dialkyl trioxides obtained in the temperature range from –20 to 18 °C using the CL method are listed in Table 11.

The rate constants for the decomposition of di-*tert*-butyl trioxide (at 0 °C) in carbon tetrachloride ($\varepsilon = 2.23$) and nitromethane ($\varepsilon = 38.6$) are 0.6×10^{-3} and 9.7×10^{-3} s^{-1}, respectively (see Ref. 88), *i.e.*, they increase with the medium polarity. The same is true of di-*tert*-butyl peroxide; however, in the latter case this effect is less pronounced. For example, at 125 °C the

Table 11. Activation parameters of the decomposition of dialkyl trioxides ROOOR in CH_2Cl_2 inferred from the chemiluminescence data.

R	Method [a]	$\log A$ (s^{-1})	E_a /kJ mol^{-1}	Ref.
Bu^t	IR	14.5 ± 2.2	87.0 ± 2.5	85
	Vis	14.5 ± 0.7	85.4 ± 3.8	86
$EtMe_2C$	IR	13.2 ± 1.0	80.3 ± 5.4	87
	Vis	16.3 ± 1.8	94.1 ± 9.6	87
$PhMe_2C$	IR	15.5 ± 0.9	92.0 ± 4.6	87
	Vis	15.0 ± 1.6	89.5 ± 8.2	87

[a] Designations: IR, infrared spectroscopy; Vis, spectroscopy in the visible region of the spectrum.

decomposition rate constants of Bu^tOOBu^t in cumene ($\varepsilon = 2.37$) and acetonitrile ($\varepsilon = 37.5$) are equal to 16.0×10^{-6} and 34.7×10^{-6} s^{-1}, respectively. A symmetrical transition state of the peroxide RO···OR is stabilised by the solvent to a lesser degree than the non-symmetrical transition state of the trioxide RO···OOR. Therefore, the dependence of the activation energy on the medium polarity is expressed to a greater degree for the latter.

Di-*tert*-butyl trioxide is an effective initiator of the chain decomposition of ozone in $CFCl_3$ (−23 °C).[89] The consumption of O_3 occurs in accordance with the first-order kinetic law; the value of the effective rate constant k_{eff} depends linearly on $[Bu^tOOOBu^t]^{1/2}$. This process is described by the following scheme:

$$Bu^tOOOBu^t \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Bu^tO^{\bullet} + Bu^tOO^{\bullet},$$

$$Bu^tOO^{\bullet} + O_3 \xrightarrow{k_2} Bu^tO^{\bullet} + 2O_2,$$

$$Bu^tO^{\bullet} + O_3 \xrightarrow{k_3} Bu^tOO^{\bullet} + O_2,$$

$$Bu^tO^{\bullet} \longrightarrow MeC(O)Me + Me^{\bullet},$$

$$Bu^tO^{\bullet} + RH \longrightarrow Bu^tOH + R^{\bullet},$$

$$2\,Bu^tOO^{\bullet} \longrightarrow 2\,Bu^tO^{\bullet} + O_2,$$
$$\qquad\qquad\quad \longrightarrow Bu^tOOBu^t + O_2,$$

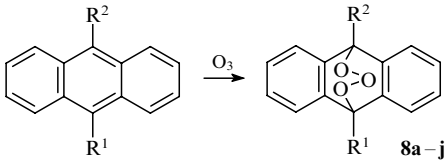
where RH = Bu^tOOOBu^t and its decomposition products.

The termination of the kinetic chains takes place as a result of cross-recombination of the radicals $Bu^tO^{\bullet}$ and $Bu^tOO^{\bullet}$ into the original trioxide; the contributions of irreversible consumption of the *tert*-butoxyl radical and the quadratic decay of the peroxy radicals are negligibly small. For this reason, the concentration of the trioxide does not change throughout the experiment ($\sim 10^4$ s), which simplifies the reaction scheme and yields the following expression for the effective rate constant for this reaction:

$$k_{eff} = 2(Kk_2k_3[Bu^tOOOBu^t])^{1/2},$$

where $K = k_1/k_{-1}$. The product of the rate constants for the reactions of O_3 with alkoxy and peroxy radicals was calculated from the linear dependence of k_{eff} on $[Bu^tOOOBu^t]_0^{1/2}$; k_3 was found to be equal to $\sim 1.7 \times 10^7$ litre mol^{-1} s^{-1} at −23 °C.

Transannular ozonides (cyclic analogues of dialkyl trioxides) are formed upon addition of ozone to anthracene and its 9,10-substituted derivative.[90–94]

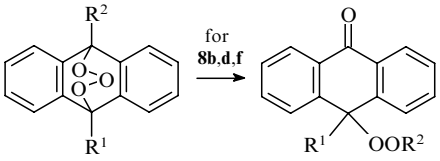


8a–j

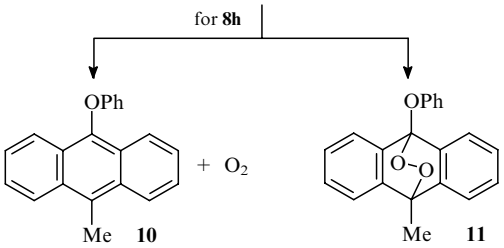
R^1 = H: R^2 = H (**a**), Me (**b**), Bu^t (**c**); R^1 = Me: R^2 = Me (**d**), Et (**e**), Bu^t (**f**), OMe (**g**), Ph (**h**), CH_2Ph (**i**); R^1 = R^2 = OMe (**j**).

The stability of transannular ozonides strongly depends on the nature of the substituents R^1 and R^2. The preparation of 9-(*tert*-butyl)-10-methylanthracene ozonide (**8f**) stable at room temperature has been described.[93] The latter was isolated in a crystalline state and studied by X-ray diffraction analysis. The decomposition of the ozonide **8f** obeys the first-order kinetic law and is characterised by the following activation parameters: $\log A = 14.6 \pm 0.3$ (s^{-1}); $E_a = 119.7 \pm 2.1$ kJ mol^{-1}. The activation energy of the decomposition of this compound exceeds those of the ozonides **8b** (E_a = 105 kJ mol^{-1})[92] and **8c** (E_a = 100 kJ mol^{-1}),[95] which points to stabilisation of transannular ozonides by bulky alkyl substituents. Interestingly, in the case of *cis*-1,2,3-trioxolanes their structures are destabilised by bulky substituents.

Heating of the ozonides **8b**, **8d** and **8f** results in their isomerisation into 10-methyl-10-(alkylperoxy)-9-anthrone (**9**) in nearly quantitative yields.[90, 91, 93]



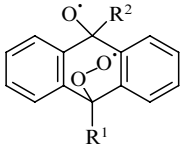
8b,d,f,h **9**



10 **11**

The decomposition of the ozonide **8h** is accompanied by evolution of molecular oxygen and a shift of the phenyl substituent to the oxygen atom; this affords 9-methyl-10-phenoxyanthracene (**10**). Endoperoxide **11** is formed in a small amount upon decomposition of the ozonide **8h**.

The radical decomposition of transannular ozonides was confirmed in the studies carried out in the presence of the free radical scavenger 2,4,6-tri-*tert*-butylphenol.[94] Selective homolysis of one of the O—O bonds is the first step in the decomposition of transannular ozonides and dialkyl trioxides.



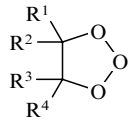
Attempts to detect the formation of singlet oxygen in the decomposition of the ozonide **8g** in the presence of the $^1O_2$ scavengers cyclohexene and 1,2-dimethylcyclohexene were unsuccessful.[94]

Table 12. Activation parameters of the thermal decomposition of 1,2,3-trioxolanes.

Ozonide	$\log A$ (s^{-1})	E_a /kJ mol^{-1}	Ref.
trans-**12a**	5.3	28.9	96
trans-**12b**	8.4	39.7	96
trans-**12c**	11	59.8	96
cis-**12b**	—	< 13.8	96
cis-**12d** (see [a])	—	—	97
12e (see [b])	14	37.7	97
12f	—	< 13.8	96
	—	33.5	96
	9	29.3	98

[a] $\tau_{1/2}$ = 0.06 s at −92 °C; [b] $\tau_{1/2}$ = 0.74 s at −92 °C.

Data on the kinetic regularities of the thermolysis of 1,2,3-trioxolanes (**12**) (primary ozonides) are relatively scarce (Table 12).



12a–f

$R^1 = R^3$ = H: $R^2 = R^4$ = Et (**a**), Pr^i (**b**), Bu^t (**c**), Me (**d**);
$R^1 = R^2 = R^3 = R^4$ = Me (**e**); $R^1 = Bu^n$, $R^2 = R^3 = R^4$ = H (**f**).

Their decomposition was studied by IR [96] and ^{1}H NMR spectroscopy [97] by following the changes in the ozonide concentration and the accumulation of the ozonide transformation products.[98] In all cases studied, the thermolysis of 1,2,3-trioxolanes obeyed the first-order kinetic law.[96–98]

The decomposition of primary ozonides yields a carbonyl compound $R^1R^2C{=}O$ and a carbonyl oxide R^3R^4COO; the existence of the latter in the liquid phase was confirmed by spectroscopic data.[99] The final decomposition products (1,2,4-trioxolanes, peroxides and polymeric peroxides) are formed in subsequent reactions of carbonyl oxide molecules with one another, with carbonyl compounds and with the solvent or special additives.

The homolytic cleavage of the O—O bond is the most typical reaction of all trioxides under consideration. Thermal stability of peroxides is the main feature which makes them different from trioxides. For example, the same rates of decomposition of di-*tert*-butyl trioxide and di-*tert*-butyl peroxide ($k = 1 \times 10^{-5}$ s^{-1}) are observed at −40 and 120 °C, respectively.

VII. Hydrotrioxides

Thermolysis of hydrotrioxides ROOOH was considered in detail in a recently published review;[100] therefore, here we shall confine ourselves to the description of the main characteristic features of this process.

The decomposition of ROOOH occurs in accordance with the first-order kinetic law.[101–110] The activation parameters for the decomposition of some hydrotrioxides are listed in Table 13. High proneness of hydrotrioxides to homoassociation and complexation with a solvent determines a broad range of activation energies and preexponential factors which are interrelated in a compensation law. The thermal decomposition rate constant of ROOOH increases with the enhancement of the electron-withdrawing properties [101–104] and polarity [105] of the substituent R.

In the thermal decomposition of hydrotrioxides, part of O_2 is evolved in a singlet excited state. In addition, the decomposition of some hydrotrioxides is accompanied by chemiluminescence in the visible region of the spectrum, which suggests the formation of free radicals during the thermolysis.

The thermal decomposition of hydrotrioxides may occur by different pathways:

$$\mathrm{ROOOH} \xrightarrow{a} \text{molecular products},$$

$$\mathrm{ROOOH + X^{\bullet}} \xrightarrow{b} \mathrm{ROOO^{\bullet} + XH} \longrightarrow \mathrm{RO^{\bullet} + O_2 + XH},$$

$$\mathrm{ROOOH} \xrightarrow{c} \mathrm{RO^{\bullet} + {}^{\bullet}OOH},$$

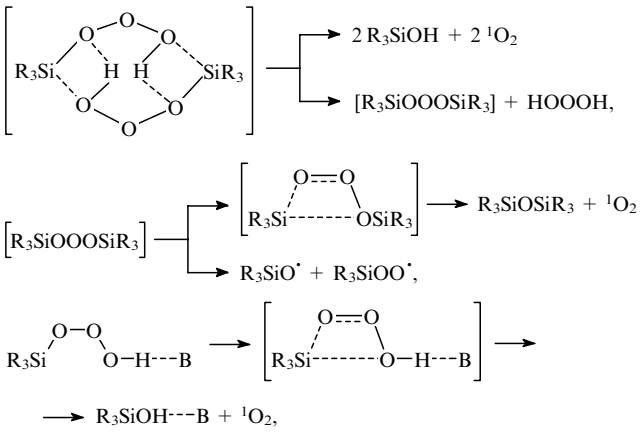
where $X^{\bullet}$ is any radical leaving the solvent cage and inducing the decomposition of ROOOH.

The first reaction (route *a*) takes place in the case of silyl hydrotrioxides. The decomposition mechanism of these compounds was studied in detail in the example of dimethylphenylsilyl hydrotrioxide.[104] The kinetic and activation parameters of this decomposition (high negative values of entropy of activation), considerable effects of substituents, dependence of the decomposition rate on the solvent polarity and the absence of the effect of the radical inhibitor (ionol) on the decomposition kinetics correlate with the predominantly molecular (> 90%) decomposition mechanism of silyl hydrotrioxides.

Table 13. Kinetic parameters of the thermal decomposition of hydrotrioxides.

Hydrotrioxide	Solvent	T /°C	$\log A$ (s^{-1})	E_a /kJ mol^{-1}	Ref.
$Me_2C(OMe)OOOH$	RH	−38 to −9	11.5	69.5	106
$PhMeC(OMe)OOOH$	Me_2CO	−30 to −10	16.0	83.3	103
$Me_2C(OPr^i)OOOH$	RH	−50 to 30	11.0	67.8	101
$MeC(OMe)_2OOOH$	RH	−20 to −10	15.6	86.6	102
$MeC(OEt)_2OOOH$	RH	−50 to −10	18.2	95.4	107
$MeCH(OH)OOOH$	RH	−70 to −30	3.08	29.3	108
$Me_2C(OH)OOOH$	RH	−30 to 8	7.93	56.1	105
$PhMeC(OH)OOOH$	Me_2CO	−35 to −15	13.4	70.7	103
Ph_3COOOH	CH_2Cl_2	−2 to 20	9.0	55.6	54
$EtMe_2COOOH$	CH_2Cl_2	7 to 27	11.5	77.8	54
$PhMe_2SiOOOH$	$(CD_3)_2CO$	−60 to −20	5.5	39.7	104
$Bu_3SiOOOH$	RH	−70 to −50	6.84	25.1	109
HOOOH	$(CD_3)_2CO$	−50 to 10	6.1	46.0	110

Note. RH is a starting compound used for the preparation of the corresponding hydrotrioxide.



B is a base.

The decomposition of ROOOH induced by free radicals (route *b*) is especially well pronounced in the case of cumyl hydrotrioxide.[111,112] The thermal decomposition of this compound in acetone ($E_a = 66.9 \pm 0.4$ kJ mol^{-1}; $\log A = 10.4 \pm 0.1$) is significantly retarded in the presence of ionol. The activation parameters of the reaction ($E_a = 100.0 \pm 0.4$ kJ mol^{-1}; $\log A = 16.4 \pm 0.1$) change under these conditions. In the absence of the inhibitor, the reaction products are dimethylphenylmethanol (the main product), acetophenone and isopropylphenyl hydroperoxide. The decomposition occurs in accordance with the following scheme:

$$PhMe_2COOOH \longrightarrow PhMe_2CO^{\bullet} + {}^{\bullet}OOH,$$

$$PhMe_2CO^{\bullet} ({}^{\bullet}OOH) + PhMe_2COOOH \longrightarrow$$

$$\longrightarrow PhMe_2COH\ (HOOH) + PhMe_2COO^{\bullet},$$

$$PhMe_2COO^{\bullet} \longrightarrow PhMe_2CO^{\bullet} + O_2,$$

$$PhMe_2CO^{\bullet} \longrightarrow PhC(O)Me + Me^{\bullet},$$

$$PhMe_2CO^{\bullet} + MeC(O)Me \longrightarrow PhMe_2COH + {}^{\bullet}CH_2C(O)Me,$$

$$PhMe_2C^{\bullet} + O_2 \longrightarrow PhMe_2COO^{\bullet},$$

$$PhMe_2COO^{\bullet} + MeC(O)Me \longrightarrow PhMe_2COOH + {}^{\bullet}CH_2C(O)Me.$$

In the presence of ionol (ArOH), the induced decomposition is suppressed and dimethylphenylmethanol is formed as the only organic reaction product.[111,112]

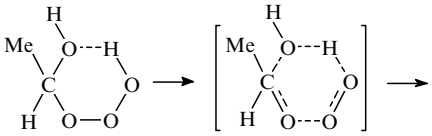
$$ROOOH \longrightarrow RO^{\bullet} + {}^{\bullet}OOH,$$

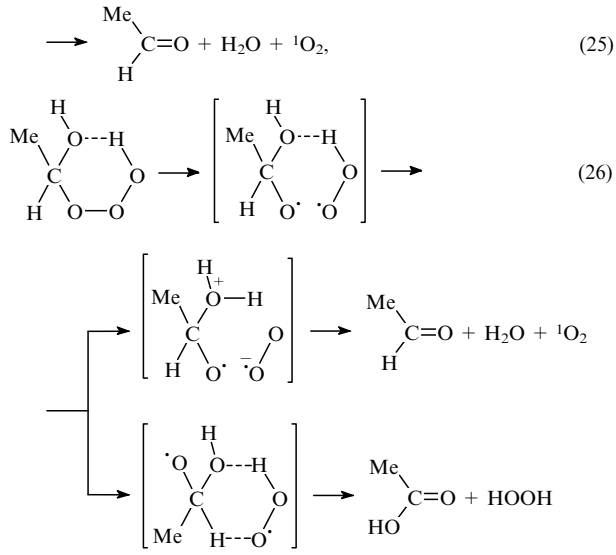
$$RO^{\bullet} ({}^{\bullet}OOH) + ArOH \longrightarrow ROH\ (HOOH) + ArO^{\bullet},$$

$$RO^{\bullet} ({}^{\bullet}OOH) + ArO^{\bullet} \longrightarrow \text{non-radical products},$$

R = $PhMe_2C$.

Intramolecular hydrogen bonds can be formed in hydrotrioxides that are derivatives of alcohols, esters and acetals containing an additional oxygen atom at the α-C atom. For these compounds, the molecular mechanism for the decomposition [reaction (25)] is feasible.[113] However, the experimental data altogether are more consistent with the radical mechanism of ROOOH decomposition; its first step includes the homolysis of the RO−OOH bond [reaction (26)] (the cleavage of ROOOH was demonstrated for α-hydrotrioxyethanol).





Self-association of ROOOH and the formation of intermolecular hydrogen bonds are responsible for the low exit of the radicals from the solvent cage.[114,115] The main factors determining the direction of decomposition of ROOOH are as follows:[100]

1. The nature of the atom bound to the hydrotrioxide group. The polarity of the X−O bond in the hydrotrioxide $R^1R^2R^3XOOOH$ is the higher, the greater is the difference between the electronegativities of X and O atoms. It may therefore be expected that in the case of silyl hydrotrioxides (X = Si) the contribution of the molecular route will be greater than in the case of C-hydrotrioxides.

2. Temperature. Hydrotrioxides are typical peroxide compounds. An increase in temperature determines the relative increase in the proportion of radical processes characterised by higher values of activation energies and preexponential factors. At low temperatures, polar rearrangements without formation of radical intermediates are more probable.

3. Solvent. Polar solvents accelerate molecular decomposition of ROOOH, whereas the homolysis of the O−O bond is less dependent on the nature of the solvent.

4. Presence of an oxygen atom in the α-position with respect to the hydrotrioxide group. Such hydrotrioxides are characterised by the formation of an intramolecular hydrogen bond. Their decomposition occurs by a non-chain radical route.

VIII. Acyl peroxides

1. Peroxy acids

Peroxycarboxylic acids RC(O)OOH possess high oxidative properties and low thermal stabilities.[6,116] Diverse reactions involving peroxy acids occur in solution and thus complicate the thermolysis itself. For example, hydrolysis in aqueous solutions is catalysed by mineral acids:

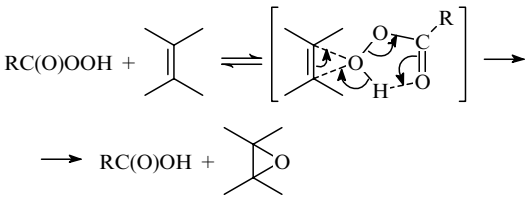
$$RC(O)OOH + H_2O \rightleftharpoons RC(O)OH + H_2O_2.$$

The non-catalytic decomposition of aliphatic and aromatic peroxy acids in aqueous solutions is second order with respect to the peroxy acid:[117,118]

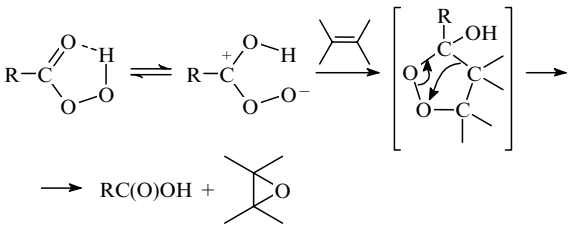
$$\frac{d[RC(O)OOH]}{dt} = k_{eff}[RC(O)OOH]^2.$$

The dependence of k_{eff} on the pH of the medium is described by a curve with a maximum at pH ≈ pK_a of the peroxy acid.[6]

Reactions of alkenes with peroxy acids yield epoxides.[119,120]



In addition to the cyclic concerted epoxidation mechanism, the following scheme for the 1,3-dipolar cycloaddition has been proposed:[121]



The reversible reaction of peroxy acids with aldehydes yields 1-hydroxyperoxides:

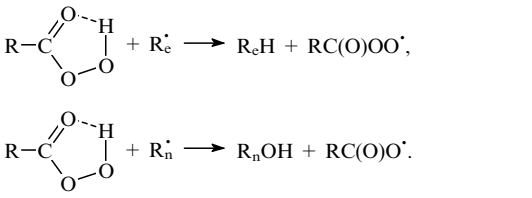
$$R^1C(O)OOH + R^2CHO \rightleftharpoons R^1C(O)OOCH(OH)R^2.$$

The kinetic regularities of the thermolysis of peroxy acids depend on the reaction conditions. According to the published data,[122,123] the thermolysis of peroxy acids in solutions occurs by a radical mechanism:

$$RC(O)OOH \longrightarrow RC(O)O^{\bullet} + HO^{\bullet},$$

$$RC(O)O^{\bullet} \xrightarrow{\text{fast}} R^{\bullet} + CO_2.$$

A significant contribution to the thermolysis of peroxy acids is made by induced decomposition steps:



Oxygen-containing electrophilic radicals $R_e^{\bullet}$ attack the hydrogen atom, but do not react with the O—O bond. This reaction yields acylperoxy radicals. Nucleophilic radicals $R_n^{\bullet}$ (mainly, alkyl radicals) attack the peroxide group to give alcohols R_nOH. The presence or the absence of oxygen in the solution is the crucial factor which determines the route of radical decomposition of peroxy acids. In the presence of O_2, nucleophilic radicals $R_n^{\bullet}$ are converted into electrophilic radicals $R_nOO^{\bullet}$. In the absence of oxygen, nucleophilic radicals $R_n^{\bullet}$ react with the solvent (provided that the latter acts as a donor of hydrogen atoms) to give radicals $Sol^{\bullet}$ or with a peroxy acid to give an alcohol R_nOH:

$$RC(O)OOH + R_n^{\bullet} \longrightarrow R_nOH + R^{\bullet} + CO_2.$$

Radicals $Sol^{\bullet}$ react in a similar way.

Table 14. Thermolysis of the aliphatic peroxy acids RC(O)OOH in methanol at 25 °C.[124]

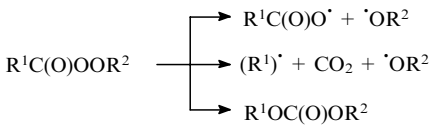
R	$10^5 k_1$ /s^{-1}	R	$10^5 k_1$ /s^{-1}
n-C_7H_{15}	1.75	n-$C_{11}H_{23}$	2.35
n-C_8H_{17}	2.23	n-$C_{12}H_{25}$	1.75
n-C_9H_{19}	2.93	n-$C_{13}H_{27}$	1.75
n-$C_{10}H_{21}$	1.60		

The thermal stabilities of peroxy acids also depend on the nature of the acid. The data illustrating the dependence of decomposition rate constants of peroxy acids on the length of the aliphatic chain are listed in Table 14.[124]

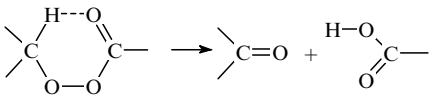
2. Peroxy esters and peroxy carbonates

Thermolysis of peroxy esters has been discussed in several reviews.[125–130] The main peculiarities of their decomposition mechanisms are related to asymmetry and the presence of an acyl group, which favour competition between the homolytic and heterolytic decomposition routes and their rearrangements.

Depending on the structure of peroxy esters, their thermolysis involves the homolysis of one or two bonds simultaneously. Peroxy esters can also undergo rearrangements.



The presence of α-hydrogen atoms favours the formation of a ketone and a carboxylic acid as a result of cyclic redistribution of the bonds.



Bartlett[130] proposed the classification of the peroxy esters $R^1C(O)OOR^2$ into two groups according to the mechanism of their thermal decomposition. In peroxy esters of the first group, the radical R^1 cannot exist in the form of a relatively stable free radical, whereas in peroxy esters of the second group the radicals R^1 can be stabilised due to delocalisation of the unpaired electron.

To the first type one may assign such peroxy esters as *tert*-butyl peroxyacetate and peroxybenzoate. The second group includes, in particular, *tert*-butyl peroxyphenyl acetate and its derivatives along with fairly unstable peroxy esters with $R^1 = Ph_3C$. Peroxy esters of the second group decompose much faster than their first-group analogues; their thermolysis is usually accompanied by simultaneous cleavage of two bonds, *viz.*, O—O and R—C. The decomposition rate of peroxy esters is usually the lower, the stronger is the starting carboxylic acid.

Denisov[131,132] and Pokidova[133] used the semi-empirical parabolic model of a bimolecular reaction modified for the calculation of kinetic and thermodynamic parameters of decomposition of molecules into radicals with simultaneous cleavage of several bonds for the determination of the corresponding parameters for a series of peroxy esters that dissociate presumably with simultaneous cleavage of R—C and O—O bonds. It was found also that with regard to the structure of the reaction centre, concerted decomposition is similar to addition reactions of carbon-centred radicals to the carbonyl group and of oxygen-centred radicals to alkenes.

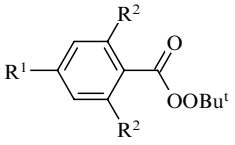
A comparison of decomposition rates of dialkyl peroxides, peroxy esters and diacyl peroxides revealed that the presence of a carbonyl group at the α-carbon atom favours the cleavage of the O—O bond due to the conjugation of the free valence formed with the C=O group. On the whole, the effects of the substituents in the starting peroxide are rather diverse. The introduction of vinyl, phenyl and alkyl groups into the acyl fragment sharply increases the decomposition rate. Besides the inductive effect of substituents, this entails changes in the decomposition mechanism: fragmentation with simultaneous cleavage of two bonds caused by the weakening of the R—C(O) bond even in the transition state and stabilisation of the radical R^1 due to mesomeric and hyperconjugation effects of the substituents takes place instead of the cleavage of one O—O bond. The dependence of the homolytic decomposition of the peroxy esters $R^1R^2R^3CC(O)OOBu^t$ on the size of the alkyl substituents can be illustrated by the data

Table 15. Kinetic parameters of the thermolysis of $R^1R^2R^3CC(O)OOBu^t$ in ethylbenzene at 60 °C.[134]

R^1	R^2	R^3	k_1 (relative)
Me	Me	Me	1.0
Me	Me	Et	1.29
Me	Me	n-C_8H_{17}	1.73
Me	Me	Bu^i	2.30
Et	Et	Et	3.19
Et	Et	Pr^i	6.50
Me	Me	Bu^t	3.40
Me	Me	Bu^tCH_2	2.60
Pr^i	Pr^i	Pr^i	32

presented in Table 15.[134] Here, both the steric strain created in a peroxy ester by the substituents R^1-R^3 and the inductive effects must be taken into consideration.

The introduction of *ortho*-substituents into the phenyl group of peroxybenzoates **13** leads to destabilisation of the ground state due to rotation of the carboxy group and its exit from the conjugation with the aromatic ring. As a result, the decomposition rates of peroxides **13c**,**d** are increased dramatically (Table 16).[135]



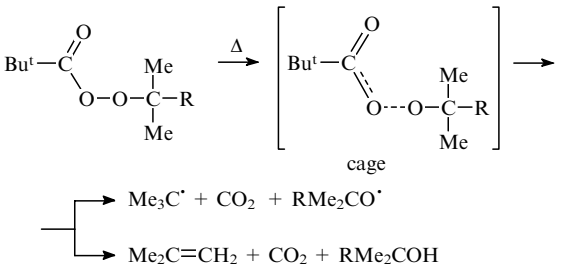
13a–d

$R^1 = R^2 =$ H (**a**); $R^1 =$ Me: $R^2 =$ H (**b**), Me (**c**); $R^1 = R^2 = Bu^t$ (**d**).

Table 16. Kinetic and thermodynamic parameters of the thermal decomposition of peroxybenzoates **13a–d**.[135]

Peroxide **13**	R^1	R^2	k_1 /s^{-1} (at 100 °C in cumene)	$\Delta H^{\neq}$ /kJ mol^{-1}
a	H	H	9.7×10^{-6}	142.3
b	Me	H	1.2×10^{-5}	134.7
c	Me	Me	1.1×10^{-4}	133.5
d	Bu^t	Bu^t	2.8×10^{-4}	137.7

It is of note that the decomposition of peroxyacetate occurs several times more slowly than that of peroxybenzoates. The thermolysis of *tert*-alkyl peroxypivalates in the solvent cage[136–138] affords equimolar amounts of *tert*-butyl and *tert*-alkoxyl radicals as a result of concerted cleavage of two bonds.



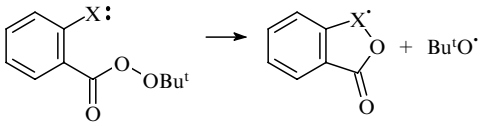
R = Me, Et, Pr, Pr^i, Bu^i, $PhCH_2$.

The reaction products correspond to nearly quantitative β-dissociation into alkyl and alkoxyl radicals and CO_2.

The transition from the simple cleavage of the O–O bond to the decomposition with simultaneous cleavage of the O–O bond and decarboxylation results in a simultaneous decrease in the enthalpy and entropy of activation.

In the case of thermolysis of peroxy esters containing an ^{18}O-labelled carbonyl group, the reverse recombination of the $RC(O)O^{\bullet}$ radical in the solvent cage leads to the averaging of the distribution of the label between the carbonyl and peroxide oxygen atoms. An increase in the solvent viscosity favours reverse recombination and increases the degree of averaging of the label content. The secondary isotope effect (k^H/k^D) observed in the thermal decomposition of *tert*-butyl peroxyacetate is equal to unity,[139] which points to a non-synchronous cleavage of the bonds in its decomposition. At the same time, the magnitude of the isotope effect for *tert*-butyl *p*-methylphenylperoxyacetate and its derivatives markedly exceeds unity [1.03–1.06 per one H(D) atom], which unequivocally testifies to a synchronous mechanism of their decomposition.[139–142]

The effects of substituents able to interact directly with the peroxide group and thus accelerate the homolysis of the peroxide bond are presented in Table 17.[143] As can be seen from these data, the presence of an unshared electron pair in the groups X in the *ortho*-position of the benzene rings of *tert*-butyl peroxybenzoates favours the formation of relatively stable radicals due to the cleavage of the O–O bond.



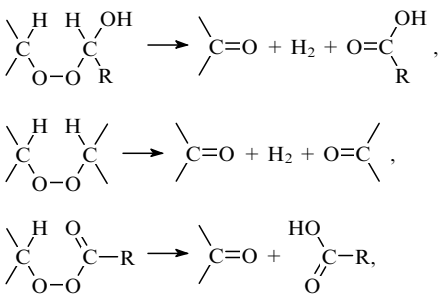
This effect of the substituent was termed by Martin[143] as 'anchimeric acceleration'. Presumably, such substituents have a similar effect on the decomposition of diacyl peroxides.

Table 17. Kinetic and thermodynamic parameters of the decomposition of *tert*-butyl *o*-X-peroxybenzoates in chlorobenzene.[143]

X	k (relative) at 60 °C	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J mol^{-1} K^{-1}
PhS	2.8×10^4	96.2	−14.2
MeS	1.8×10^4	94.6	−23.0
PhS(O)	73	12.3	18.8
$Ph_2C{=}CH$	67	110	−20.9
I	54	117	−2.9
Bu^t	3.8	143.1	52.3
$MeS(O)_2$	0.4[a]	159	39.7
$PhC{\equiv}C$	1.8	148.1	62.8
H	1.0	142.7	41.8

[a] With respect to H at 120 °C.

The presence of a C–H bond at the α-carbon atom enables the decomposition of peroxy esters according to a scheme acceptable for various classes of peroxides.[144]

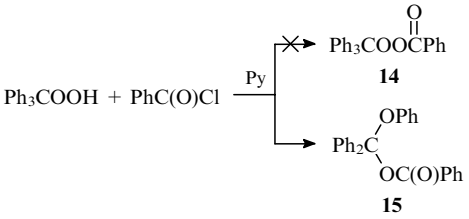


R = H, Alk, Ar.

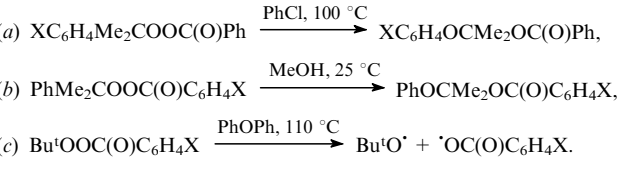
In solution, the decomposition of peroxy esters by this concerted mechanism yields carboxylic acids and aldehydes or ketones.

The thermolysis of primary (n-butyl and isobutyl) and secondary (*sec*-butyl and cyclohexyl) peroxyacetates in the liquid phase proceeds by a concerted six-centred decomposition mechanism (see above) and affords a carboxylic acid and a carbonyl compound. Upon thermal decomposition in the gas phase, the same peroxy esters yield products corresponding to ordinary decomposition with a primary cleavage of one O—O bond. Thus, the solvent favours the non-radical concerted mechanism of thermolysis of primary and secondary peroxy esters.

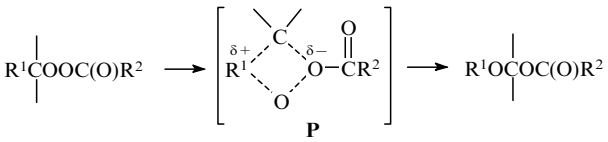
In addition to homolysis, the decomposition of peroxy esters can be realised by a heterolytic route. Back in 1931, Wieland and Mayer [145] obtained α-phenoxy ester (**15**) instead of trityl peroxybenzoate (**14**):



This reaction has been named the Criegee rearrangement.[146] The kinetic parameters of the isomerisation (*a*, *b*) and homolysis (*c*) of various tertiary peroxybenzoates are listed in Table 18.[5, 127]

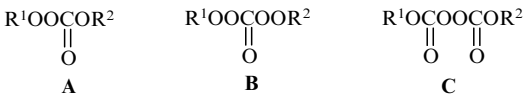


Heterolysis of the peroxide bond under the influence of neighbouring groups with oppositely directed effects is accompanied by migration of a hydrocarbon radical from the carbon atom to the oxygen atom. Aralkyl, decalyl, 1,3,3-trialkylcyclohexyl and some other groups and fragments of strong carboxylic acids (trifluoroacetic, trichloroacetic, *p*-nitrobenzoic, *etc*.) in the ester moiety favour the heterolytic rearrangement in the hydroperoxide moiety. In many cases, the heterolysis competes with the homolysis in the decomposition of peroxy esters. The heterolysis is enhanced with an increase in the ionising ability of the medium and in the presence of acidic or basic catalysts. According to Yablokov,[127] the heterolytic rearrangement occurs *via* cyclic complex **P**.



Charge separation does not reach the state of free ions or contact ion pairs as can be judged from the retention of the ^{18}O label in the carbonyl group and the lack of transesterification upon the rearrangement (the peroxy ester anion is not interchanged for the salt anion).

Organic peroxide derivatives of carbonic acid (peroxycarbonates) are divided into three main groups, *viz*., monoperoxycarbonates (**A**), diperoxycarbonates (**B**) and peroxydicarbonates (**C**).



All these compounds are 'overloaded' with oxygen atoms and are therefore rather unstable (Table 19). (For comparison, effective kinetic characteristics of other types of peroxides are listed). Low stability of peroxycarbonates also manifests itself in a significant contribution of induced decomposition to the overall process.

Table 18. Kinetics of decomposition of various peroxy esters in solution.

Type of reaction	*p*-X	$10^4 k$ /s^{-1}	E_a /kJ mol^{-1}	log *A* (s^{-1})
a	H	5.8	115	12.94
	Cl	1.92	121	13.28
	Br	2.68	119	13.19
	NO_2	0.945	129	14.09
b	H	26	90	14.14
	Me	19	83	12.80
	Br	70	87	14.05
	NO_2	282	84	13.15
c	H	0.28	156	16.85
	Me	0.32	151	16.11
	Cl	0.16	164	17.66
	NO_2	0.16	172	18.22

The decomposition of symmetrical peroxydicarbonates occurs in accordance with a simple scheme which involves primary cleavage of the O—O bond followed by fast decarboxylation of the acyloxy radicals.

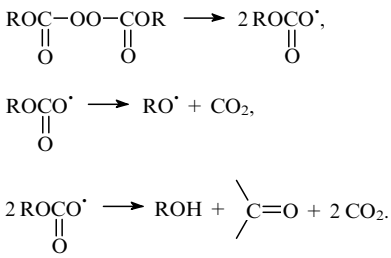


Table 19. Effective kinetic parameters of the thermolysis of peroxides in dilute benzene solutions.

Peroxide	*T* corresponding to $\tau_{1/2}$ /°C		E_a /kJ mol^{-1}
	1 min	1 h	
Acetylperoxy isopropyl carbonate	110	90	122.9
Acetylperoxy 2-ethylhexyl carbonate	110	90	122.9
Benzoylperoxy isopropyl carbonate	112	90	127.6
Diisopropyl peroxydicarbonate	102	47	112
tert-Butylperoxy isopropyl carbonate	165	102	137.3
tert-Butylperoxy 2-ethylhexyl carbonate	164	99	144.5
tert-Butylperoxy octadecyl carbonate	170	104	139.2
tert-Butylperoxy cyclohexyl carbonate	160	103	136.2
tert-Butylperoxy benzoyl carbonate	164	109	142.0
tert-Butylperoxy 2-phenoxyethyl carbonate	167	101	137.3
Benzoyl peroxide	133	72	126
tert-Butyl peroxybenzoate	166	105	143
Di-*tert*-butyl peroxide	193	126	152

The thermolysis of dicyclohexyl peroxydicarbonate in a pressure range from 0.1 to 500 MPa [147, 148] revealed that its first step includes the cleavage of the O—O bond and the formation of oxycarboxy radicals. The volume effects of activation in benzene, toluene and acetonitrile are equally high (11 ± 0.5 cm^3 mol^{-1}), which is attributed to the changes in the ratios of diffusion and recombination reactions occurring in the solvent cage and is regarded as evidence in favour of the cleavage of one O—O bond in the first decomposition step.

For a detailed description of peroxycarbonate thermolysis see Refs 10 and 149.

3. Diacyl peroxides

Decomposition of diacyl peroxides upon heating in solution was the subject of extensive studies which allowed identification of reaction products and elucidation of mechanisms and kinetic regularities of this process. The thermolysis of such peroxides occurs by two main competing routes with radical and non-radical mechanisms.

The homolytic decomposition begins with the cleavage of the O—O bond:

$$R^1C(O)OOC(O)R^2 \longrightarrow R^1C(O)O^{\bullet} + {}^{\bullet}OC(O)R^2.$$

The solvent cage retains the radicals in the form of a radical pair and thus favours their recombination. Therefore, in the case of incomplete decomposition of a peroxide containing an isotopically labelled carbonyl oxygen the distribution of the latter will be averaged as a result of intraradical exchange:



This is followed by decarboxylation

$$RC(O)O^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

and further reactions of the radicals with themselves and the solvent.

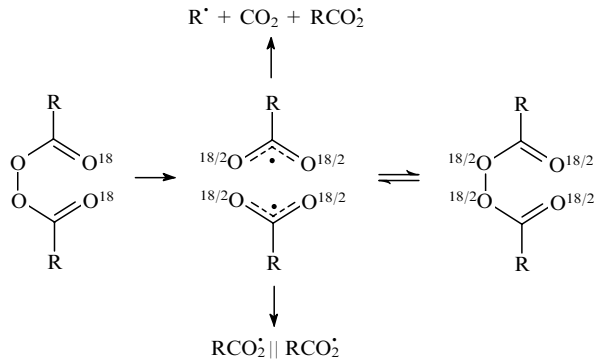
The averaging of the ^{18}O label over the carbonyl oxygen atom of the starting diacyl peroxide upon its partial thermolysis provides direct evidence for the initial formation of a contact radical pair. This is confirmed by the following facts:[150, 151]

1. The thermolysis rate of cyclopropanecarbonyl peroxide decreases with an increase in the solvent viscosity, whereas the averaging rate of ^{18}O diminishes to a much lesser degree.

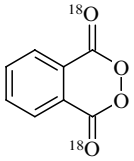
2. The enthalpy of activation of the decomposition of this peroxide exceeds the enthalpy of activation of the averaging of the ^{18}O content in CCl_4 by 8.4–11.7 kJ mol^{-1}. The entropy of activation of the averaging of ^{18}O is characterised by a small, although positive value in contrast to high negative values of entropies of activation of ordinary concerted sigmatropic rearrangements.

3. Substitution of the phenyl group for the cyclopropyl group leads to a decrease in the averaging rate of the label.

Hence, the mechanism of averaging of the isotopic label fits into the following scheme:



It is interesting to note that in the cyclic phthaloyl peroxide



the averaging of the isotopic label in solution at 80 °C occurs 40 times faster than its decomposition.[151]

Quantum-chemical studies (B3LYP calculations) of formyl peroxide [152] confirmed the averaging mechanism involving the formation of a σ-acyloxy radical pair.

A high contribution of induced decomposition of acyl peroxides to the overall rate of their thermolysis in solution is yet another characteristic feature.[153–155] For example, induced decomposition of benzoyl peroxide includes the following steps:

$$PhC(O)OOC(O)Ph \xrightarrow{k_d} \underset{\text{in the cage}}{\left[2\,PhCO_2^{\bullet}\right]} \xrightarrow{k_i} 2\,PhCO_2^{\bullet},$$

$$\left[2\,PhCO_2^{\bullet}\right] \longrightarrow PhOC(O)Ph + CO_2,$$

$$PhCO_2^{\bullet} + SolH \xrightarrow{k} PhC(O)OH + Sol^{\bullet},$$

$$Sol^{\bullet} + PhC(O)OOC(O)Ph \longrightarrow PhC(O)OSol + PhCO_2^{\bullet},$$

$$Sol^{\bullet} + Sol^{\bullet} \xrightarrow{2k_t} Sol{-}Sol.$$

The corresponding expression for the reaction rate appears as:

$$W = k_d[PhC(O)OOC(O)Ph] + k_{ind}[PhC(O)OOC(O)Ph]^{3/2},$$

where $k_{ind} = kk_i^{1/2}(2k_t)^{-1/2}$ and $k_i = 2ek_d$, e is the proportion of radicals that exit the cage into the bulk.

The kinetic parameters of reactions of the radicals $Me^{\bullet}$, $(Bu^t)^{\bullet}$ and $PhCH_2^{\bullet}$ with various peroxides were calculated [154] using a parabolic model for bimolecular reactions (Table 20).

The rate of chain decomposition of benzoyl peroxide in the alcohols R^1R^2CHOH is increased by an order of magnitude due to the reaction of the radicals $R^1R^2C^{\bullet}OH$ with the peroxide. This reaction was also studied using the aforementioned model.[155, 156]

The ester RC(O)OR is formed from acetyl and benzoyl peroxides as a result of recombination of $R^{\bullet}$ and $RC(O)O^{\bullet}$.

The volume of activation $\Delta V^{\neq}$, *i.e.*, the change in the volume of a molecule upon the formation of an activated complex, in the cleavage of one bond approximates to 10 cm^3 mol^{-1}, whereas that in the concerted cleavage of two bonds is 2–5 cm^3 mol^{-1} (see Ref. 11). The $\Delta V^{\neq}$ values for the thermolysis of diacyl peroxides without rearrangement vary from 2 to 5 cm^3 mol^{-1}. The volumes of activation for the thermolysis of the following compounds are listed in the table below: [157, 158]

Peroxide	$\Delta V^{\neq}$ /cm^3 mol^{-1}
Bis(3,5,5-trimethylhexanoyl) peroxide	2–3
Dioctanoyl peroxide	2–3
Dibenzoyl peroxide	1–2

Asymmetric structures of diacyl peroxides and the use of polar solvents favour their decomposition into esters by non-radical routes involving both ionic and concerted mechanisms.

The formation of an ester ArC(O)OC(O)OAlk in the thermolysis of ArC(O)OOC(O)Alk as a result of a concerted rearrangement concomitant with a carboxy inversion was first reported by Leffler.[159, 160] Here, the alkyl group migrates to the electron-deficient oxygen atom resulting in a nearly complete inversion of the configuration of the migrating group.

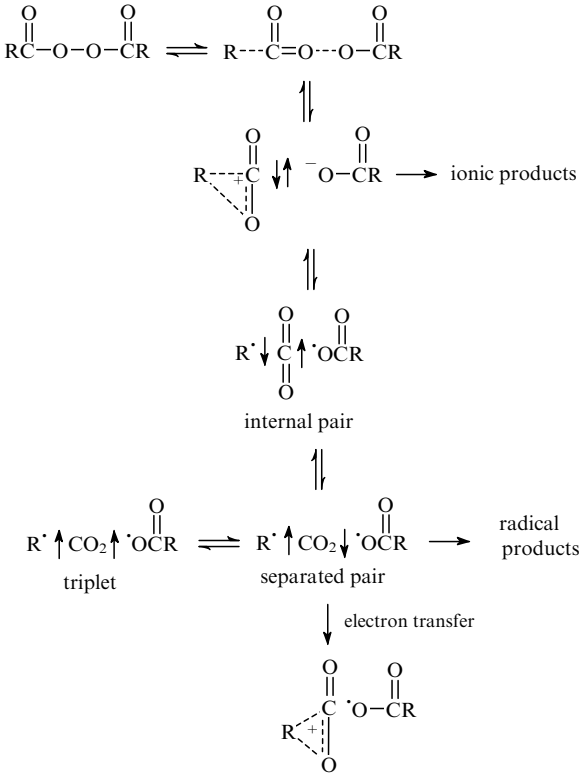
Table 20. Kinetic parameters of the bimolecular reactions of the radicals $Me^{\bullet}$, $(Bu^t)^{\bullet}$ and $PhCH_2^{\bullet}$ with some peroxides at 80 °C.

Peroxide	E_a /kJ mol^{-1}			k_1 /litre mol^{-1} s^{-1}		
	$Me^{\bullet}$	$(Bu^t)^{\bullet}$	$PhCH_2^{\bullet}$	$Me^{\bullet}$	$(Bu^t)^{\bullet}$	$PhCH_2^{\bullet}$
H_2O_2	36.7	33.6	48.6	1.51×10^4	1.31×10^4	3.14×10^2
Bu^tOOH	27.5	24.8	37.9	7.76×10^4	1.96×10^5	2.17×10^3
$[MeC(O)O]_2$	37.3	39.8	48.0	5.40×10^3	2.40×10^3	1.40×10^2
$[PhC(O)O]_2$	38.7	41.1	49.6	3.30×10^3	1.50×10^3	78.0
Bu^tOOBu^t	50	56	–	68	8.6	–

In this case, the redistribution of the ^{18}O label between the carbonyl and the peroxide oxygen atoms is either insignificant or altogether absent.[161–170] The carboxy inversion is enhanced in the presence of Brønsted and Lewis acids.

Carboxy inversion is characterised by higher negative volume of activation and lower energy and entropy of activation than an ordinary radical decay.[167] The ionic type of this reaction was confirmed by a strong dependence of the decomposition rate on the changes in the electron-donor or electron-withdrawing properties of the aryl and alkyl groups.

The formation of compound RSol in the reaction of the radicals with the solvent and the formation of the recombination and disproportionation products ArR, RH and ArC(O)OR is yet another characteristic feature of the decomposition route of diacyl peroxides. An analysis of kinetics and compositions of decomposition products led Walling to suggest[165–167] that both the radical and ionic pathways are realised through the same rate-limiting step in accordance with the following scheme:

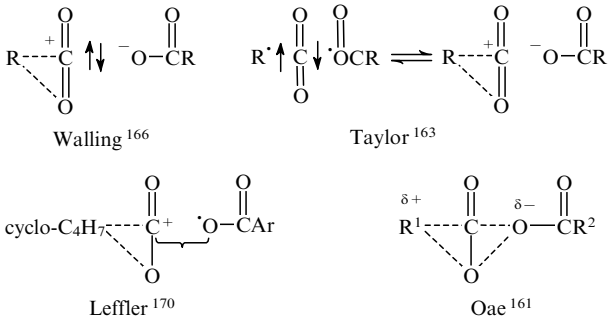


This scheme includes the interaction and disproportionation of radicals. Supporting evidence for this mechanism was obtained in the studies of chemically induced dynamic nuclear polarisation (CIDNP) in the rearrangement products formed upon decomposition of *tert*-butylacetyl-*m*-chlorobenzoyl peroxide.

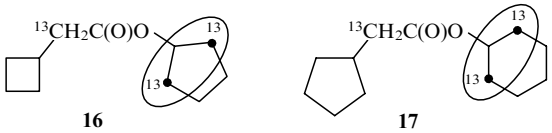
The formation of an ester from diacyl peroxide ($PhMe_2CCH_2.COO)_2$ as a result of rearrangement on silica gel was also attributed to the electron transfer in the neophylcarbonyloxy radical pair $\{PhMe_2CCH_2C(O)O^{\bullet}\ {}^{\bullet}OC(O)CH_2CMe_2Ph\}$.[171] If the reaction is carried out on silica gel, the reaction rate increases considerably in comparison with the reaction carried out in solution. The decomposition products of $(PhMe_2CCH_2COO)_2$ obtained in solution and on the surface of silica gel are also different. In the latter case, alkanes are not formed.

According to Taylor,[163] the electron transfer mechanism cannot be used for interpreting the results of thermal decomposition of cyclopropylacetyl cyclobutanecarbonyl peroxide and 4-pentanoyl *m*-chlorobenzoyl peroxide. Evidence in favour of the formation of an ion pair-like intermediate in the decomposition of a peroxide containing an R group able to form a stable cation was obtained.[164] An argument against the formation of a radical pair is the low value of CIDNP or its complete absence from the systems under study. However, some authors[162] made reference to the difficulty in detecting polarised signals in complex samples and the strong dependence of experimental values of CIDNP on the relative rate of the reaction and on spin relaxation.

The following structures have been proposed for the intermediate species formed in the first step by different groups of investigators:



Special mention should be made of the studies[172–174] of chemical polarisation of nuclei in the decomposition products formed in the thermolysis of cycloalkanoyl and cycloalkylacetyl peroxides in benzene and a benzene–$CHBr_3$ mixture; the data obtained testify to a radical mechanism of their formation. However, chemical polarisation of nuclei takes place only in those cases where relatively long-living radicals (methyl, cyclopropyl) or radicals stabilised by the π-bond are formed. No CIDNP was observed in other peroxy esters, which points either to a non-radical decomposition mechanism or the exclusive formation of short-living (less than 10^{-10} s) radicals in the solvent cage. The thermolysis of cyclobutyl and cyclopentylacetyl peroxides yields esters **16** and **17**, respectively. ^{13}C labelling studies have shown that in this case we deal with a skeletal rearrangement in the absence of hydride transitions.



The absence of hydride transitions points to the formation of an ion–radical pair in the transition state where the carbocation-like species undergo skeletal rearrangement:

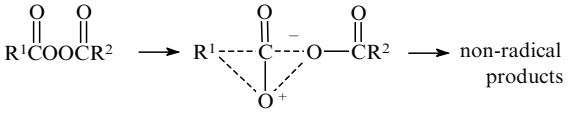
$$RC(O)OOC(O)R \longrightarrow [R^{\bullet}CO_2^{\bullet}OC(O)R \rightleftharpoons R^{+}CO_2^{-}OC(O)R],$$

R = cyclo-$C_4H_7CH_2$, cyclo-$C_5H_9CH_2$.

However, the energies and lifetimes of these species are not high enough for hydride transitions to occur.

Studies of a series of asymmetrical diacyl peroxides [175–177] have shown that in the case of electron-donor and/or polar substituents thermolysis in nonpolar solvents proceeds by a radical route and yields acyl alkyl carbonates, alkenes, carboxylic acids and/or esters.

The proportion of heterolytic processes increases with stabilisation of the negative charge formed in the transition state.



The contribution of the homolytic process to the thermal decomposition of diacyl peroxides shows a good correlation with the energy of dissociation of the R–H bond, which characterises the stability of the radical R.

Studies on chemical polarisation of nuclei ^1H and ^{13}C in the thermolysis products of these peroxides in CCl_4 revealed [178] that the contribution of secondary processes occurring outside the solvent cage diminishes with an increase in temperature.

IX. Sulfonyl peroxides

1. Alkanesulfonylperoxy acids

The thermal decomposition of the decanesulfonylperoxy acid $C_{10}H_{21}SO_2OOH$ (R^1SO_2OOH) in n-decane (R^2H) in an atmosphere of argon results in quantitative yields of $C_{10}H_{21}SO_2OH$ (R^1SO_2OH) and a relatively high yield of the alcohols $C_{10}H_{21}OH$ (R^2OH) (ketones and H_2O are formed in trace amounts).[179]

According to data from gas chromatography/mass spectrometry, the decomposition of decanesulfonylperoxy acid yields a mixture of primary and secondary alcohols. n-Decanol is not formed in noticeable amounts, whereas the ratio of decan-2-, -3-, -4- and -5-ols formed is close to the statistical value (1.2 : 1.0 : 1.2 : 1.15). With an increase in the initial concentration (c_0) of the peroxy acid, the total yield of *sec*-decanols with respect to the peroxy acid decreases (Table 21). The yield of the alcohols does not virtually depend on the nature of the bubbling gas (O_2 or Ar). This suggests that sulfonylperoxy acids are effective reagents for oxidative functionalisation of even non-activated C–H bonds of organic compounds.[180]

Table 21. Yields of the secondary alcohols in the decomposition of decanesulfonylperoxy acid in oxygen-saturated n-decane at 50 °C.

$10^2\ c_0$ /mol litre^{-1}	$10^2\ \Delta c$ /mol litre^{-1}	10^2 [sec-$C_{10}H_{21}OH$] /mol litre^{-1}	[sec-$C_{10}H_{21}OH$]/Δc (%)
0.82	0.77	0.58	75
2.6	2.6	1.5	57
6.5	6.5	2.3	35
7.6	7.5	2.0	27
11.0	11.0	2.4	22

Ketones are accumulated in much smaller amounts in comparison with alcohols (~0.6%–0.7% of the alcohol yield) owing to their ability to react fast with the peroxy acid. For example, the effective rate constant for the reaction of decanesulfonylperoxy acid with ethyl methyl ketone in n-decane at 50 °C is 0.5 litre mol^{-1} s^{-1} (see Ref. 181). Indeed, decanesulfonylperoxy acid is an extremely potent oxidant of ketones in the Baeyer–Villiger reaction.[182–184]

The thermolysis of decanesulfonylperoxy acid is complicated by its reaction with the solvent and homoassociation. As a consequence, the rate of this thermal decomposition depends on reaction conditions, in the first place, on the concentration of the sulfonylperoxy acid used. For this very reason, the kinetics of thermal decomposition of the sulfonylperoxy acid was formally characterised by an effective first-order rate constant.[179] The value of k_{eff} increases with an increase in the temperature and initial concentration of the peroxy acid (c_0).

Substitution of CCl_4 for n-decane leads to a significant decrease in the decomposition rate. Thus at 70 °C and $c_0 = 0.07$ mol litre^{-1} the half-lives of decanesulfonylperoxy acid in *n*-decane and CCl_4 are 4 and 33 min, respectively.

Some experimental results suggest the formation of free radicals in the thermolysis of sulfonylperoxy acids.

1. The thermal decomposition of an $R^1SO_2OOH-R^2H-O_2$ system is accompanied by consumption of oxygen.

2. The decomposition of R^1SO_2OOH in an atmosphere of argon proceeds much faster than that in the presence of oxygen. For example, at $c_0 = 9\times10^{-3}$ mol litre^{-1} the initial decomposition rates of sulfonylperoxy acid in an atmosphere of O_2 and Ar are 1.3×10^{-5} and 4×10^{-6} s^{-1}, respectively. In an atmosphere of argon, the reaction rate decreases with time; for the 60% conversion of R^1SO_2OOH in Ar and O_2, the decomposition rates are levelled off.

3. The decomposition rate of peroxy acid in an $R^1SO_2OOH-R^2H-Ar$ system in the presence of the free radical scavenger 2,2,6,6-tetramethyl-4-hydroxypiperidin-*N*-oxyl is essentially the same as that in the $R^1SO_2OOH-R^2H-O_2$ system.

Based on the data obtained, the following mechanism has been proposed for the thermal decomposition of the alkanesulfonylperoxy acids R^1SO_2OOH in R^2H in an atmosphere of O_2:[179, 181]

$$R^1SO_2OOH \longrightarrow R^1SO_2O^{\bullet} + {}^{\bullet}OH,$$

$$R^1SO_2OOH + R^2H \longrightarrow \begin{cases} R^1SO_2OH + R^2OH, \\ R^1SO_2O^{\bullet} + H_2O + (R^2)^{\bullet}, \end{cases}$$

$$R^1SO_2OOH + R^1SO_2OOH \rightleftharpoons K,$$

$$K \longrightarrow \begin{cases} 2\,R^1SO_2OH + O_2, \\ R^1SO_2O^{\bullet} + H_2O + R^1SO_2OO^{\bullet}, \end{cases}$$

$$HO^{\bullet} + R^2H \longrightarrow H_2O + (R^2)^{\bullet},$$

$$R^1SO_2O^{\bullet} + R^2H \longrightarrow R^1SO_2OH + (R^2)^{\bullet},$$

$$R^1SO_2OO^{\bullet} + R^2H \longrightarrow R^1SO_2OOH + (R^2)^{\bullet},$$

$$(R^2)^{\bullet} + O_2 \longrightarrow R^2OO^{\bullet},$$

$$R^2OO^{\bullet} + R^2OO^{\bullet} \longrightarrow \rangle C{=}O + R^2OH + O_2,$$

$$\rangle C{=}O + R^1SO_2OOH \longrightarrow {-}O\rangle C{=}O + R^1SO_2OH,$$

where C is a complex comprising two sulfonylperoxy acid molecules.

With regard to their oxidative capacities, alkanesulfonylperoxy acids are in no way inferior to such a potent oxidant as trifluoroperoxyacetic acid, but even surpass it in many aspects.

2. Acetyl cyclohexylsulfonyl peroxide

Of prime interest among other representatives of sulfonylperoxy acid derivatives is acetyl cyclohexylsulfonyl peroxide [cyclo-$C_6H_{11}SO_2OOC(O)Me$ (ACSP)] which has found wide industrial application.

A significant contribution of radical processes to the thermolysis of ACSP can be illustrated by the chemiluminescence (CL)

observed during its decomposition.[185] However, whereas in the presence of O_2 the spectral pattern of CL (*i.e.*, the maxima at 400–440 and 500–540 nm) indicates the formation of excited triplet carbonyl groups as CL emitters, in an inert atmosphere the situation is less apparent. The intensity of CL decreases with ACSP consumption. In addition to a distinct maximum at 580–600 nm, the CL spectrum contains two signals of lower intensities with maxima around 650 and 690 nm. The intensity of CL decreases after addition of alkyl radical traps to ACSP. Presumably, the radiation emitter is formed in reactions involving alkyl radicals.

The kinetics of thermal decomposition of ACSP in an atmosphere of O_2 obeys the first-order kinetic law.[186] The activation parameters of the thermal decomposition of ACSP in various solvents are listed in Table 22.

Table 22. Effect of the solvent on the activation parameters of the decomposition of acetyl cyclohexylsulfonyl peroxide.[186]

Solvent	$\log A$ (s^{-1})	E_a /kJ mol^{-1}
n-$C_{10}H_{22}$	16.2	123
cyclo-C_6H_{12}	14.0	101
CCl_4	16.5	127
PhH	14.5	114
PhMe	13.8	108
PhEt	13.1	104
$PhPr^i$	14.7	115
MeCN	15.8	126
EtOH	12.5	103
Pr^iOH	14.0	113

In argon, the kinetics of ACSP thermolysis is different. The kinetic order of this reaction with respect to peroxide increases to 1.5. Thus in n-decane:

$$\log k_{ind} = (13.2 \pm 0.5) - (93 \pm 3)/2.3\,RT \ (\text{litre}^{1/2}\ \text{mol}^{-1/2}\ \text{s}^{-1}).$$

An analysis of the whole body of experimental data has made it possible to propose the following mechanism for ACSP decomposition:[187]

$$\text{cyclo-}C_6H_{11}SO_2OOC(O)Me \longrightarrow \text{cyclo-}C_6H_{11}SO_2O^{\bullet} + MeC(O)O^{\bullet}, \quad (27)$$

$$\text{cyclo-}C_6H_{11}SO_2OOC(O)Me \longrightarrow \text{cyclo-}C_6H_{11}SO_2OMe + CO_2,$$

$$\text{cyclo-}C_6H_{11}SO_2O^{\bullet} + RH \longrightarrow \text{cyclo-}C_6H_{11}SO_2OH + R^{\bullet},$$

$$MeC(O)O^{\bullet} \longrightarrow Me^{\bullet} + CO_2,$$

$$Me^{\bullet} + RH \longrightarrow CH_4 + R^{\bullet},$$

$$R^{\bullet} + \text{cyclo-}C_6H_{11}SO_2OOC(O)Me \longrightarrow \text{cyclo-}C_6H_{11}SO_2OR + MeC(O)O^{\bullet}, \quad (28)$$

$$R^{\bullet} + R^{\bullet} \longrightarrow \text{molecular products},$$

where RH is n-decane.

Reaction (28) is the limiting step in the chain process. Oxygen inhibits induced chain decomposition of ACSP due to rapid oxidation of alkyl radicals to $ROO^{\bullet}$. Peroxy radicals are inactive with respect to ACSP and undergo recombination resulting in chain termination. The following expression was proposed for the rate constant of induced decomposition of ACSP in n-decane [reaction (28)]: $\log k = 10.8 - 36/2.3\,RT$ (litre mol^{-1} s^{-1}). For the rate constant for the monomolecular decomposition of ACSP in $C_6H_4Cl_2$ [reaction (27)], $\log k = 14.5 - 115.4/2.3\,RT$ s^{-1} (the activation energy is expressed in kJ mol^{-1}).

X. Peroxide derivatives of carbonyl compounds

Upon heating in neutral media, hydroxyperoxides formed in the reaction of hydrogen peroxide and hydroperoxides with carbonyl compounds easily dissociate into the original compounds.[188]

$$HOOH + O{=}C \underset{k_1}{\overset{k_2}{\rightleftharpoons}} HOOC{-}OH,$$

$$ROOH + O{=}C \underset{k_1}{\overset{k_2}{\rightleftharpoons}} ROOC{-}OH.$$

The rate constants for the forward (k_2) and reverse (k_1) reactions are listed in Tables 23 and 24 (see Refs 39 and 188).

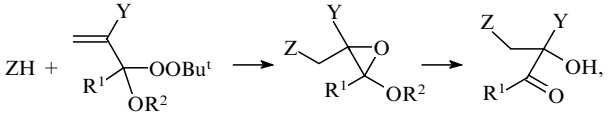
Different peroxy acetals and peroxy ketals including

$$R^1OOC(\text{|})OOR^2,$$

and cyclic polyperoxides are formed in acidic media as a result of condensation of aldehydes or ketones with 1-hydroxyperoxides.[188,189]

The thermolysis of monoperoxy ketals[190] is characterised by the parameters listed in Table 25. Despite the large distance between the peroxide group and the substituent, the structure of the latter has a strong effect on the kinetic parameters of the thermolysis. In particular, non-valent interactions of the oxygen atoms of the substituent with the peroxide group are possible.

In the presence of an allyl substituent, the thermolysis of monoperoxy ketal occurs in accordance with the following scheme:[191]



Z = cyclo-C_6H_{11}; Y = H, Me, Ph; R^1 = H, Me; R^2 = Me, Et,

Table 23. Kinetic parameters of the decomposition of 1-hydroxyperoxides and their formation from hydroperoxides and aldehydes at 20 °C.

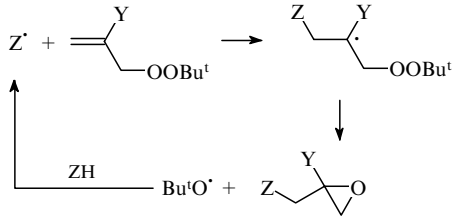
Aldehyde	Hydroperoxide	Solvent	$10\,k_2$ /litre mol^{-1} min^{-1}	$10^2\,k_1$ /min^{-1}	$10^2\,K$ /mol $litre^{-1}$	E_a /kJ mol^{-1}	
						E_2	E_1
Acetaldehyde	*tert*-butyl	CCl_4	7	1.3	1.8	13	42
	tetralyl	CCl_4	11	0.9	0.8	13	38
	cumyl	CCl_4	6	1.3	2.2	17	38
	diphenylethyl	CCl_4	3.5	1.5	4.3	17	42
	tert-butyl	Pr^n_2O	0.9	0.4	4.8	25	42
	tert-butyl	$CHCl_3$	1.7	0.8	4.7	21	46
Butyraldehyde	*tert*-butyl	CCl_4	6	1.1	1.9	17	38
Crotonic aldehyde	*tert*-butyl	CCl_4	0.08	5.0	6.0	–	–

Table 24. Kinetic parameters of the formation of 1-hydroxyperoxides (from tetralyl hydroperoxide and ketones) and their dissociation.

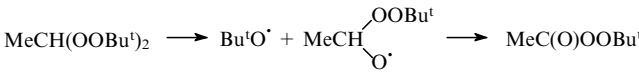
Ketone	$10\,k_2$ /litre mol^{-1} min^{-1}	$10^2\,k_1$ /min^{-1}	$10^2\,K$ /mol litre^{-1}	E_a /kJ mol^{-1}	
				E_2	E_1
Cyclohexanone	18	6	0.33	33	40
4-Methylcyclohexanone	17	7	0.41	33	40
3-Methylcyclohexanone	14	8	0.57	33	38
2-Methylcyclohexanone	3.1	11	3.5	–	–
Acetone	3.7	7	1.9	–	–
Ethyl methyl ketone	3.5	9	2.6	–	–
Isopentyl methyl ketone	2.1	9	4.3	–	–
Acetophenone		no reaction			
Benzyl ethyl ketone		no reaction			

Note. Concentrations: tetralyl hydroperoxide, 0.18 mol litre^{-1}; ketone, 0.02 mol litre^{-1}; solvent, CCl_4–tetralin (1 : 1), 20 °C.

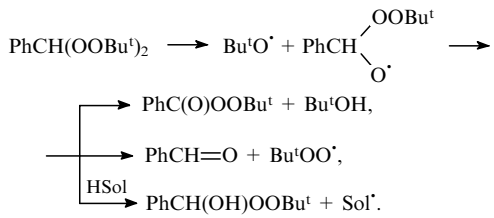
which includes the well-established reactions of induced decomposition of allyl peroxides:



The decomposition of diperoxyacetals is accompanied by the transient formation of peroxy esters [192]

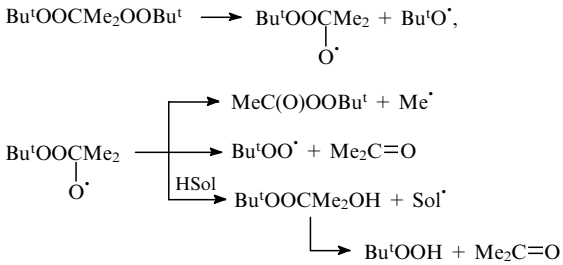


The decomposition of aromatic peroxy acetals occurs in accordance with the same scheme, *i.e.*, with the formation of peroxybenzoates as intermediates:[193]



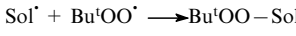
Under these conditions, the contribution of other parallel conversions of the initially formed radical increases.

The thermolysis of 2,2-bis(*tert*-butylperoxy)alkanes [194–197] proceeds through selective cleavage of the O–O bonds rather than by a concerted mechanism. This confirms the similarity of the activation parameters of 2,2-bis(*tert*-butylperoxy)propane ($\Delta H^{\neq}$ = 145.6 kJ mol^{-1}, $\Delta S^{\neq}$ = 47.3 J mol^{-1} K^{-1}) and di-*tert*-butyl peroxide ($\Delta H^{\neq}$ = 153.6 kJ mol^{-1}, $\Delta S^{\neq}$ = 48.1 J mol^{-1} K^{-1}) at 90–120 °C in the absence of induced decomposition (in cumene). The products formed are consistent with the following decomposition scheme:



A high volume of activation ($\Delta V^{\neq}$ = 22.3 ml mol^{-1} at 200 °C) [198] is an argument in favour of a concerted decomposition mechanism. However, at relatively high temperatures this mechanism can be different.

A method for the introduction of Bu^{t}OO groups into organic molecules by the thermolysis of 2,2-bis(*tert*-butylperoxy)propane has been proposed.[197] Diperoxy ketals that simultaneously generate the radical Bu^{t}O˙, causing the abstraction of the active hydrogen atom from the substrate, and the radical Bu^{t}OO˙, which undergoes recombination with the radical Sol˙,



were used as sources of Bu^{t}OO˙ radicals.

The thermolysis of 1,1-bis(*tert*-butylperoxy)cycloalkanes [18, 199–201] in solution occurs with homolytic cleavage of one O–O bond which occurs at a much faster rate than the thermolysis of the corresponding alkyl *tert*-butyl peroxides

Table 25. Thermolysis of monoperoxy ketals RMeC(OMe)OOBu^t in alkylaromatic hydrocarbons.

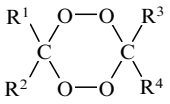
R	$-\ln k$ (s^{-1}) at 20 °C	E_a /kJ mol^{-1}
Me	9.21	138.3
Et	8.27	128.7
Pr	8.27	131.7
Bu	8.23	135.8
Bu^i	7.90	127.5
Pr^i	7.07	127.1
$MeOCH_2$	4.77	113.7
$EtOC(O)CH_2$	9.58	143.8

Table 26. Rate constants (at 110 °C) and activation parameters of the thermolysis of peroxides in cumene.[201]

Peroxide	$10^5\,k$ /s^{-1}	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J mol^{-1} K^{-1}
$(CH_2)_4C(OOBu^t)_2$	21.7	33.3	11.0
$(CH_2)_5C(OOBu^t)_2$	16.2	33.8	12.0
$(CH_2)_7C(OOBu^t)_2$	13.6	33.8	14.4
$(CH_2)_{11}C(OOBu^t)_2$	9.9	34.6	13.2
$Me_2C(OOBu^t)_2$	2.97	34.9	11.3
$EtMeC(OOBu^t)_2$	3.89	34.9	11.7
$Bu^tMeC(OOBu^t)_2$	13.8	33.8	11.6
Bu^tOOBu^t	0.25	36.9	11.5
$EtMe_2COOBu^t$	0.39	36.8	12.3
$Pr^iMe_2COOBu^t$	0.71	36.8	12.3

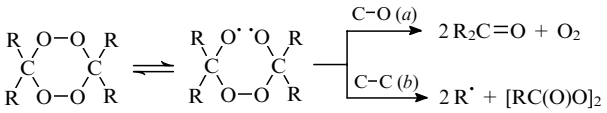
(Table 26). For cycloalkanes, the decomposition rate decreases in the following order: cyclopentane > 3,3,5-trimethylcyclohexane > cyclohexane > cyclooctane > cyclodecane. The dependence of the decomposition rate on the ring size suggests that stabilisation of the transition state due to the electron-donor effect of the cycloalkyl substituent and repulsion of free electron pairs of the oxygen atoms of the O—O group is a critical factor which determines the decomposition kinetics of geminal diperoxides.

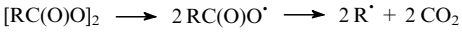
The decomposition of cyclic diperoxides of the type



R^{1-4} = Alk, Ar

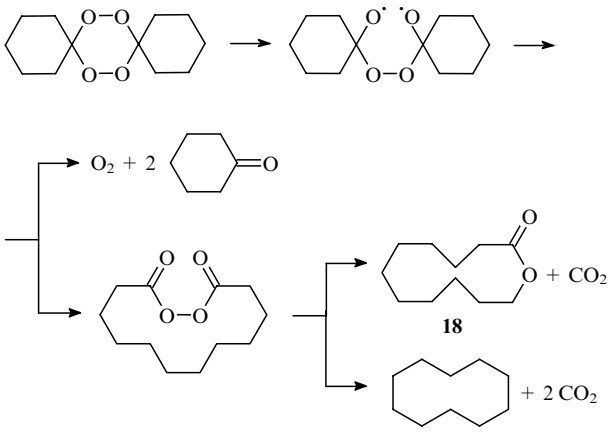
occurs with primary homolysis of one O—O bond with subsequent destruction of the biradical and cleavage of a C—O or a C—C bond.[199, 202–206]





The choice of a decomposition route (*a* is the formation of ketones, *b* is the formation of hydrocarbon radicals) depends on the structure of the substituents: for R = Ar, the yields of ketones are 90%, whereas for R = Alk they are as low as 10%–20% (in benzene) and even smaller. The higher the stability of the radical R the higher the yield of the ketone.

Cyclic diperoxides prepared from cyclohexanone undergo decomposition to give cyclohexanone and O_2, lactone **18** and CO_2, or cyclodecane and CO_2.[207]

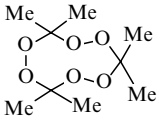
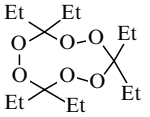
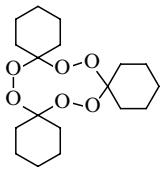
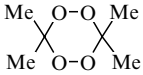
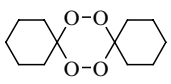


On the whole, cyclic diperoxides are more stable than their non-cyclic analogues.[199, 207]

The generation of a biradical in the first step of the thermolysis of a cyclic diperoxide prepared from an indene derivative was confirmed by analysis of polarisation of nuclei in the decomposition products (the thermolysis of acyl peroxides, peroxycarbonates and other peroxy derivatives (see above) was studied using a similar approach).[208]

The thermolysis of cyclic triperoxides, like the thermolysis of cyclic diperoxides, begins with the formation of a radical pair which undergoes further destructive rearrangements. As a result, the kinetics of decomposition of cyclic triperoxides characterised by high degrees of conversion is first order. The kinetic data on the thermolysis of cyclic di- and triperoxides in solution are generalised in Table 27.[209] The contribution of induced decomposition is insignificant, thus the activation parameters listed in the Table refer exclusively to the monomolecular decomposition.

Table 27. Kinetic parameters of the thermolysis of cyclic di- and triperoxides.

Peroxide	Solvent	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J mol^{-1} K^{-1}	$10^5 k$ /s^{-1} (145 °C)
	toluene	174.5	77.4	0.49
	acetone	174.5	76.6	0.37
	toluene	203.8	169.5	6.6
	"	193.7	142.7	14.3
	acetone	191.6	142.3	29.3
	toluene	120.9	−57.3	0.28
	"	167.4	70.7	5.5

XI. Conclusion

Depending on the structure of the compounds undergoing decomposition and the nature of the solvent, the thermolysis of organic peroxides in solution proceeds by both a homolytic mechanism with the cleavage of the O—O or OO—X bond and non-radical routes, through concerted rearrangement, in particular. Radical and non-radical decomposition reactions of peroxides normally occur in parallel. The formation of complexes and associates can increase the rates of both thermolysis routes.

Induced decomposition and recombination of radicals in the solvent cage diminish the proportion of radicals (*e*) released into the solvent. Kinetic estimates [210] show that the values of *e* for the peroxides R^1OOR^2 are the closest to unity. In the case of symmetrical diacyl peroxides, *e* does not usually exceed 0.3–0.6 (*cf.* 0.3–0.7 for diaroyl peroxides; 0.2–0.4 for dialkylperoxy ketals; and 0.5–0.9 for aromatic acids of *tert*-butyl peroxyesters).

This multivariant mechanism of thermolysis must be taken into consideration in those cases where organic peroxides are used as radical initiators of chemical reactions.

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