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Organic hydrotrioxides

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Abstract. The results of studies on the synthesis, structure, thermochemistry and oxidising capacity of organic hydrotrioxides are generalised. Particular emphasis is placed on the analysis of thermal and catalytic decomposition of ROOOH and on generation of free radicals and singlet molecular oxygen. Problems concerning the mechanisms of formation and decomposition of organic hydrotrioxides are also considered. The bibliography includes 154 references.

I. Introduction

The chemistry of trioxides, *viz*., compounds with a $-O-O-O-$ fragment, has been a matter of considerable interest during recent decades.[1–5] The family of trioxides comprises hydrogen trioxide HOOOH, organic hydrotrioxides ROOOH, dialkyl- and diaryltrioxides ROOOR. Primary ozonides (1,2,3-trioxolanes) and transannular ozonides can be considered as cyclic analogues of dialkyl- and diaryltrioxides. Phosphite ozonides [*e.g*., $(RO)_3PO_3$], ozone–arene complexes $ArX \cdot O_3$ as well as alkali metal and ammonium ozonides also belong to trioxides.

The nomenclature of compounds with the general formula RO_nR' has not been settled yet. For $n = 2$, this formula corresponds to the class of peroxides, the simplest representative of which is hydrogen peroxide (or hydrogen dioxide), HOOH. Extension of the oxygen chain by an O atom gives compound HOOOH, which by analogy should be named 'hydrogen trioxide'. Replacement of H atoms by organic radicals leads to 'hydrotrioxides' (HTO), ROOOH, and 'trioxides', ROOOR. 'Tetraoxides' RO_4R are formed in the radical-chain oxidation of organic compounds, in the stage of quadratic termination of the oxidation chain induced by peroxyl radicals $ROO^{\bullet}$. Hydrotrioxides of different classes of organic compounds have the general formula ROOOH and should probably be named by analogy with hydroperoxides ROOH. For instance, the term 'acylhydrotrioxides' refers to aldehyde hydrotrioxides.

In this review, we analyse the publications devoted to the synthesis, structure and decomposition of HTO and their use as oxidants of various organic compounds. The latest review concerning this topic was published by Plesničar in 1992.[4] Since then, numerous papers dealing with various aspects of the chemistry of HTO have appeared and a considerable body of new information on their structures and reactivity has been obtained. Progress in the studies of HTO necessitates generalisation of these data, refinement or even revision of some statements in Plesničar's review [4] concerning, *e.g*., the efficiency of generation of $^1O_2$ in the decomposition of HTO. In addition, the kinetics of the synthesis of ROOOH, the synthesis of ROOOH on surfaces, thermochemistry of HTO and related compounds, radical and catalytic decomposition of HTO, the use of HTO as oxidants of unsaturated, organophosphorus, nitrogen- and sulfur-containing organic compounds are considered in detail in the present review. We also present comprehensive information on the kinetics of thermal decomposition of HTO and report a critical analysis of the data on the efficiency of generation of singlet molecular oxygen in the thermal decomposition of ROOOH. In his review,[4] Plesničar did not dwell on these problems or only briefly outlined them.

Finally, it should be noted that studies carried out by the researchers from the Russian Federation have been incompletely covered in that review.[4] Therefore, we deemed it our duty to consider in the present review not only the results of studies carried out during the last eight years but also those reported before 1992.

For a rather long time, HTO were thought of only as hypothetic labile intermediates in the studies of the mechanisms of ozonisation of saturated organic compounds. However, once the fact that hydrotrioxides are stable at low temperatures had been revealed, the chemistry of HTO has progressed rapidly. Methods for the synthesis of HTO have been developed which allow the preparation of HTO at concentrations as high as ~ 1 mol litre^{-1}. Organic HTO appeared to be both efficient oxidants in reactions with various organic substrates and convenient chemical sources of singlet molecular oxygen in organic media.

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A hypothesis that hydrotrioxides are formed as intermediates in the ozonisation of certain organic compounds RH was first put forward independently by Price and Tumolo [6] and by White and Bailey [7] to rationalise the results obtained in studies of the reactions of ozone with ethers [6] and aromatic aldehydes.[7] Rapidly, this hypothesis has gained acceptance and was nearly simultaneously used by different authors in their studies on ozonisation of saturated hydrocarbons,[8–10] alcohols,[9] acetals [11] and silanes.[12]

Murray *et al.*[13–15] were the first who have provided strong experimental evidence for the existence of HTO. They have shown that unstable peroxide compounds **1a**, **2** and **3a** (Table 1) accumulated in the reaction medium during the low-temperature ozonisation of benzaldehyde, 2-methyltetrahydrofuran and isopropyl methyl ether, respectively. A signal at δ 13.1 was present in the ^{1}H NMR spectra of compounds **1a**, **2** and **3a**, which was tentatively assigned to the OOOH proton.

In further studies, ^{1}H NMR spectroscopy has become the basic method for identification and quantification of HTO in solution. Table 1 lists hydrotrioxides derived from aromatic aldehydes, ethers, linear and cyclic acetals, alcohols and ketones and Table 2 presents hydrotrioxides derived from hydrocarbons known to date. Organic compounds of other carbon subgroup elements also form hydrotrioxides upon oxidation by ozone. Hydrotrioxides of organosilicon and organogermanium com-

Table 1. Hydrotrioxides derived from aromatic aldehydes, ethers, linear and cyclic acetals, alcohols and ketones.

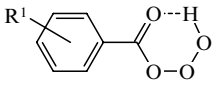
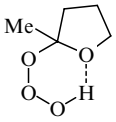
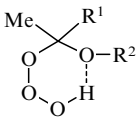
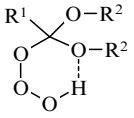
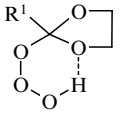
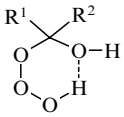
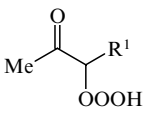
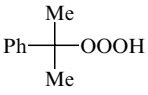
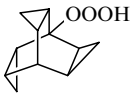
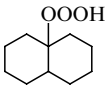
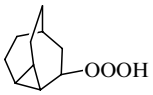
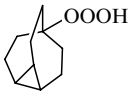
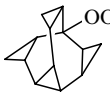
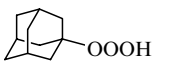
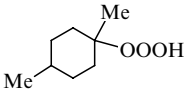
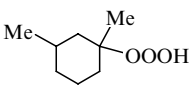
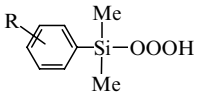
Formula	Compound	R^1	R^2	Ref.
	**1a**	H		15, 16
	1b	2-Cl		16
	1c	3-Cl		16
	1d	4-Cl		16
	1e	2-F		16
	1f	4-OMe		16
	**2**			15
	**3a**	Me	Me	13
	3b	Ph	Me	17
	3c	4-MeC_6H_4	Me	17
	3d	4-$MeOC_6H_4$	Me	17
	3e	4-FC_6H_4	Me	17
	3f	4-ClC_6H_4	Me	17
	3g	4-BrC_6H_4	Me	17
	3h	H	Et	18
	3i	Ph	Et	17
	3j	4-MeC_6H_4	Et	17
	3k	4-ClC_6H_4	Et	17
	3l	4-BrC_6H_4	Et	17
	3m	Me	Pr^i	16
	**4a**	Me	Me	19, 20
	4b	Ph	Me	19, 20
	4c	3-MeC_6H_4	Me	19, 20
	4d	4-$MeOC_6H_4$	Me	19, 20
	4e	4-FC_6H_4	Me	19, 20
	4f	4-ClC_6H_4	Me	19, 20
	4g	4-BrC_6H_4	Me	19, 20
	4h	Me	Et	19–21
	4i	Ph	Et	19, 20
	**5a**	H		22, 23
	5b	Me		23
	5c	Pr^n		18
	5d	Ph		19, 20, 22
	5e	4-MeC_6H_4		19, 20
	5f	3-ClC_6H_4		19, 20
	**6a**	H	H	18
	6b	Me	H	18, 24, 25
	6c	CH_2Cl	H	26
	6d	Et	H	26
	6e	Pr^n	H	26
	6f	Me	Me	18, 26
	6g	CH_2OH	Me	26
	6h	Et	Me	26
	6i	MeCHOH	Me	26
	6j	CH_2CH_2OH	Me	26
	6k	Ph	Me	17
	**7a**	Me		27
	7b	Pr^n		27

Table 2. Hydrotrioxides derived from hydrocarbons.

Formula	Compound	Ref.
	**8**	28, 29
	**9**	30
	**10a**	30
	**10b**	30
	**11**	18, 31
	**12**	30
	**13**	30
	**14**	30
	**15**	18, 31, 32
	**16**	18, 31
	**17**	18, 31
Ph_3COOOH	**18**	18, 31
$EtMe_2COOOH$	**19**	18, 31

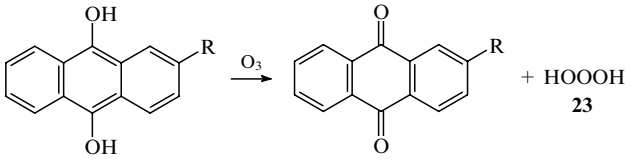
pounds have been detected (Table 3). Presumably, HTO represent labile intermediates in the ozonisation of stannanes,[36] though their formation from organotin compounds has not been reported so far.

Table 3. Hydrotrioxides derived from organoelement compounds.

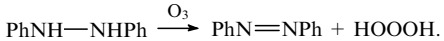
Formula	Compound	R	Ref.
	**20a**	H	33, 34
	20b	4-Me	33
	20c	4-MeO	33
	20d	4-Cl	33
$R_3SiOOOH$	**21a**	Et	35, 36
	21b	Bu^n	37
$Et_3GeOOOH$	**22**		36

II. Synthesis of hydrotrioxides

It was only recently that the methods for the synthesis of the simplest trioxide, HOOOH (**23**), have been proposed. Hydrogen trioxide **23** is formed upon oxidation of 9,10-dihydroxyanthracene, 2-ethyl-9,10-dihydroxyanthracene or hydrazobenzene by ozone (−78 °C, acetone-d_6 or methyl acetate).[34]



R = H, Et.



Hydrogen trioxide **23** is also formed in the decomposition of silane hydrotrioxides.[33, 34]

All HTO listed in Tables 1–3 can be synthesised using a rather simple and virtually identical procedure consisting of bubbling a cooled O_3-O_2 or O_3-N_2 gas mixture through a liquid substrate RH or its solution at reduced temperature (−20 to −78 °C). After completion of the reaction, the unconsumed ozone is removed by blowing air or (if necessary) an inert gas and then the concentration of HTO in the solution is determined by NMR spectroscopy. The yield of ROOOH with respect to the consumed RH depends on the substrate structure and varies from 1%–2% for cumene hydrotrioxide **8** to 70%–90% for acetal, alcohol and silane hydrotrioxides.

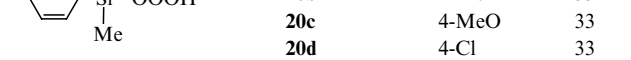
A modified procedure for the synthesis of HTO involves ozonisation of organic compounds on the surface of silica gel (the so-called 'dry' ozonisation).[18, 31, 32, 38, 39] It was used to obtain the hydrotrioxides **11** and **15**–**19**, which could not be prepared in the liquid-phase ozonisation.[18, 31, 32] Highly polar silica gel surface stabilises the ionic intermediates of the ozonisation reaction, thus favouring the formation of ROOOH even from non-activated hydrocarbons. It can be hypothesised that 'dry' ozonisation will also be convenient for the synthesis of other HTO which cannot be obtained by liquid-phase ozonisation.

The kinetics of formation of compounds **3m**,[16] **4h**,[21] **6d**,[25] **6f**[16] and **7b**[27] have been studied. At sufficiently low temperatures where thermal decomposition of HTO can be ignored the kinetic curves of accumulation of HTO have the shape of saturation curves, which means that the yield of ROOOH (α) calculated with respect to the ozone consumed decreases with an increase in conversion. The extent of the reaction is related to the amount of the ozone absorbed $\Delta(O_3)$ and the yield of ROOOH is calculated by the formula

$$\alpha = \frac{[ROOOH]}{\Delta(O_3)}.$$

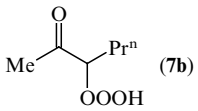
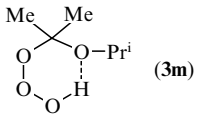
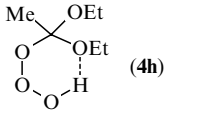
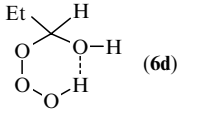
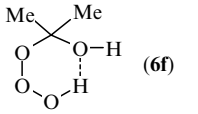
The yield calculated with respect to the ozone consumed (α_0) is obtained by extrapolating the value of α to the zero time [$\Delta(O_3) = 0$].

The α_0 values for a number of HTO are listed in Table 4. The decrease in the yield with the increase in the extent of the reaction is explained by consumption of the HTO in the reactions with ozone.



The rate constants for the first (k_1) and second (k_2) stages of ozonisation of 1,1-diethoxyethane at −60 and −80 °C are $k_1 = 6.8 \times 10^{-4}$ and 2.5×10^{-5} litre mol^{-1} s^{-1} and $k_2 = 3.0 \times 10^{-3}$ and 1.2×10^{-4} litre mol^{-1} s^{-1}, respectively.[21]

Table 4. Yields of hydrotrioxides (α_0) calculated with respect to the consumed ozone.

Compound	Temperature /°C	α_0 /mol mol^{-1}	Ref.
 (**7b**)	−60	0.5	27
 (**3m**)	−78	0.45	16
 (**4h**)	−78	0.51	21
	−60	0.45	21
 (**6d**)	−98	0.90	25
	−78	0.80	25
	−50	0.20	25
 (**6f**)	−78	0.98	16
	−40	0.80	16

III. The structure, thermochemistry and spectroscopy

1. The structure

a. Equilibrium molecular geometry of hydrotrioxides

Experimental data on the spatial structure of HTO are lacking and this was established only from the results of semiempirical (EHT, CNDO/2, MINDO/3, AM1)[40–43] and *ab initio* quantum-chemical calculations.[33, 44–54]

Ab initio calculations of the equilibrium molecular geometry of HOOOH have been carried out at different levels of theory, from simple calculations in the one-determinant approximation with the STO-2G basis set to sophisticated calculations with different TZP basis sets augmented with diffuse functions and intensive treatment of electron correlation. Both partial[44–48, 50] and full optimisation of the molecular geometry[33, 49, 51, 52, 54] were employed. Tables 5 and 6 present the results of *ab initio* calcu-

Table 5. Results of *ab initio* calculations of the equilibrium geometries and total energies of HOOOH.

Basis set	r(HO) /Å	r(OO) /Å	θ(HOO) /deg	θ(OOO) /deg	φ /deg	E_{total}	Ref.
RHF/STO-3G	1.002	1.392	102.5	105.9	84.2	−222.58049	49
RHF/4-31G	0.959	1.437	103.6	106.0	83.5	−225.21862	49
RHF/6-31G	0.958	1.432	104.1	106.5	83.9	−225.44304	33
RHF/6-31G*	0.953	1.373	103.2	107.2	80.1	−225.53362	49
RHF/6-31G**	0.949	1.373	103.5	107.4	80.8	−225.54584	51
MP2/4-31G	0.992	1.539	99.6	104.4	78.3	−225.62077	49
MP2/6-31G*	0.980	1.442	100.3	106.1	78.5	−226.09075	49
MP2/6-31++G*	0.982	1.445	100.8	106.4	79.6	−226.10273	52
MP2/6-31G**	0.972	1.441	100.2	106.2	78.7	−226.11275	51

Note. Hereafter, the E_{total} are given in hartree.

Table 6. Results of *ab initio* calculations [54] of the equilibrium geometries and total energies of hydrotrioxides H_3COOOH and $H_3SiOOOH$.

Basis set	r(XO) /Å	r(XOO) /Å	r(OOH) /Å	r(OH) /Å	θ(OOH) /deg	θ(OOO) /deg	θ(XOO) /deg	φ(HXOO) /deg	φ(XOOO) /deg	φ(OOOH) /deg	E_{total}
Compound H_3COOOH											
RHF/STO-3G	1.453	1.396	1.392	1.003	102.4	105.9	106.5	179.1	87.8	83.5	−261.16718
RHF/4-31G	1.438	1.436	1.440	0.958	103.4	106.1	107.7	179.0	85.8	82.4	−264.18963
RHF/6-31G	1.439	1.430	1.433	0.957	103.9	106.5	108.1	179.0	86.0	82.6	−264.45417
Compound $H_3SiOOOH$											
RHF/6-31G	1.771	1.441	1.429	0.958	103.9	106.2	109.6	180.2	84.1	79.3	−515.49701

lations [53] of the molecular structures of HOOOH, H_3COOOH and $H_3SiOOOH$ with full geometry optimisation.

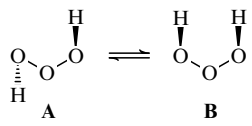
The data listed in Tables 5 and 6 reveal salient features of the molecular geometry of hydrotrioxides.

1. The r(O−O) distances in trioxides are close to those in peroxides. Blint and Newton [46] found that the O−O bond length can be calculated with a reasonable accuracy using the empirical Pauling equation

$$r_e = r_e^s - \alpha \ln(n), \quad (1)$$

where r_e is the equilibrium bond length (Å); r_e^s is the equilibrium length of a bond with the order of unity; $\alpha = 0.351$ Å is the empirical constant; and n is the bond order. According to calculations with the 4-31G basis set, r(O−O) ≈ 1.41 − 1.44 Å in polyoxides. The O−O bond in HOOOH is 0.03 to 0.04 Å shorter than in HOOH. A similar tendency of changes in the O−O bond length is observed for the pairs H_3COOOH/H_3COOH and $H_3SiOOOH/H_3SiOOH$,[54] which seems to be a general feature.

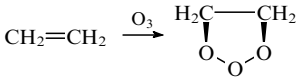
2. The torsion (dihedral) angle φ in the HTO molecules characterises the positions of the substituent atoms with respect to the plane passing through three O atoms. According to the most sophisticated calculations,[49, 54] $\varphi \approx 75 - 80°$. The calculations revealed two stable conformations, *anti* (**A**) and *syn* (**B**), for the hydrogen trioxide molecule, which differ in positions of the H atoms with respect to the trioxide plane.



A **B**

The assumption of the existence of stable *anti* and *syn* conformations of hydrogen trioxide molecule (**23**) is indirectly confirmed by the results of IR and microwave spectroscopic studies of hydrogen trisulfide, a close analogue of HOOOH.[55] According to the results of quantum-chemical calculations carried out at the MP2/TZ+P and QCISD/TZ+P levels of theory, the *anti* conformation of HSSSH molecule is 0.25 kcal mol^{-1} (87 cm^{-1}) more stable than the *syn* conformation.

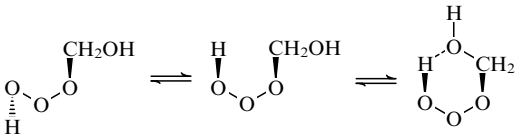
For the HOOOH molecule, conformation **A** is more energetically favourable (by 3.5±1.0 kcal mol^{-1}) than conformation **B** (see Refs 43, 44, 46, 49). This gives a rationale of the low stability of 1,2,3-trioxolanes, which are intermediates of the ozonolysis of alkenes, compared to linear trioxides. The molecule of primary ozonide (1,2,3-trioxolane **24**) adopts an 'envelope' conformation [56, 57] in which the positions of methylene groups formally correspond to the *syn* conformation of the trioxide.



24

Hence, the energy of conformational transition and strain energy in the five-membered ring [∼6 kcal mol^{-1} (see Ref. 58)] contribute to the destabilisation of the primary ozonide. As a consequence, the activation energy of further transformations of compound **24** is ∼10 kcal mol^{-1} lower than those of thermal decomposition of dialkyl trioxides.[5]

Hydrotrioxides derived from alcohols, ethers and acetals can form intramolecularly hydrogen-bonded structures only if these molecules adopt the *syn* conformation.[13, 14, 16, 17, 19, 20, 24]



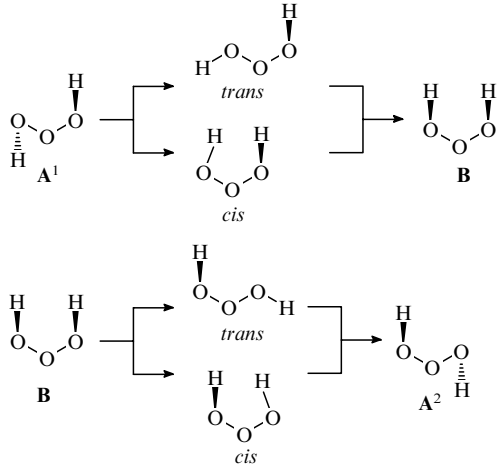
Hence, the enthalpy of formation of a hydrogen bond, $\Delta H°$, includes the *anti*–*syn* interconversion energy.[18] Radical decomposition of the cyclic intermediate removes the conformational strain, thus decreasing the activation energy for this process.

3. The H−O−O and C−O−O bond angles (see Tables 5 and 6, respectively) in hydrotrioxide molecules are somewhat larger than in the corresponding hydroperoxides. The O−O−O bond angles in different HTO (104 − 107°) are in good agreement with the IR spectroscopic estimate.[59]

4. Conformational analysis of the HOOOH molecule has been carried out.[49] The potential energy surface for simultaneous

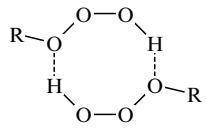
rotation of the OH groups about the O—O axes in the molecule was calculated. Analogous semiempirical AM1 calculations were carried out for hydrogen trioxide and tetraoxide.[43] The nature of the barriers to rotation was interpreted based on the results of the Fourier analysis of the conformational potential of the polyoxides. The conformational behaviour of polyoxides is dominated by the repulsion between the lone electron pairs of the neighbouring oxygen atoms and by stabilisation of the hydropolyoxide owing to delocalisation of the lone electron pair (n_O) over the σ*-antibonding orbital of the neighbouring O—O bond (or O—C and O—H bonds).[18, 54] The latter effect provides an explanation for the shortening of the r(O—O) distance in trioxides compared to peroxides, since the stabilising effect of hyperconjugation $n_O - \sigma^*_{O-O}$ on the trioxide molecule is more pronounced than that of hyperconjugation $n_O - \sigma^*_{O-OH}$ on the peroxide molecule, thus favouring a decrease in the O—O bond length.[54]

Analysis of the potential surface for internal rotation of hydrogen trioxide suggests that the most favourable conversional process between two global energy minima (**A**[1] and **A**[2]) for the *anti* conformation of HOOOH involves a two-step flip-flop rotation rather than simultaneous rotation of the OH groups.[43, 49]



b. Association of hydrotrioxides

The binding energies of the intermolecularly hydrogen-bonded dimers were calculated taking dimerisations of HOOOH, H_3COOOH and $H_3SiOOOH$ as examples.[33, 53]

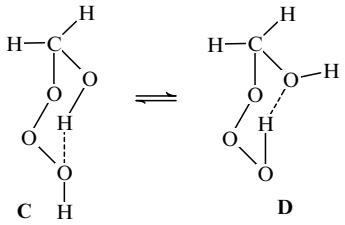


R = H, CH_3, SiH_3.

Relatively high binding energies (E = 6–8 kcal mol^{-1} per O—H bond) are close to the hydrogen bond energy in cyclic dimers of carboxylic acids.[60, 61] This confirms the assumption that self-association is a salient feature of HTO molecules. It should be noted, however, that the computational method (RHF/6-31G) employed by Plesničar *et al.*[33, 53] overestimates the energies of hydrogen bonds. Indeed, augmentation of the basis set with *p*-polarisation functions for hydrogen and *d*-polarisation functions for other atoms leads to more realistic results, *viz.*, the binding energy of H_3COOOH in the eight-membered dimer is 4.5 kcal mol^{-1} per hydrogen bond.[18]

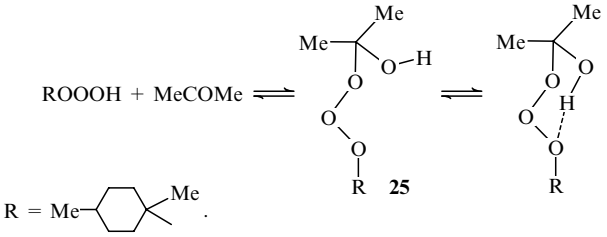
The effect of water on the decomposition of HOOOH has been studied.[52, 54] The water molecule acts as a bifunctional catalyst, thus facilitating the decomposition of hydrogen trioxide into H_2O and $^1O_2$. This reaction is preceded by the formation of a six-centred hydrogen-bonded complex. The binding energy in this complex is 1.5 kcal mol^{-1} lower than in the cyclic dimer of HOOOH. The calculated height of the potential barrier to decomposition of hydrogen trioxide (15.1 kcal mol^{-1} relative to noninteracting reagents) is in good agreement with the experimentally found effective activation energies for the decomposition of HOOOH.[34, 52, 62]

Ab initio calculations of intramolecularly hydrogen-bonded structures ROOOH have been carried out taking methanol hydrotrioxide (**6a**) as an example.[18] The most stable conformers of the molecule are the *anti* (**C**) and *syn* (**D**) conformers with nearly equal energies.



The *anti* conformer **C** is stabilised by the hydrogen bond between the H atom of the alcoholic hydroxy group and the most distant (from the carbon atom) O atom of the trioxide fragment. The *syn* conformation **D** favours the formation of a hydrogen bond between the OOOH hydrogen and alcoholic O atom. The binding energies of structures **C** and **D** calculated at the MP2//RHF/6-31G** level of theory are 2.2 and 5.4 kcal mol^{-1}, respectively.

In conclusion, mention should be made that HTO can form associates with carbonyl compounds.[18] In addition to the signal at δ = 13, the ^{1}H NMR spectrum of 1,4-dimethylcyclohexyl hydrotrioxide (**16**) in acetone exhibits two peaks at δ = 4.15 and 4.35 which disappear irreversibly upon heating. It is well known that hydrogen peroxide[63] and hydroperoxides[64, 65] readily react with aliphatic and alicyclic ketones to give α-hydroxy hydroperoxides and α-hydroxy peroxides. Presumably, a similar reversible reaction occurs in the system HTO **16** – acetone resulting in a derivative of 2-R-trioxy-2-hydroxypropane **25**.[18] Compound **25** exists in two forms, which accounts for the presence of two OH proton resonance peaks in its ^{1}H NMR spectrum.



2. Thermochemistry

In this Section, we outline briefly the possibilities of estimation of the enthalpies of formation and bond dissociation energies in hydrotrioxides. For more detailed data, see a recent review.[66]

The experimentally determined thermodynamic characteristics of HTO (enthalpies of formation and of phase transitions, entropies, *etc.*) are lacking. Therefore, thermochemical calculations of the thermal effects of the reactions involving ROOOH were carried out using approximate computational schemes, in particular, the approach of additivity of thermochemical increments developed by Benson *et al.*[58, 67, 68] In the framework of Benson's scheme, the enthalpies of formation of hydropolyoxides are related by simple relationships

$$\Delta_f H^\circ(\text{ROOOH}) = \Delta_f H^\circ(\text{ROOH}) + \Delta_f H^\circ[\text{O}-(\text{O})_2], \quad (2)$$

$$\Delta_f H^\circ(\text{ROOOOH}) = \Delta_f H^\circ(\text{ROOOH}) + \Delta_f H^\circ[\text{O}-(\text{O})_2], \quad (3)$$

where the second term in the right side of Eqns (2) and (3) is the polyoxide group increment, which characterises the enthalpy contribution of the central O atom of the trioxide fragment. As will be shown below, the assumption that the enthalpy of formation changes linearly in the order ROOH—ROOOH—

ROOOOH is rough and leads to substantial discrepancies between the results of thermochemical studies carried out by different authors.

Practically, the most convenient way of calculating the $\Delta_f H^\circ$(ROOOH) values is to use Eqn (2). A number of experimentally determined enthalpies of formation of hydroperoxides has been reported.[69] Good agreement with experimental $\Delta_f H^\circ$(ROOH) values is also observed when using the method of isodesmic reactions as well as *ab initio* calculations with extended basis sets and inclusion of electron correlation (CI or perturbation theory).[70, 71] Unfortunately, high computational cost of real-time calculations of $\Delta_f H^\circ$(ROOH) allows them to be carried out only for the simplest substituents R. Thermochemistry of peroxides has been analysed using a large body of experimental data on the enthalpies of formation (see Ref. 72 and references cited theirein), increments for calculating $\Delta_f H^\circ$(ROOH) in both the gas phase and condensed phase were proposed.

The polyoxide group increment, $\Delta_f H^\circ[O-(O)_2]$, which plays the key role in calculations of the enthalpies of formation of hydrotrioxides, cannot be calculated from the available experimental data on $\Delta_f H^\circ$ and bond dissociation energies in related compounds. Since the accuracy of indirect estimates is insufficient, the numerical value of $\Delta_f H^\circ[O-(O)_2]$ has been the subject of systematic revisions.[70, 73–77]

a. Comparison of the enthalpies of formation

The first estimates of $\Delta_f H^\circ[O-(O)_2]$ (25±6 and 19±4 kcal mol^{-1}, see Refs 73 and 74, respectively) were made based on the assumption that thermodynamic properties change linearly in the order ROR′–ROOR′–ROOOR′ and from comparison of the enthalpies of formation for pairs of compounds H_2O and H_2O_2,[73, 74] MeOH and MeOOH and MeOMe and MeOOMe.[74] This approach was found to be very rough. In particular, the results obtained suggested that tetraoxides can be synthesised at temperatures below 80–100 K.[74] Later, it has been shown[78–80] that tetraoxides ROOOOR (R = *tert*-Alk, ArAlk) are rather stable at $T \leqslant 170$ K, which indicated overestimation of the $\Delta_f H^\circ[O-(O)_2]$ value reported in earlier studies.[73, 74]

b. Comparison of thermal effects of reactions

Another procedure for the calculation of the polyoxide group increment was used by Nangia and Benson.[75] Based on the reaction equations

$$Bu^tOOOOBu^t \longrightarrow 2\,Bu^tOO, \quad (4)$$

$$Bu^tOOOBu^t \longrightarrow Bu^tO + Bu^tOO, \quad (5)$$

$$Bu^tOOBu^t \longrightarrow 2\,Bu^tO \quad (6)$$

with the known thermal effects $\Delta H^\circ(4) = 9.0\pm1.5$[78, 79] and $\Delta H^\circ(6) = 38.0\pm1.0$ kcal mol^{-1} (see Ref. 81) and using the additivity rule, according to which

$$\Delta H^\circ(5) = 0.5[\Delta H^\circ(4) + \Delta H^\circ(6)],$$

they found that $\Delta H^\circ(5) = 23.5\pm0.8$ kcal mol^{-1} and $\Delta H^\circ(6) - \Delta H^\circ(5) = \Delta H^\circ(5) - \Delta H^\circ(4) = 14.5\pm0.8$ kcal mol^{-1}. By representing the enthalpies of formation of the molecules under study as the sums of the enthalpies of formation of the thermochemical groups, one can readily obtain the expression for the calculation of the polyoxide group increment

$$\Delta H^\circ(6) - \Delta H^\circ(5) = \Delta_f H^\circ(RO) - \Delta_f H^\circ(ROO) + \Delta_f H^\circ[O-(O)_2]. \quad (7)$$

Using the known values of the enthalpies of formation of the MeO$^\bullet$ and MeOO$^\bullet$ radicals, the new polyoxide group increment $\Delta_f H^\circ[O-(O)_2]$ was found to be 16.8±2.2 kcal mol^{-1} (see Ref. 75). A year later, Nangia and Benson corrected this estimate and reported that $\Delta_f H^\circ[O-(O)_2] = 14.8$ kcal mol^{-1}.[76] This approach has a drawback consisting of the assumption of linear changes in the ΔH° of the reactions (4)–(6). Recent experiments showed that $\Delta H^\circ(5) = 20-21$ kcal mol^{-1} (see Refs 18, 82, 83). Mention has been made of the nonlinear character of changes in the enthalpies of formation in the order 'peroxide–trioxide–tetraoxide'.[84]

c. Quantum-chemical calculations of the enthalpies of formation

The use of quantum-chemical methods has opened new possibilities for the thermochemical analysis of the reactions of HTO and higher polyoxides.[44, 46, 50, 70, 71, 77, 82, 84–87] However, direct calculations of the enthalpies of formation of polyoxides can lead to large errors owing to incomplete inclusion of electron correlation in the *ab initio* computational schemes and inadequate parametrisation of semiempirical methods. This can be illustrated as follows. The enthalpy of formation of MeOOOH obtained from MP4SDTQ/6-31G*//MP2/6-31G* calculations is −22.2 kcal mol^{-1} and must correspond to the energy of dissociation of the weakest O–O bond, D(MeO–OOH); however, D(MeO–OOH) = 35.8 kcal mol^{-1} (see Ref. 70). The value cannot be regarded as realistic despite the high level of quantum-chemical calculations. It is only 2 to 3 kcal mol^{-1} lower than the corresponding bond dissociation energies in peroxides. However, the temperature intervals of stability of these compounds are not comparable: peroxides are rather stable at room temperature, while the lifetimes of HTO under these conditions are within several minutes. Therefore, the numerical estimates of the polyoxide group increment obtained from both semiempirical MNDO[77] and *ab initio*[70] calculations of $\Delta_f H^\circ$ of polyoxides {$\Delta_f H^\circ[O-(O)_2] = 13.1\pm1.5$ and 9.6±0.1, respectively} should be used with caution.

d. Quantum-chemical calculations of bond dissociation energies

The best results can be obtained from calculations of bond dissociation energies (strengths). This is due to mutual cancellation of the errors of calculations of $\Delta_f H^\circ$ for polyoxide and its decomposition products. Systematic studies of the O–O and O–H bond dissociation energies in organic polyoxides (see Table 7) have been carried out.[18, 82, 84–86] This allowed calculations of the enthalpies of formation for a number of peroxides, trioxides and tetraoxides. It was found that the difference $\Delta_f H^\circ$(ROOOR′) − $\Delta_f H^\circ$(ROOR′) is 5 to 8 kcal mol^{-1} larger than $\Delta_f H^\circ$(ROOOOR′) − $\Delta_f H^\circ$(ROOOR′). The reason for this discrepancy was explained based on the results of analysis of the conformational potentials of polyoxide compounds H_2O_x (x = 2,

Table 7. Bond strengths D (kcal mol^{-1}) in organic hydropolyoxides.

Bond type	D	Ref.
R–OOOH [a]	63.6 ± 1.2	18
RO–OOH [b]	20.4 ± 1.0 (MNDO)	86
	20.8 ± 1.1 (AM1)	86
	23.4 [c]	88
ROO–OH [b]	(25.5 ± 0.6) + (1.97 ± 0.49)·σ*(R) (MNDO)	86
	(23.8 ± 0.6) + (1.38 ± 0.49)·σ*(R) (AM1)	86
	30.1 [c]	88
HO–OOH	24.8 (CI(SDQ))	50
	25.0 (MNDO)	86
	25.2 (AM1)	86
HOOO–H	82.6	70
ROOO–H [d]	80.8 ± 0.8	18
R–OOOOH [a]	63.6 ± 1.2	18
RO–OOOH [a]	20.8 ± 1.4	18
ROO–OOH [a]	8.7 ± 1.2	84
HOO–OOH	7.1 (MNDO)	82
	12.1 (MNDO)	77
ROOO–OH [a]	25.1 ± 0.5	18
ROOOO–H [a]	80.8 ± 0.8	18

[a] R = Alk. [b] R is unsubstituted, halo-, hydroxy- or alkoxy-substituted alkyl. [c] R = Me. [d] R is unsubstituted, halo-, hydroxy- or alkoxy-substituted alkyl, H, HCO or MeCO.

3, 4).[43] It was shown that the enthalpies of formation in the series 'peroxide – trioxide – tetraoxide' do not change linearly as it would follow from the additivity method owing to additional stabilisation of peroxides by the dipole – dipole interaction between the alkoxy groups. Therefore, the $\Delta_f H^\circ[O-(O)_2]$ group increment can be calculated as the difference between the enthalpies of formation of a trioxide and tetraoxide with the same substituents. Calculations of the enthalpies of formation of trioxides from the corresponding peroxides should be carried out with inclusion of the energy of conformational rearrangement of the molecule (~ 5 kcal mol^{-1}).

For practical calculations of $\Delta_f H^\circ$ values in polyoxides we recommend the following relationships

$$\Delta_f H^\circ(\mathrm{ROOOR}') = \quad (8)$$
$$= \Delta_f H^\circ(\mathrm{ROOR}') + (17.6 \pm 1.6) \text{ kcal mol}^{-1},$$
$$\Delta_f H^\circ(\mathrm{ROOOOR}') = \quad (9)$$
$$= \Delta_f H^\circ(\mathrm{ROOOR}') + (11.1 \pm 1.0) \text{ kcal mol}^{-1}.$$

Calculations using Eqns (8) and (9) allow correct reproduction of the intervals of thermal stability of trioxides and tetraoxides and give the bond dissociation energies that are close to the activation energies for decomposition of polyoxides (provided that E_a is corrected for the normal value of the pre-exponential factor).

3. Spectroscopic studies

a. UV, IR and Raman spectra

Scarce experimental data indicate that the electronic spectra of HTO are similar to those of related peroxide compounds. The optical spectrum of HOOOH obtained in the pulse radiolysis experiments is similar to that of hydrogen peroxide and exhibits a somewhat larger molar extinction, $\varepsilon \approx 100$ litre mol^{-1} cm^{-1} ($\lambda = 240$ nm).[62] Weak absorption at $\lambda > 320$ nm in the spectrum of benzaldehyde hydrotrioxide (**1a**) can be assigned to the S_1 ($\pi^*_{O-O} \rightarrow \sigma^*_{O-O}$) transition. The position and spectral features of this signal are similar to those of aromatic endoperoxides.[89] Thus, the UV spectra of HTO exhibit no characteristic bands suitable for identification and determination of the concentration of ROOOH. Since almost any reaction of the synthesis or decomposition of HTO proceeds to give peroxides as side or major products, one can conclude that investigations into the chemical nature of organic HTO based on the UV spectra is hardly probable.

Specific features of the IR spectra of hydrogen and deuterium trioxides and tetraoxides allowed Giguere and Herman [59] to relate the observed frequencies to vibrations of the zigzag chain of the O atoms linked by single bond. They estimated the O – O bond length at ~ 1.5 Å and the O – O – O bond angle at 100 to 120 ° and concluded that internal rotation of the OH groups in free molecules is only weakly hindered, whereas in the solid state their orientation will be strongly dependent on the possibility of hydrogen bonding, as in hydrogen peroxide. More recently,[90] normal coordinate analyses for HOOOH and HOOOOH molecules were performed. Nonplanar hydrogen polyoxide structures exhibited fairly good correspondence between the calculated frequencies and experimental IR spectrum and the existence of several spatial isomers was suggested. Further quantum-chemical studies have confirmed in general the above-mentioned conclusions [59, 90] (see Table 3).

Raman spectra of hydrogen polyoxides have been studied.[91, 92] The fundamental skeletal vibrations of the HOOOH and HOOOOH molecules and their deuterated analogues were identified and interpreted (Table 8). The frequencies observed are consistent with the C_2 symmetry of the molecular structure in the form of a skew chain of O atoms linked by single bonds.

Vibrational spectra of organic hydroperoxides have not been studied as yet.

Table 8. Vibrational spectra of hydrogen polyoxides.[92]

Compound	Frequencies /cm^{-1}		Assignment
	Raman	IR	
HOOOH	~ 855	~ 855	ν_s(O – O)
	500	–	δ(O – O – O)
	755	755	ν_{as}(O – O)
DOOOD	~ 857	~ 857	ν_s(O – O)
	497	–	δ(O – O – O)
	760	760	ν_{as}(O – O)
HO(1)O(2)O(3)O(4)H	~ 855	–	ν_s(O – O)
	~ 764	–	ν[O(2) – O(3)]
	450	–	δ_s(O – O – O)
	~ 98	–	δ_{tors}[O(2) – O(3)]
	~ 823	~ 823	ν_{as}(O – O)
	–	435	δ_{as}(O – O – O)
DO(1)O(2)O(3)O(4)D	~ 857	–	ν_s(O – O)
	~ 768	–	ν[O(2) – O(3)]
	~ 440	–	δ_s(O – O – O)
	~ 98	–	δ_{tors}[O(2) – O(3)]
	~ 828	~ 828	ν_{as}(O – O)
	–	~ 430	δ_{as}(O – O – O)

b. NMR studies

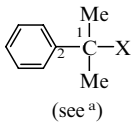
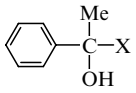
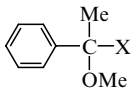
Organic HTO can be conveniently identified by NMR spectroscopy owing to the presence of characteristic signals of the hydrotrioxide fragment. Resonance absorptions of other groups are less characteristic. The chemical shifts of the ^{1}H, ^{13}C and ^{29}Si nuclei in the NMR spectra of a number of HTO and related compounds [17, 29, 33] are listed in Tables 9 and 10.

Typical of HTO is the signal of the OOOH proton at $\delta \sim 13$ in the ^{1}H NMR spectra, the position of the signal being virtually independent of the nature of ROOOH.[13 – 17, 19 – 21, 23 – 30, 33, 34, 36, 37] In the series ROH – ROOH – ROOOH, the chemical shift of H increases from δ 0.5 – 5.5 for ROH to δ 7.6 – 9.2 for ROOH [93] and δ 12 – 14 for ROOOH. Unlike alcohols and hydroperoxides,[93] dilution of HTO solutions has little effect on the chemical shift of the trioxide proton. Based on these observations, it was concluded that hydrotrioxides form strong intramolecularly hydrogen-bonded complexes.[13, 14]

A peculiarity of the ^{1}H NMR spectra of hydrotrioxides is the appearance, in some cases, of the splitting of the OOOH proton signal into two signals.[14, 16, 17, 19, 20, 24] The chemical shifts of these signals also show little change with dilution. Heating of the samples results in broadening and coalescence of the lines. The coalescence temperature depends on the chemical nature of both ROOOH and the solvent. For instance, two peaks in the ^{1}H NMR spectrum of 2-methyltetrahydrofuran hydrotrioxide (**2**) coalesce at -27 °C.[14] For hydrotrioxide **3b** obtained from methyl α-methylbenzyl ether in Freon 11/12, two peaks appear in its ^{1}H NMR spectrum only at -50 °C and lower temperatures, whereas no peak coalescence is observed in diethyl ether, acetone-d_6 and ethyl acetate even at -10 °C.[17] The origin of two resonance signals for the OOOH proton is still to be clarified. This can be due to either the 'chair – boat' conformational transition of the six-membered ring resulting from the formation of intramolecular hydrogen bond or the presence of two conformations with the R group at the O atom in either axial or equatorial position. Hydrotrioxides derived from cyclic acetals [19, 20] can form various complexes owing to nonequivalence of the two acetal O atoms with respect to the OOOH group.

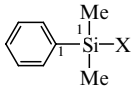
Studies of the ^{1}H NMR spectra of hydrotrioxides in different solvents [17] showed that though the chemical shifts of two peaks vary insignificantly, their relative intensities can vary over a rather wide range (see Table 9). In diethyl ether, the more intense low-field peak of the hydrotrioxide **3b** disappears upon heating with a somewhat higher rate compared with the high-field signal. The

Table 9. Chemical shifts and multiplicities of signals in the ^1H and ^{13}C NMR spectra of organic hydrotrioxides and related compounds.

Compound	X	δ ^1H	δ ^{13}C			
			C(1)	C(2)	C(Me)	other C atoms
 (see [a])	H	1.17 d (Me)	34.6	148.8	24.3	–
	OH	1.50 (Me), 5.18 (OH)	72.1	150.7	32.3	–
	OOH	1.52 (Me), 10.95 (OOH)	84.0	145.5	26.6	–
	OOOH (**8**)	1.64 (Me), 13.67 (OOOH)	104.3	134.5	–	–
	H	1.33 d (Me), 4.65 q (H), 5.3 (OH)	69.9	147.3	25.1	–
	OOOH (**6k**)	13.20, 13.23 (1.2 : 1) (OH, OOOH)	105.26	–	–	–
	OOOH [b] (**6k**)	12.95, 13.12 (1 : 1) (OH, OOOH)	105.15	–	–	–
	H	–	79.7	144.4	24.7	56.2
	H [c]	1.35 d (Me), 3.05 (OMe), 4.12 q (H)	79.7	143.9	24.0	56.1
	OOH	10.6 (OOH)	106.4	142.5	25.4	49.7
	OOH [c]	1.65 (Me), 3.35 (OMe), 8.85 (OOH)	106.7	140.5	24.6	49.9
	OOOH (**3b**)	1.60 (Me), 3.25 (OMe), 13.19, 13.54 (1 : 1.2)	108.1	134.3	26.0	–
	OOOH [b] (**3b**)	1.80 (Me), 12.81, 13.04 [1 : (7 – 10)] (OOOH)	103.2, 104.1	–	–	–
	OOOH [d] (**3b**)	1.57 (Me), 12.90, 13.15 (1 : 1.2) (OOOH)	108.1	–	–	–

Note. The spectra were measured in $(CD_3)_2CO$ at −60 °C, the chemical shifts are given in ppm relative to tetramethylsilane; the signals in the ^1H NMR spectra are singlets unless otherwise specified; the ratios of the signal intensities are given in parentheses.
[a] At −73 °C. [b] In Et_2O. [c] In $CDCl_3$. [d] In $MeCO_2Et$.

Table 10. Chemical shifts of signals in the ^1H, ^{13}C and ^{29}Si NMR spectra of hydrotrioxides derived from organosilicon compounds and related compounds.

Compound	X	δ ^1H	δ ^{13}C		δ $^{29}Si(1)$
			C(1)	C(Me)	
	H	0.30 (Me), 4.40 (H)	140.6	−1.1	−16.95
	OH	0.32 (Me), 4.5 – 5.5 (OH)	143.5	3.1	3.30
	OOH	0.43 (Me), 11.2 (OOH)	139.6	2.8	14.31
	OOOH (**20a**)	0.55 (Me), 13.96 (OOOH)	138.5	2.7	17.31
	OOOH (**20a**) [a]	13.64 (OOOH)	–	–	–
	OOOH (**20a**) [b]	13.40 (OOOH)	–	–	–
	$OSiMe_2Ph$	0.33 (Me)	143.1	3.9	−0.96
	$OOSiMe_2Ph$	0.40 (Me)	139.5	2.8	16.6

Note. The spectra were measured in $(CD_3)_2CO$ at −78 °C; the chemical shifts are given in ppm relative to tetramethylsilane.
[a] In $MeCO_2Et$. [b] In Me_2O.

possibility of assigning the weaker signal to the ROOOH formed from the solvent was rejected.[17]

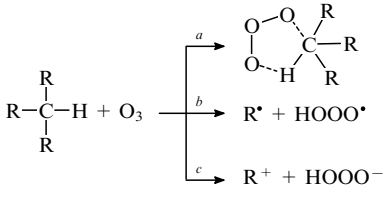
Based on the results of the concentration dependence and temperature variation studies, Plesničar *et al.*[17] concluded that HTO can form either intramolecularly hydrogen-bonded structures or rather strong eight-membered intermolecular associates.

In conclusion mention may be made of the first identification of isopropyl alcohol hydrotrioxide (**6f**) and hydrogen trioxide (**23**) by ^{17}O NMR spectroscopy.[94,95] The experimental results are in reasonable agreement with those of the *ab initio* GIAO/MP2/6-311++G** calculations of the ^{17}O chemical shifts. For HO(1)O(2)O(3)H (**23**), the experimental and calculated chemical shifts for the O(2) atom are 421 and 433 ppm, respectively, while δ[O(1,3)] = 305 (*cf.* the calculated value δ = 306). Hydrotrioxide $Me_2C(OH)$[O(1)O(2)O(3)H] (**6f**) is characterised by δ[O(1)] = 368, δ[O(2)] = 445 and δ[O(3)] = 305 (relative to $H_2{}^{17}O$). Probably, ^{17}O NMR spectroscopy of hydrotrioxides would serve as the basis for a breakthrough in understanding of the structure of organic HTO in the condensed phase.

IV. The mechanism of formation of organic hydrotrioxides

1. Experimental results

The reactions of ozone with C–H bonds of organic compounds leading to hydrotrioxides have been proposed to follow three main mechanisms, *viz*., a concerted 1,3-dipolar insertion of ozone (route *a*),[6,8,11,96,97] homolytic abstraction of an H atom by ozone followed by cage recombination of the radical pair (route *b*)[9,10,96,98] and ionic (molecular) mechanism (route *c*).[10,11,76,98]



Obviously, the variety of transformations of organic compounds in the reactions with ozone to give HTO cannot be described by a common mechanism. In this connection, the

study by Giamalva, Church and Pryor[99] is remarkable. They proposed that the reactions of O_3 with a number of cage hydrocarbons proceed by the insertion mechanism (route *a*) with the feasible transition states considered to be a set of resonance structures including both the radical (route *b*) and ionic (route *c*) mechanisms as the limiting cases.

The dominating reaction mechanism depends on the nature of the substrate and oxidation conditions. Let us consider the experimental grounds that serve as the basis for inferences about the most plausible mechanism of the ozone reaction with the C–H bond.

a. Reaction kinetics

The pre-exponential factors for the reaction RH + O_3 (Table 11) are 2 to 3 orders of magnitude lower than those of typical radical abstraction reactions of the H atom.[101] The estimate $\log A \approx 6.5$ obtained for the 1,3-addition reaction (route *a*) (see Ref. 76) is close to the activation parameters listed in Table 11; however, the experimental activation energies are incompatible with the energies of formation of pentacoordinated carbon. Taking into account the strain energy in the five-membered ring in the transition state of the 1,3-addition reaction, the expected E_a value must lie between 20 and 26 kcal mol^{-1} (see Ref. 76).

Table 11. Activation parameters of the reactions of organic compounds with ozone.[100]

Substrate	Solvent	$\log A$ /litre mol^{-1} s^{-1}	E_a /kcal mol^{-1}
cyclo-C_6H_{12}	cyclo-C_6H_{12}	7.71	13.7
$PhPr^i$	$PhPr^i$	6.4	8.7
EtOH	EtOH	4.88	7.3
	MeCOOH	6.15	9.1
	CCl_4	6.81	10.0
cyclo-$C_6H_{11}OH$	CCl_4	6.26	7.9
MeCOEt	CCl_4	10.7	18.5

b. Kinetic isotope effect

Relatively high k_H/k_D values (see Table 12) indicate substantial weakening of the C–H bond in the transition state of the reaction RH + O_3. A large kinetic isotope effect is evidence for the linear transfer of a proton and its symmetric localisation in the transition state.[102] This conclusion contradicts the mechanism of 1,3-cycloaddition and precludes linear arrangement of the C, H and O atoms.

Table 12. Kinetic isotope effect in the oxidation of organic compounds by ozone.[10, 96, 100]

Substrate	Solvent	T/K	k_H/k_D
cyclo-C_6D_{12}	cyclo-C_6H_{12}–cyclo-C_5H_{10}	295	4.1–4.5
$PhCD_2OCMe_3$	Freon 11	273	3.8–4.1
$MeCD_2OCMe_3$	Me_2CO	273	2.4–4.5
$MeCD_2OH$	CCl_4	293	5.9

c. Relative reactivity

Ozone exhibits a much higher selectivity toward primary, secondary and tertiary C–H bonds (0.003 : 1 : 87) as compared to alkoxyl (0.08 : 1 : 33.7) and peroxyl (0.024 : 1 : 10) radicals.[4]

d. Structure of a substrate

It is remarkable that compounds used as substrates in the liquid-phase ozonisation to give HTO, *viz*., oxygen-containing compounds (acetals, ethers, alcohols), hydrocarbons (cumene, cage compounds, including those containing the cyclopropane fragment) and silanes exhibit a common feature consisting of the possibility of effective stabilisation of the derived carbocation. Ozone was found to react with the benzylic C–H bond of fluorene at a much lower rate than with the analogous bond in diphenylmethane and 9,10-dihydroanthracene derivatives.[103] The low reactivity of fluorene is due to the fact that the formation of a carbocation from fluorene is less energetically favourable than from the other two compounds.[103]

Studies within the same class of compounds showed that electron-donor substituents accelerate the reaction of the RH + O_3 type and that the apparent rate constant for the reaction series for substituted toluenes ($\rho = -2.07$) substantially differs from the ρ values for peroxyl (-0.76) and alkoxyl (-0.34) radicals.[4]

e. Solvent effect

The yields of HTO in the oxidation of aliphatic and aromatic acetals by ozone in polar solvents (acetone, diethyl ether) are much higher than in dichloromethane and pentane.[4, 19, 20]

f. Formation of charge-transfer complexes

Taking into account the high electron affinity of ozone, one can assume that the reaction with the appropriate substrate will proceed with partial transfer of the electron density to the O_3 molecule. Indeed, the reaction of ozone with alkylaromatic compounds (*e.g*., cumene) results in a charge-transfer complex, which was proved by spectroscopic methods.[104–107] Further nonradical transformation of the complex results in the hydrotrioxide. This is confirmed by a substantial increase in the yield of the hydrotrioxide **8** upon irradiation of the reaction mixture by light in the spectral region corresponding to absorption of the charge-transfer complex;[28, 29] the absence of kinetic isotope effect in the reaction of ozone complex with toluene-d_8[108] and by acceleration of the decomposition of ozone–arene complexes in polar solvents.[109]

2. Thermochemical analysis of the mechanisms of formation of ROOOH

Thermochemistry of the reactions of ozone with the C–H bonds was investigated taking the reaction with ethanol as an example. Detailed kinetic studies[24, 100] of the reaction revealed its first order with respect to both reagents, the rate constants were determined over a wide temperature range (see Table 11) and the dependence of the rate constant on the chemical nature of solvent was investigated.

At $T = 293$ K, the rate constant for the gas-phase reaction EtOH + O_3 is 0.72±0.06 litre mol^{-1} s^{-1}.

Let us consider a feasible mechanism for this reaction. α-Hydroxyethyl hydrotrioxide **6b** was reliably established[24, 100] to be the major product. As mentioned above, the mechanism of 1,3-dipolar insertion (route *a*), for which $\log A \approx 6.5$ and $E_a \approx 20-26$ kcal mol^{-1}, is inconsistent with the observed Arrhenius parameters (see Table 11).

The enthalpies of the reactions proceeding by routes *b* and *c* can be calculated using the following values (in kcal mol^{-1}): $\Delta_f H^\circ$(EtOH) = −56.1,[110] $\Delta_f H^\circ(O_3)$ = 34.0,[110] $\Delta_f H^\circ$(MeĊHOH) = −14.5±3,[111] $\Delta_f H^\circ$(MeC$^+$HOH) = 139±3[111] and $\Delta_f H^\circ$(HOOO$^\bullet$) = 15.3.[18] The $\Delta_f H^\circ$(HOOO$^-$) value can be found using the gas-phase acidity of HOOOH (352 kcal mol^{-1} obtained from the *ab initio* MP4//MP2/6-31++G* calculations[52]) and $\Delta_f H^\circ$(HOOOH) = −12.2 kcal mol^{-1} (see Ref. 18). Thus we get $\Delta_f H^\circ$(HOOO$^-$) = −25.9 kcal mol^{-1}.

The activation energy of the gas-phase reaction of ethanol with ozone was estimated using the experimental rate constant $k = 0.72$ litre mol^{-1} s^{-1} provided that $A = 1 \times 10^8$ litre mol^{-1} s^{-1} (see Ref. 112); this gives $E_a = 10.9$ kcal mol^{-1}.

The enthalpy of a reaction proceeding by the radical route *b* is

$$\Delta H^\circ(b) = \Delta_f H^\circ(\mathrm{MeC\dot{H}OH}) + \Delta_f H^\circ(\mathrm{HOO\dot{O}}) -$$
$$- \Delta_f H^\circ(\mathrm{EtOH}) - \Delta_f H^\circ(\mathrm{O_3}) =$$
$$= 15.3 - 14.5 - 34.0 + 56.1 = 22.9 \text{ kcal mol}^{-1}.$$

Comparison of the $\Delta H^\circ(b)$ and E_a values suggests that the homolytic mechanism for the formation of the hydrotrioxide **6b** is energetically unfavourable. In addition, both thermochemical estimates [18, 66] and quantum-chemical calculations [70, 71, 113] predict that the radical HOOO$^\bullet$ is less stable compared to its decomposition products (HO$^\bullet$ and O_2) and decomposes almost barrierlessly. This reduces the role of the radical HOOO$^\bullet$ in the formation of HTO from saturated organic compounds to a minimum. Thus, the homolytic mechanism (route *b*) is inconsistent with thermochemical estimates.

The enthalpy of the gas-phase reaction of the hydride ion transfer (route *c*) can be calculated using the following equation

$$\Delta H^\circ(c) = \Delta_f H^\circ(\mathrm{MeC^+HOH}) + \Delta_f H^\circ(\mathrm{HOOO^-}) -$$
$$- \Delta_f H^\circ(\mathrm{EtOH}) - \Delta_f H^\circ(\mathrm{O_3}) + E_q\,.$$

Here, E_q is the energy of the Coulomb interaction within the ion pair ($-e^2/r$), where r is the inter-charge separation. Assuming that $r = 2.65 \pm 0.05$ Å,[76] we get

$$\Delta H^\circ(c) = 139 - 25.9 - 34.0 + 56.1 - 125 = 10.2 \text{ kcal mol}^{-1}.$$

As can be seen, the calculated E_a value is in good agreement with $\Delta H^\circ(c)$.

Calculations of $\Delta H^\circ(c)$ values for liquid-phase reactions face considerable difficulties owing to the lack of reliable methods for calculating the solvation energies of reactants, $\Delta H^\circ(\mathrm{solv})$. A qualitative estimate, $\Delta H^\circ(\mathrm{solv}) < 0$, can be obtained by simply reasoning that the ionic character of the transition state will favour its solvation compared to the electrically neutral EtOH and O_3. It is also clear that $\Delta S_0(\mathrm{solv}) < 0$. Therefore, the $\log A$ and E_a values for the liquid phase will be smaller than those obtained for the gas phase, which is consistent with the experimental results (see Table 11). Nangia and Benson [76] used the Kirkwood formula for calculating the change in the Gibbs free energy of solvation. However, it was noted [100] that this approach *a priori* implies too strong a dependence of the rate constant for the reaction on the dielectric constant of the medium. We believe that a consistent explanation is that the actual transition state is not purely ionic but includes to a great extent the contribution of charge transfer from $\mathrm{MeC^+HOH}$ to $\mathrm{HOOO^-}$.

3. Formation of hydrotrioxides in the ozonisation of hydrocarbons

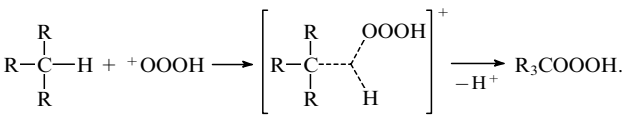
Experiments show that the most plausible mechanism for the reaction of ozone with the C–H bonds of organic compounds involves a hydride transfer of hydrogen to ozone followed by cage recombination of the ion pair (route *c*). The reaction is favoured by some factors responsible for the stabilisation of the carbocation formed: the structure of the substrate, polar substituents in the substrate, the presence of electron-donor substituents at the reaction centre.

In the absence of these factors the most plausible mechanism for the reaction $RH + O_3$ involves a homolytic abstraction of a H atom by the ozone molecule. The energy profiles of the reactions of ozone with the C–H bonds of methane, ethane, propane and isobutane have been studied.[113] In the transition state, the H atom is nearly orthogonal to the plane passing through three oxygen atoms, which indicates the involvement of the π-MO of ozone in the formation of a new bond. The C–H–O angle is rather large (167 to 174°) and the C–H and H–O distances are close (1.28 and 1.25 Å for methane and 1.27 and 1.34 Å for isobutane, respectively). This is consistent with the results obtained in studies of the kinetic isotope effect (see Section IV.1). According to quantum-chemical calculations, all the localised transition states have large contributions of biradical structures. The radical HOOO$^\bullet$ formed in the reaction is extremely unstable and decomposes into the oxygen molecule and the hydroxyl radical

$$RH + O_3 \longrightarrow R^\bullet + HOOO^\bullet \longrightarrow R^\bullet + O_2 + {}^\bullet OH.$$

Thus, the probability of the homolytic mechanism of the ozonisation of hydrocarbons containing non-activated C–H bonds in the gas phase (or in non-polar solvents) is very low.

On the other hand, the contribution of radical structures to the transition state decreases as the number of alkyl substituents in the α-position relative to the C–H bond involved in the reaction increases.[113] Hence under specific conditions (*e.g.*, with appropriate substituents and medium) the ionic mechanism can become even more energetically favourable. This can occur in the ozonisation of alkanes in superacidic solutions at −78 °C.[114, 115] The reaction proceeds *via* a transition state with the 3c-2e bond between the protonated ozone, $HOOO^+$, and the C–H bond. The pentacoordinated carbonium ion either undergoes further decomposition or loses a proton to give the corresponding hydrotrioxide:



Yet another specific procedure for the preparation of hydrotrioxides of non-activated organic compounds is 'dry' ozonisation, *i.e.*, the reaction of ozone with hydrocarbons adsorbed on a polar surface. The synthesis of HTO **11** and **15**–**19** by 'dry' ozonisation of aliphatic, alicyclic and alkylaromatic hydrocarbons on silica gel has been reported.[18, 31, 32]

$$RH \xrightarrow[-70\ ^\circ C]{O_3,\ SiO_2} \underset{\mathbf{11,\ 15-19}}{ROOOH}.$$

It was also noted in these studies that hydrotrioxides **11** and **15**–**19** cannot be obtained by conventional liquid-phase oxidation.

Triphenylmethylhydrotrioxide **18** can be prepared not only by 'dry' ozonisation but also in solution. However, low solubility of triphenylmethane at temperatures near −70 °C precludes the synthesis of Ph_3COOOH in solution. In addition, this synthesis requires thermal activation or photoactivation of the intermediate complex $ArH \cdot O_3$, as in the case of cumyl hydrotrioxide.[28, 29] In 'dry' ozonisation, the polar surface acts as an activator.

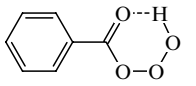
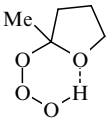
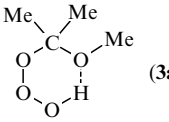
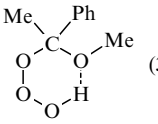
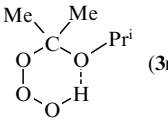
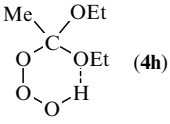
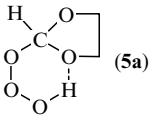
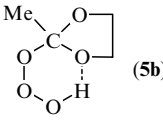
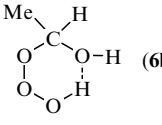
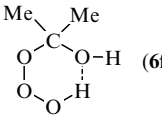
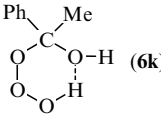
We can distinguish several factors responsible for the differences between the low-temperature ozonisation of hydrocarbons on the surface and the ozonisation in solution. First, the concentrations of reagents on the surface of the adsorbent can be very high, which cannot be achieved in solution at low temperature. As a result, ozonisation on the surface proceeds much faster.[116] Second, low mobility of the adsorbed reagents, intermediates and products reduces the probability of side reactions and, hence, increases selectivity of the process. Finally, the surface of silica gel is a highly polar anisotropic medium, which stabilises the ionic intermediates. Thus, the formation of hydrotrioxides ROOOH by 'dry' ozonisation is yet another argument in favour of the ionic mechanism of the reactions of ozone with the C–H bonds of saturated organic compounds.

V. Decomposition of hydrotrioxides

1. Reaction products. Chemiluminescence

The thermolysis products of hydrotrioxides **1a**, **2**, **3d**, **3m**, **4h**, **5a**,**b**, **8** and **20a** are presented in Table 13. It should be noted that with a few exceptions (see notes to Table 13) the decomposition products were analysed together with the products formed in the synthesis of ROOOH; because of this, the yields of each of the products were calculated with respect to ozone consumed to give the

Table 13. Thermal decomposition products of ROOOH.

ROOOH	Solvent	Product	Yield [a] /mol mol^{-1}	Ref.
 (**1a**)	RH	$PhCO_2H$	0.96	14
 (**2**)	RH	$MeCOCH_2CH_2CH_2OH$	0.70 [b]	14
 (**3a**)	CD_3COCD_3	Me_2CO MeOH HOOH $Me_2C(OMe)OOH$	0.32 0.29 0.05 0.03	95
 (**3b**)	Me_2CO $MeCO_2Et$	PhCOMe MeOH $PhCO_2Me$ $PhCO_2H$	0.50 0.14 0.20 0.05	17
 (**3m**)	RH	$Me_2CO : Me_2CHOH : MeCO_2Pr^i = 1 : 1.3 : 2.7$		96
 (**4h**)	RH	$MeCO_2Et$ EtOH	0.80 – 0.85 0.75 – 0.80	20
 (**5a**)	RH	$HCOOCH_2CH_2OH$	1.0	23
 (**5b**)	RH	$MeCO_2CH_2CH_2OH$	1.0	23
 (**6b**)	RH	MeCHO $MeCO_2H$ HCOOH HOOH	0.31 0.56 0.12 0.58	25, 100
 (**6f**)	Bu^tCOMe	Me_2CO $MeCO_2H$ HOOH	0.37 0.39 0.11	95
 (**6k**)	Me_2CO $MeCO_2Et$	PhCOMe $PhCO_2H$	0.65 0.05	17
$PhMe_2COOOH$ (**8**)	CD_3COCD_3	$PhMe_2COH$ PhCOMe	0.8 – 0.9 [c] 0.1 – 0.2 [d]	29
$PhMe_2SiOOOH$ (**20a**)	CD_3COCD_3	$PhMe_2SiOH$ $PhMe_2SiOSiMe_2Ph$ H_2O_2 $PhMe_2SiOOH$	0.9 [c] 0.08 0.09 0.05	33

Note. Hydrotrioxides ROOOH were obtained by oxidation of the corresponding substrates RH. [a] The yields are given with respect to ozone consumed in the reactions, $\Delta(O_3)$. [b] The product undergoes further cyclisation and dehydration to give 2-methyl-4,5-dihydrofuran. [c] The yields are given with respect to HTO. [d] The yield is given with respect to Δ[ROOOH]; decomposition of the hydrotrioxide **8** in the presence of ionol results in $PhMe_2COH$ as the only reaction product.

particular product, $\Delta[P]/\Delta(O_3)$. All the reactions are accompanied by evolution of molecular oxygen including $^1O_2$.

According to the data listed in Table 13 thermal decomposition reactions of the hydrotrioxides derived from benzaldehyde (**1a**), acetals (**4h**, **5a**,**b**), cumene (**8**) and dimethylphenylsilane (**20a**) in which the reaction products are formed in nearly 100% yields exhibit the highest selectivities. As was mentioned above, silane-derived hydrotrioxides decompose to give, in particular, HOOOH.[33,34] Taking hydrotrioxide **6b** as an example, it was shown that the yields of the major decomposition products, *viz*., $\Delta[P]/\Delta(O_3) = 0.30\pm0.04$ for MeCHO, 0.56 ± 0.03 for MeCOOH, 0.11 ± 0.03 for HCOOH and 0.57 ± 0.03 for H_2O_2, are virtually independent of temperature in the range between -78 and 0 °C.[25]

Decomposition of HTO is accompanied by chemiluminescence in the visible spectral region.[16,21,27,117–119] The chemiluminescence spectra of compounds **8**, **6d**, **6f**, **6e**, **7a**, **3m** and **1** exhibit maxima (λ) at 425, 425, 405, 405, 405, 405 and 515 nm, respectively. No chemiluminescence was observed in the thermolysis of the hydrotrioxide **6b**. Based on comparison of both the fluorescence and phosphorescence spectra of the carbonyl compounds which resulted from decomposition of ROOOH and the chemiluminescence spectra in the visible spectral region it was concluded that the emitters of chemiluminescence are excited carbonyl groups ($>C=O^*$).

One of the most interesting and important properties of hydrotrioxides is their ability to generate $^1O_2$ during thermal decomposition.[13,14,16,17,19–21,27,31–33,35,52,89,117,118,120–122] The formation of singlet molecular oxygen was proved by carrying out specific reactions of singlet oxygenation of unsaturated organic compounds (see Section VII.1). Yet another convincing proof of the formation of $^1O_2$ is intense chemiluminescence in the IR spectral region with a maximum at $\sim$1270 nm, which is typical of O_2 ($^1\Delta_g$).[123]

Chemiluminescence in the visible and IR spectral regions has also been observed in the decomposition of adamantyl hydrotrioxide **15** on the surfaces of silica gel and alumina.[32,39] Spectral characteristics of chemiluminescence were found to be identical with those observed in the liquid phase. The yield of singlet molecular oxygen was determined by three methods.

The first method involved measurements of the amount of the $^1O_2$ acceptor consumed (1,3-diphenylisobenzofuran, 1,2-dimethylcyclohexene or tetraphenylcyclopentadienone).[13–15,17,19,20,28,29,35] The yield of singlet molecular oxygen ($\Phi_0 = \Delta[^1O_2]/\Delta[ROOOH]$ /mol mol^{-1}) was calculated based on the assumption that the amount of $^1O_2$ that evolved in the reaction ($\Delta[^1O_2]$) is equal to the amount of acceptor consumed ($\Delta[A]$). However, this approach provides only semiquantitative data on the yield of $^1O_2$,[124] so it is not surprising that the results obtained in the experiments with different $^1O_2$ acceptors differ substantially. For instance, the $\Delta[^1O_2]/\Delta[ROOOH]$ values for 1,1-diethoxyethane-derived hydrotrioxide (**4h**) found using tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran were $20\pm5\%$ and $54\pm5\%$, respectively.[20] Quantitative determination of the yield of $^1O_2$ requires a kinetic approach based on rigorous analysis of all possible consumption channels for the $^1O_2$ acceptor, hydrotrioxide and singlet molecular oxygen. The drawback of this method is that the acceptor of singlet molecular oxygen can be oxidised by the hydrotrioxide, which leads to overestimation of the results of measurements of the Φ_0 values.

Generation of $^1O_2$ in the decomposition of ROOOH, its deactivation and quenching by acceptors A was found [16] to follow a mechanism similar to that of the thermolysis of organic phosphite ozonides [124]

$$ROOOH \xrightarrow{k_0} P_0 + O_2,\ ^1O_2,$$

$$^1O_2 \xrightarrow{k_d} O_2, h\nu,$$

$$^1O_2 + A \xrightarrow{k_r} AO_2,$$

$$^1O_2 + A \xrightarrow{k_q} A + O_2,$$

where k_0, k_d, k_r and k_q are the rate constants for thermal decomposition of the hydrotrioxide, radiative deactivation of singlet molecular oxygen and chemical and physical quenching of $^1O_2$ by the acceptor A, respectively; and P_0 is the decomposition product of the hydrotrioxide.

Based on this mechanism, for the steady state we get

$$\ln\left(\frac{I_0}{I_t}\right) = k_0 t, \tag{10}$$

$$\frac{I_0}{I_A} = 1 + k\tau_d[A], \tag{11}$$

$$\frac{[A]_0 - [A]_\infty}{[ROOOH]_0} = \Phi_0\Phi_r - (k\tau_d)^{-1}\left\{\frac{\ln([A]_0/[A]_\infty)}{[ROOOH]_0}\right\}. \tag{12}$$

Here I_0 and I_A are the initial intensities of chemiluminescence in the absence and in the presence of the acceptor A, respectively; I_t is the current intensity of chemiluminescence in the absence of the acceptor; t is time; $k = k_r + k_q$; $\tau_d = 1/k_d$ is the lifetime of $^1O_2$ in the solvent specified; $[A]_\infty$ is the concentration of the acceptor in the reaction mixture after complete decomposition of ROOOH ($t \to \infty$); and $\Phi_r = k_r/(k_q + k_r)$.

Equation (10) can be used to follow the kinetics of the overall decomposition of ROOOH in the absence of the acceptor A. The Stern–Volmer equation (11) allows determination of the parameter $k\tau_d$ and calculation of the overall rate constant for quenching of singlet molecular oxygen by the substrate A provided that τ_d is known. This approach was used [120–122] for calculations of the k values for quenching of $^1O_2$ that evolved during the decomposition of hydrotrioxides **4h**, **6b**,**f** and **7b** by alkenes, dienes, phenols, glycosides and flavonoids.

The yield of $^1O_2$ can be determined from Eqn (12) using the Φ_r and $(k\tau_d)^{-1}$ values that can be found experimentally. Preference should be given to those acceptors which are characterised by high k_r values and $\Phi_r \approx 1$ (*e.g.*, 1,3-diphenylisobenzofuran). The results obtained by this method for hydrotrioxides **3m**, **4h** and **6b**,**f** are listed in Table 14. This approach is appropriate in the case of systems with relatively low concentrations of the acceptor (10^{-5} to 10^{-3} mol litre^{-1}). If the initial concentrations of the acceptor ($[A]_0$) are high, account must be taken of the reaction of the acceptor with HTO.

Yet another procedure for the determination of Φ_0 involves measurements and comparison of total light emissions for the reactions of thermal decomposition of ROOOH under study and a standard source of $^1O_2$ (*e.g.*, triphenyl phosphite ozonide).[18] This method has been employed for the determination of Φ_0 in the recombination of peroxyl radicals [125] and decomposition of di(*tert*-butyl) trioxide in various solvents.[126] The Φ_0 values were calculated using Eqn (13)

$$\Phi_0 = \Phi_{st}\frac{S_{ROOOH}}{S_{st}}\frac{k_d}{k_d^{st}}\frac{k_r^{st}}{k_r}\frac{[(PhO)_3PO_3]_0}{[ROOOH]_0}, \tag{13}$$

where Φ_0 is the yield of singlet molecular oxygen per 1 mol of HTO decomposed; $\Phi_{st} = 1$ (see Ref. 124) is the yield of singlet molecular oxygen in the decomposition of the standard source of $^1O_2$ (triphenyl phosphite ozonide); and S_{ROOOH} and S_{st} are the areas under the chemiluminescence decay curves for the decomposition of ROOOH and the standard source of $^1O_2$, respectively.

The Φ_0 values for a number of HTO are listed in Table 14. In all cases, except for hydrotrioxide **6f** in propan-2-ol, methods A and D give close Φ_0 values which are much smaller than the yields of $^1O_2$ calculated by methods B and C. This suggests that HTO are efficient sources of singlet molecular oxygen, though their efficiency has sometimes been overestimated.

Table 14. The yield of singlet molecular oxygen upon thermolysis of hydrotrioxides.[14, 16, 18, 20, 89]

Hydrotrioxide	Solvent	T /°C	Φ_0 (%)	Method of determination of Φ_0 [a]
1a	CH_2Cl_2	4.5	0.04	A
	Et_2O	−30	0.02	see [b]
	RH	⩾ −50	96	B
2	RH	⩾ −70	80	B
3a	RH	⩾ −23	30	B
3b	Me_2CO	–	45	B
	Me_2CO	–	22	C
3h	CH_2Cl_2	3.0	10.1	A
3m	CH_2Cl_2	6.0	5.0	A
	RH	−10	1.7	D
4h	CH_2Cl_2	7.5	19.0	A
	RH	−58	7.3	D
	RH	−45	5.2	D
	RH	⩾ −50	54	B
	RH	⩾ −50	20	C
5c	CH_2Cl_2	5.0	0.5	A
6a	CH_2Cl_2	6.0	2.5	A
6b	CH_2Cl_2	6.5	13.6	A
	RH	−20	10.3	D
6f	CH_2Cl_2	8.0	8.0	A
	PhCl	0	7.0	D
	RH	−29	78	D
	RH	−20	70	D
	RH	−10	55	D
	RH	−2.5	48	D
6k	Me_2CO	–	60	B
	Me_2CO	–	25	C
7a	CH_2Cl_2	6.0	3.0	A
11	CH_2Cl_2	6.0	1.2	A
15	CH_2Cl_2	−3.0	7.2	A
	CH_2Cl_2	12.0	6.4	A
16	CH_2Cl_2	15.0	15.0	A
18	CH_2Cl_2	5.0	2.6	A
19	CH_2Cl_2	12.0	5.2	A
	CH_2Cl_2	6.0	5.6	A
20a	CD_3COCD_3	⩾ −78	65	B
	CD_3COCD_3	⩾ −78	25	C

Note. Hydrotrioxides ROOOH were obtained by oxidation of the corresponding substrates RH. [a] For methods A and D, the yield of $^1O_2$ was determined from Eqn (10) and Eqn (12), respectively; for methods B and C, the Φ_0 value was determined by following the consumption of the acceptors of singlet molecular oxygen, *viz*., 1,3-diphenylisobenzofuran (B) and tetraphenylcyclopentadienone (C). [b] The HTO was decomposed by a light pulse (λ = 266 nm), the Φ_0 value was determined from the relative intensity of chemiluminescence at λ = 1270 nm.

The influence of the reaction conditions on the yield of singlet molecular oxygen has been studied.[16, 18] It was found that the Φ_0 value decreases as the initial concentration of hydrotrioxide **3m** ([**3m**]$_0$) increases. This effect was explained by an increase in the contribution of 'blank' decomposition (without production of $^1O_2$) of ROOOH induced by free radicals with an increase in [**3m**]$_0$.[18] Taking hydrotrioxides **6f** [16] and **6b** [18] as examples, it was shown that the increase in temperature leads to a decrease in Φ_0. For compound **6b**, the temperature dependence of Φ_0 is satisfactorily described by the Bagdasaryan equation.[127] It seems likely that singlet molecular oxygen can be produced either by molecular conversion of ROOOH or as a result of disproportionation of the solvent-caged radical pair, [RO$^{\bullet}$ $^{\bullet}$OOH]. In a recent study,[18] preference has been given to the latter mechanism for the formation of ROOOH.

Table 15. Effect of solvents on the rate constant for decomposition and on the yield of singlet molecular oxygen in thermolysis of the hydrotrioxide **6b** {5 °C, [MeCH(OH)OOOH] = 0.011 mol litre^{-1}}.

Solvent	$10^3 k$ /s^{-1}	Φ_0 (%)	Solvent	$10^3 k$ /s^{-1}	Φ_0 (%)
$CFCl_3$	47.7	18.1	$C_6D_5CD_3$	21.4	13.6
CCl_4	57.4	10.1	$PhCH_2Cl$	10.6	10.4
$CHCl_3$	42.5	15.2	$PhCH_2OH$	40.0	1.6
CH_2Cl_2	31.5	13.3	PhEt	22.6	7.6
$C_2H_4Cl_2$	22.7	11.6	$PhPr^i$	32.8	5.6
PhH	28.9	8.0	Me_2CO	3.6	14.6
PhCl	34.0	6.4	MeCN	9.0	12.7
PhMe	24.4	13.0	$MeNO_2$	22.0	0.9

Solvent has a pronounced effect on Φ_0 in the case of thermal decomposition of the hydrotrioxide **6b** (Table 15). Using the Koppel – Palm correlation equation, the yield of $^1O_2$ was analysed as the function of the properties of the solvent and it was found that the yield of singlet molecular oxygen, Φ_0, increases as the solvent polarity increases, whereas enhancement of specific solvation in the transition state leads to a decrease in Φ_0.[18]

2. The kinetics of overall decomposition of hydrotrioxides

The kinetics of overall decomposition of HTO is studied by ^{1}H NMR spectroscopy (as the basic method) and chemiluminescence technique. Within the limits of experimental errors, both methods give usually the same results. Decomposition of ROOOH proceeds as a first-order reaction [14–21, 23, 24, 26–29, 31, 33, 35, 89, 119, 128]

$$-\frac{d[ROOOH]}{dt} = k_0[ROOOH].$$

The available rate constants k_0 and activation parameters of the reaction are collected in Table 16. The $\log A_0$ and E_0 values are related by a linear dependence (the compensation effect):

$$\log A_0 = -3.5 + 0.95\,E_0\,.$$

This dependence holds for a very broad range of changes in E_0 (from 1.7 to 25.1) and $\log A_0$ (from 0.2 to 21.6). It covers almost all available experimental data (Fig. 1) and suggests a common mechanism for the decomposition of ROOOH. The linear dependence between $\log A_0$ and E_0 indicates that the linear free energy relationship and the correlation equations based on it which relate the reactivity of HTO to their structure and to the physicochemical properties of the medium should also hold in the case of thermal decomposition of ROOOH in the liquid phase.

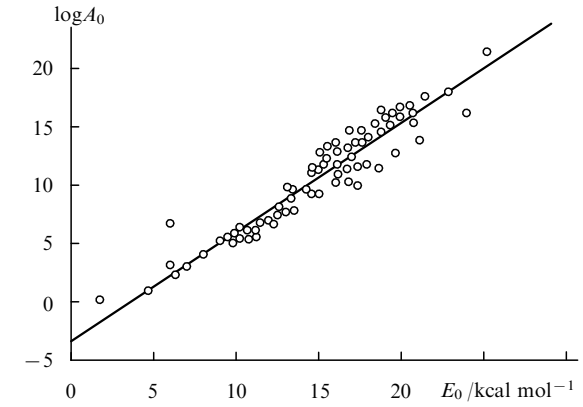


Figure 1. Compensation effect in the thermal decomposition of hydrotrioxides.

Table 16. Kinetic parameters of the overall decomposition of hydrotrioxides.

Compound	Solvent	Temperature /°C	$\log A_0$ ($\log k_0$)	E_a /kcal mol^{-1}	$\Delta G^{\neq}$ /kcal mol^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /cal mol^{-1} K^{-1}	Ref.
1a	RH	−34 – 12	5.4	10.7	19.2	10.2	−35.5	14
	RH : Et_2O = 21.3 : 78.7 (mass %)	−39 to −19	11.1	16.4	18.3	15.9	−9.4	14
	Et_2O	–	10.1	17.2	20.3	16.7	−14.1	89
	RH	0	(−3.16)	–	–	–	–	129
1b	CH_2Cl_2 : MeOH = 1 : 1 (vol.%)	−50 – 30	7.7	13.0	–	–	–	16
1c	CH_2Cl_2 : MeOH = 1 : 1 (vol.%)	−50 – 30	5.45	10.1	–	–	–	16
1d	CH_2Cl_2 : MeOH = 1 : 1 (vol.%)	−50 – 30	2.3	6.3	–	–	–	16
1e	CH_2Cl_2 : MeOH = 1 : 1 (vol.%)	−50 – 30	5.45	10.3	–	–	–	16
1f	CH_2Cl_2 : MeOH = 1 : 1 (vol.%)	−50 – 30	5.7	11.2	–	–	–	16
2	RH	−68 to −6	4.1	8.0	18.0	7.5	−41.4	14
	RH : Et_2O = 15.4 : 84.6 (mass %)	−33 to −11	11.7	17.4	18.6	16.9	−6.6	14
3a	RH	−38 to −9	11.5	16.6	18.0	16.1	−7.6	14
3b	Me_2CO	−30 to −10	16.0	19.9	16.1	19.4	13.0	17
	$MeCO_2Et$	−25 to −15	14.2	18.0	16.3	17.5	4.8	17
	$MeCO_2Et$ [a]	−25 to −15	15.3	19.3	16.3	18.8	9.8	17
	Freon 11/12	−20	(−1.73)	–	–	–	–	17
	Freon 11/12	−25	(−1.98)	–	–	–	–	17
	Et_2O	−45 to −35	12.9	15.1	16.4	14.6	7.2	17
	Me_2CO [a]	−30 to −15	16.4	20.6	16.3	20.1	14.8	17
	Et_2O [a]	−45 to −35	13.3	15.5	14.8	15.0	0.7	17
3c	Me_2CO	−30 to −10	13.8	17.6	16.4	17.1	3.0	17
	$MeCO_2Et$	−30 to −15	11.8	15.3	16.4	14.8	−6.2	17
	Et_2O	−50 to −35	16.4	18.8	14.9	18.3	13.4	17
3d	Et_2O	−45 to −30	13.7	16.0	14.9	15.5	2.5	17
3e	$MeCO_2Et$	−25	(−1.73)	–	–	–	–	17
	$MeCO_2Et$	−20	(−1.42)	–	–	–	–	17
	Et_2O	−45 to −35	13.2	15.5	15.0	15.0	0.2	17
3f	Et_2O	−55 to −40	14.8	16.8	15.1	16.3	4.9	17
3g	Me_2CO	−30 to −20	16.8	20.4	15.7	19.9	16.7	17
	$MeCO_2Et$	−20 to −10	11.5	14.8	16.2	14.3	−7.6	17
	Et_2O	−55 to −35	14.7	16.9	15.9	16.4	2.1	17
3i	Et_2O	−40 to −25	12.3	15.4	15.9	14.9	−3.9	17
3j	Et_2O	−40 to −30	11.6	14.6	15.9	14.1	−7.1	17
3k	Et_2O	−50 to −35	16.4	19.2	14.9	18.7	14.9	17
3l	Et_2O	−50 to −35	14.8	17.6	15.2	17.1	7.5	17
3m	RH	−50 – 30	11.0	16.2	–	–	–	16
4a	RH	−20 to −10	15.6	20.7	17.4	20.2	11.2	20
	RH : CH_2Cl_2 = 3 : 7 (mass %)	−10	(−1.40)	–	–	–	–	20
	RH : Et_2O = 3 : 7 (mass %)	−20 to −10	11.8	16.1	17.2	15.6	−6.2	20
4b	RH : Et_2O = 3 : 7 (mass %)	−40 to −30	15.9	19.0	15.3	18.5	12.6	20
4c	RH : Et_2O = 3 : 7 (mass %)	−35 to −20	17.8	21.4	15.5	20.9	21.3	20
4d	RH : Et_2O = 3 : 7 (mass %)	−35 to −25	13.7	17.2	16.1	16.7	2.5	20
4e	RH : Et_2O = 3 : 7 (mass %)	−40 to −30	16.4	19.5	15.2	19.0	14.9	20
4f	RH : Et_2O = 3 : 7 (mass %)	−40 to −35	15.4	18.4	15.3	17.9	10.3	20
4g	RH : Et_2O = 3 : 7 (mass %)	−35 to −25	21.6	25.1	15.7	24.6	35.1	20
4h	RH	−20 to −10	11.1	14.5	16.4	14.0	−9.4	20
	RH : Et_2O = 3 : 7 (mass %)	−20 to −10	9.8	13.2	16.6	12.7	−15.3	20
	RH [b]	−50 to −10	18.2	22.8	16.5	22.3	23.1	21
4i	RH : Et_2O = 3 : 7 (mass %)	−40 to −30	16.7	19.8	15.2	19.3	16.2	20
5a	RH	−30	(−4.15)	–	–	–	–	23
5b	RH	−30	(−3.85)	–	–	–	–	23
5d	RH : CH_2Cl_2 = 3 : 7 (mass %)	−30 to −20	16.6	20.5	16.0	20.0	15.8	20
	RH : Et_2O = 3 : 7 (mass %)	−40 to −30	13.1	15.9	15.5	15.4	−2.4	20
4n	CH_2Cl_2	−30 to −20	14.7	18.7	16.4	18.2	7.1	20
	RH : Et_2O = 3 : 7 (mass %)	−40	(−1.96)	–	–	–	–	20
5f	RH : Et_2O = 3 : 7 (mass %)	−40	(−1.57)	–	–	–	–	20
6b	RH	−70 to −30	3.08	7.0	18.2	6.5	−46.1	24
	CH_2Cl_2	−15 – 18	8.1	12.6	–	–	–	18
6c	CH_2Cl_2	−20	(−2.12)	–	–	–	–	26
6d	RH	−30 – 8	12.6	17.0	17.1	16.5	−2.5	26
	CH_2Cl_2	−20	(−1.43)	–	–	–	–	26
6e	RH	−20	(−1.51)	–	–	–	–	26
	CH_2Cl_2	−20	(−1.59)	–	–	–	–	26

Table 16 (continued).

Compound	Solvent	Temperature /°C	$\log A_0$ ($\log k_0$)	E_a /kcal mol^{-1}	$\Delta G^{\neq}$ /kcal mol^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /cal mol^{-1} K^{-1}	Ref.
6f	RH	−30 – 8	7.93	13.4	19.0	12.9	−23.9	26
6f	CH_2Cl_2	−20	(−2.55)	–	–	–	–	26
	$CHCl_3$	−20 – 5	11.9	17.8	18.8	17.3	−5.7	26
	CCl_4	−10 – 5	6.37	10.2	17.6	9.7	−31.0	26
	n-C_6H_{14}	−30 – 0	6.17	11.2	18.78	10.7	−31.9	26
	MeCN	−20 – 6	0.16	1.72	16.3	1.2	−59.5	26
	EtOH : H_2O = 4 : 1 (vol.%)	−20 – 8	5.32	9.0	17.6	8.5	−35.9	26
	EtOH : H_2O = 1 : 4 (vol.%)	0	(−2.27)	–	–	–	–	26
	Et_2O [b]	−20 – 0	10.32	16.8	19.6	16.3	−13.0	26
6g	Pr^iOH	−30 – 8	9.73	14.3	17.8	13.8	−15.7	26
6h	RH	−30 – 8	6.19	10.7	18.3	10.2	−31.9	26
	CH_2Cl_2	−20	(−2.29)	–	–	–	–	26
6i	CH_2Cl_2	−30 – 8	9.69	13.4	16.9	12.9	−15.9	26
6j	CH_2Cl_2	−30 – 8	3.15	6.0	17.1	5.5	−45.8	26
6k	Me_2CO	−35 to −15	13.4	16.9	16.1	16.4	1.1	17
	$MeCO_2Et$	−40 to −15	13.6	17.0	16.0	16.5	2.1	17
	EtO	−30 to −20	13.3	16.8	16.1	16.3	0.7	17
7b	RH	−31 – 0	6.92	11.4	18.1	10.9	−28.5	27
8	$(CD_3)_2CO$	−33 to −12	10.4	16.0	18.7	15.5	−12.6	29
	$(CD_3)_2CO$ [c]	−18 to −3	16.4	23.9	19.6	23.4	14.9	29
11	CH_2Cl_2 [d]	6 – 26	9.2	15.0	–	–	–	18
	CH_2Cl_2 [d]	5 – 30	10.2	16.0	–	–	–	18
15	CH_2Cl_2 [d]	0 – 27	9.5	15.0	–	–	–	18
	CH_2Cl_2 [d]	1 – 20	14.0	21.0	–	–	–	18
	CH_2Cl_2 [d]	0 – 27	9.3	14.6	–	–	–	18
	Me_2CO [d]	4 – 18	12.9	19.6	–	–	–	18
16	CH_2Cl_2 [d]	−7 – 17	7.0	11.9	–	–	–	18
	CH_2Cl_2 [d]	6 – 27	7.1	11.9	–	–	–	18
	Me_2CO [d]	5 – 27	5.1	9.8	–	–	–	18
18	CH_2Cl_2	−2 – 20	9.0	13.3	–	–	–	18
19	CH_2Cl_2 [d]	7 – 27	11.5	18.6	–	–	–	18
	CH_2Cl_2 [d]	7 – 27	6.8	12.2	–	–	–	18
20a	$(CD_3)_2CO$	−80 to −65	1.0	4.7	18.3	4.2	−55.6	33
	$(CD_3)_2CO$ [b]	−60 to −20	5.5	9.5	17.9	9.0	−35.0	33
	Me_2O	−60 to −30	8.2	12.6	17.8	12.1	−22.7	33
	$MeCO_2Me$	−70 to −20	5.9	10.0	17.9	9.5	−33.2	33
21a	CH_2Cl_2	−60	(−2.33) [e]	–	–	–	–	35
	CS_2	−60	(−1.16) [e]	–	–	–	–	35
	$(CD_3)_2CO$	−54 to −40	–	–	~17 [f]	17.2	1.6	36
21b	RH	−70 to −50	6.84	6.0	–	–	–	37
22	$(CD_3)_2CO$	−50 to −35	–	–	~17 [f]	13.3	−17	36
23	$(CD_3)_2CO$	−50 – 10	6.1	11.0	18.7	10.5	−32.3	34
	$(CD_3)_2CO$	−20 – 10	7.7	13.0	18.8	12.5	−25.0	34
	$MeCO_2Me$	−20 – 10	7.5	12.5	18.5	12.0	−25.9	34
	$(CD_3)_2CO$ [c]	−20 – 10	6.1	11.3	19.0	10.8	−32.3	34
	$(CD_3)_2CO$ [c]	−20 – 10	5.8	11.2	19.2	10.7	−33.6	34
	$MeCO_2Me$ [c]	−20 – 10	5.8	10.8	18.8	10.3	−33.6	34

Note. The A_0 and k_0 values are given in s^{-1}; the $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were calculated using the data taken from the corresponding references (−20 °C). Hydrotrioxides ROOOH were obtained by oxidation of the corresponding substrates RH. [a] In the presence of 2,6-di-*tert*-butyl-4-methylphenol. [b] The addition of 2,6-di-*tert*-butyl-4-methylphenol has no effect on k_0. [c] In the presence of 2,6-di-*tert*-butyl-4-methylphenol. [d] The rate constant depends on the initial concentration of hydrotrioxide which was varied between 2×10^{-3} and 8×10^{-3} mol litre^{-1}. [e] Calculated from $\tau_{1/2}$. [f] The thermodynamic parameters are given for $T = -50$ °C.

Indeed, analysis of the kinetics of decomposition of hydrotrioxides derived from benzaldehydes **1b**–**f**, acetals **4b**–**g**, benzyl methyl ethers **3b**–**g**, alcohols **6b**–**j** and silanes **20a**–**d** using the Hammett – Taft equation shows that the rate constant for thermal decomposition of ROOOH increases as the electron-acceptor properties of substituent R become stronger [16, 17, 20, 33] and its polarity increases.[26]

The effect of the solvent nature on the rate constant of the overall decomposition has been studied taking hydrotrioxides **6b**,**f** (see Table 16) as examples.[26] Both dependences can be described using the Koppel – Palm correlation equation:

$$\log k_0 = \log k_0^0 + yY + pP + eE + bB,$$

where Y, P, E, B are empirical parameters which describe the polarity, polarisability, specific electrophilic solvation ability and specific nucleophilic solvation ability of the solvent, respectively.

However, the regression coefficients at the parameters Y, P, E and B differ appreciably for the two structurally similar HTO.

Presumably, this points to a formal type of description of the dependence of the rate constant for thermal decomposition of ROOOH on the chemical nature of the solvent rather than a real influence of different solvation mechanisms on the reactivity of HTO.

The activation parameters of the overall decomposition of ROOOH in the presence of inhibitors of radical-chain processes are listed in Table 16. The rate constant for decomposition of the hydrotrioxide **8** substantially decreases in the presence of ionol.[28,29] In other cases, inhibitors have little or even no effect on the rate constant.

3. Radical decomposition of hydrotrioxides

ESR studies showed that free radicals are generated only in the decomposition of cumyl hydrotrioxide (**8**).[29] The ESR spectrum is a single line with $g = 2.0151$, which is typical of peroxyl radicals. Some other examples of detection and identification of free radicals in the presence of spin traps have been reported.[130] Decomposition of HTO synthesised from methyl oleate, 2-methyl-1,3-dioxolane, propan-2-ol, 1,1-diethoxyethane, diisopropyl ether, benzaldehyde, methyl α-methylbenzyl ether and dimethylphenylsilane was studied and the spin traps used were 2-methyl-2-nitrosopropane, *C*-phenyl-*N*-*tert*-butylnitrone and methyl-*N*-(2,3,5,6-tetramethylphenyl)nitrone. Spin trap technique has also been used to identify alkyl, acyl, alkoxyl and peroxyl radicals.[17,21,22,131]

It should be noted that this method does not allow unambiguous inference about the initial products of radical decomposition of HTO. First, spin trap technique allows detection of only those radicals which form stable adducts. Second, not only the primary reaction products but also the radicals formed in the secondary reactions (reaction with the solvent, transformation of an adduct into another one[130]) are trapped in this case. Third, the spin trap is often oxidised by the hydrotrioxide to give a paramagnetic adduct.

The ratio of the radical and non-radical routes of decomposition of ROOOH was determined[21,128,129] taking the decomposition of HTO in the presence of di(*p*-methoxyphenyl)nitroxyl (an acceptor of free radicals) as an example (Table 17). The contribution of radical decomposition, k_r/k_0, varies from 0 (**6f**, EtOH : H_2O = 1 : 4) to ~23% (**1a**, PhCHO). The contribution of homolytic decomposition of ROOOH depends on the structure of HTO and temperature. For the hydrotrioxide **6f**, $\log k_r = (16.7\pm0.9)-(25.2\pm2.5)/\theta$ ($\theta = 2.303RT$/kcal mol^{-1}).

The nature of the solvent has a pronounced effect on the rate constant for radical decomposition. However, the ratio of radical and non-radical routes of decomposition remains virtually constant (see Table 17).

Table 17. Kinetic parameters of the radical decomposition of hydrotrioxides.[21,129]

Hydrotrioxide	Solvent	T/°C	$10^5 k_r$/s^{-1}	$10^2(k_r/k_0)$
1a	PhCHO	−20	1.90	12.7
	PhCHO	0	15.7	22.8
3m	Pr^i_2CO	0	0.125	0.007
4h	$MeCH(OEt)_2$	−45	1.26	0.59
6f	Pr^iOH	−30	0.019	0.25
	Pr^iOH	−10	2.10	3.48
	Pr^iOH	0	5.75	3.89
	$CHCl_3$	0	13.20	3.47
	n-C_6H_{14}	0	1.65	0.81
	Et_2O	0	0.605	0.39
	EtOH : H_2O (4 : 1)	0	3.02	0.19
	MeCN	0	1.19	0.04
	EtOH : H_2O (4 : 1)	0	0	0

4. Catalytic decomposition of hydrotrioxides

Acid- and amine-catalysed decomposition of HTO is of interest since it allows both extension of the temperature range in which these compounds can be used for generation of singlet molecular oxygen (Section V.1) and free radicals (Section V.3) and controllability of the rate of these reactions. Catalytic effect of organic acids and amines on the decomposition of HTO has been studied.[132,133] Catalytic effects of strong mineral acids (H_2SO_4 and $HClO_4$) on the decomposition of HOOOH[134] and of *N*,*N*-dimethylacetamide on the decomposition of hydrotrioxides derived from alkyl α-methylbenzyl ethers[17] have also been reported.

a. Amine-catalysed overall decomposition of organic hydrotrioxides

The kinetics of decomposition of hydrotrioxides **1a**, **3m**, **4h** and **6f** in the presence of amines (triethylamine; pyridine; 2-methylpyridine; 3-methylpyridine; 4-methylpyridine; 2-bromopyridine; 2,4-dimethylpyridine; 2,6-dimethylpyridine and quinoline) has been studied by ^{1}H NMR spectroscopy and chemiluminescence method.[132]

In the presence of amines, the rate constant for the decomposition of the hydrotrioxide **6f** increases. A similar effect is also observed upon addition of triethylamine and pyridine to benzaldehyde-derived hydrotrioxide (**1a**). However, the addition of pyridine [$(4-50)\times10^{-3}$ mol litre^{-1}] to hydrotrioxides **3m** and **4h** has no catalytic effect on their decomposition.

Catalytic decomposition in the presence of amines seems to follow a complex mechanism. On the other hand, the main channels of consumption of the ROOOH and amine can be described by a simple scheme:

$$\mathrm{ROOOH} \xrightarrow{k_0} \mathrm{P_0}\,,$$

$$\mathrm{ROOOH} + \mathrm{Am} \xrightarrow{k_{1.1}} N\text{-oxide} + \mathrm{P_{1.1}}\,,$$

$$\mathrm{ROOOH} + \mathrm{Am} \xrightarrow{k_{1.2}} \mathrm{P_{1.2}}\,,$$

where k_0, $k_{1.1}$, $k_{1.2}$ are the rate constants for the overall thermal decomposition, formation of *N*-oxide and catalytic decomposition of ROOOH, respectively; Am is amine; and P_0, $P_{1.1}$ and $P_{1.2}$ are the reaction products.

According to this scheme, the overall rate constant for the consumption of ROOOH is given by the formula

$$k = k_0 + (k_{1.1} + k_{1.2})[\mathrm{Am}]_0\,. \qquad (14)$$

Almost no *N*-oxides are formed at low concentrations of amine. This allows determination of k_0 and $k_{1.2}$ using Eqn (14) (Table 18). The temperature dependence of the rate constant for pyridine-catalysed decomposition of the hydrotrioxide **6f** is described as follows

$$\log k_{1.2} = (12.6\pm1.1) - (15.9\pm2.0)/\theta,$$

where $\theta = 2.303RT$ kcal mol^{-1}.

Linear correlation between the $\log k_{1.2}$ values and pK_a of amines is in good agreement with the Brønsted relationship for the general acid-base catalysis.[135] Thus, the kinetic data provide

Table 18. Kinetic parameters of decomposition of the hydrotrioxide **6f** in the presence of amines in isopropyl alcohol.

Amine	T/°C	$10^3 k_0$/s^{-1}	$k_{1.2}$/litre mol^{-1} s^{-1}
Pyridine	−26	0.177	0.03
	−14	0.417	0.16
	−1	1.45	0.69
2-Bromopyridine	−2	1.32	0.0005
Quinoline	−2	1.32	0.33
2-Methylpyridine	−2	1.32	0.93
3-Methylpyridine	−2	1.32	0.95
4-Methylpyridine	−1	1.45	1.34

an explanation for low yields of *N*-oxide in the oxidation of amines by hydrotrioxides (see Section VII.2): ROOOH is not only consumed in the oxidation reaction but also undergoes conversion following other routes, *e.g.*, thermal and amine-catalysed decomposition. As the amine basicity increases, the rate of catalytic process also increases with concomitant decrease in the yield of the corresponding *N*-oxide.

b. Acid catalysis of the overall decomposition of organic hydrotrioxides

Formic, acetic, monochloroacetic, trichloroacetic, trifluoroacetic and butyric acids were found to accelerate the decomposition of hydrotrioxides **3m** and **6f**.[133]

Acid-catalysed decomposition of hydrotrioxides is described by a first-order equation, the effective rate constant being proportional to the concentration of the acid (HA)

$$k = k_0 + k_{cat}[HA].$$

The rate constants for noncatalytic (k_0) and catalytic (k_{cat}) reactions are listed in Table 19.

Table 19. Kinetic parameters for the overall decomposition of the hydrotrioxide **6f** catalysed by carboxylic acids (in isopropyl alcohol).

Acid	T /°C	$10^3 k_0$ /s^{-1}	$10^2 k_{cat}$ /litre mol^{-1} s^{-1}
HCOOH	0	1.29	1.76
$MeCO_2H$	0	1.44	1.90
$ClCH_2CO_2H$	0	1.34	4.00
Cl_3CCO_2H	0	1.89	11.00
F_3CCO_2H	0	1.70	14.60
	−10	0.74	11.00
	−20	0.16	5.40
	−32	0.09	1.90
	0	11.18 [a]	11.50 [a]
$BuCO_2H$	0	1.27	2.15

[a] The data for the hydrotrioxide **3m** in diisopropyl ether.

The temperature dependences of the rate constants k_0 and k_{cat} for decomposition of the hydrotrioxide **6f** catalysed by CF_3CO_2H are as follows:

$$\log k_0 = (7.3 \pm 1.7) - (12.6 \pm 2.0)/\theta,$$

$$\log k_{cat} = (6.1 \pm 0.9) - (8.6 \pm 1.0)/\theta,$$

where $\theta = 2.303RT$ kcal mol^{-1}.

As for amines, the $\log k_{cat}$ values and the pK_a of the acids are related by a linear dependence, which is in agreement with the Brønsted relationship for acid catalysis.[135]

We cannot perform a detailed analysis of the mechanism of consumption of ROOOH in the presence of acids based on the knowledge of the formal kinetics of the process. It can be assumed that the decomposition of the hydrotrioxides can be accelerated owing to, in particular, the formation of associates ROOOH···HA, which leads to polarisation of the O–O bond, thus facilitating thermolysis of ROOOH. Such a 'through-the-H-bond' association followed by decomposition of the associates with cleavage of the O–O bond was found in the hydroperoxide–carboxylic acid system.[136, 137]

VI. The mechanism of thermal decomposition of hydrotrioxides

Thermal decomposition of HTO can follow several routes:

$$ROOOH \longrightarrow RO^{\bullet} + {}^{\bullet}OOH, \quad (15)$$

$$ROOOH \longrightarrow ROO^{\bullet} + {}^{\bullet}OH, \quad (16)$$

$$ROOOH + X^{\bullet} \longrightarrow ROOO^{\bullet} + XH \longrightarrow RO^{\bullet} + O_2 + XH, \quad (17)$$

$$ROOOH \longrightarrow \text{molecular products}. \quad (18)$$

In reaction (17), X represents a radical which escaped from the solvent cage, thus initiating induced decomposition of HTO.

The thermal effects of reactions (15) and (16) are equal to the dissociation energies of the corresponding O–O bonds. By substituting the data listed in Table 7 we get $\Delta H^{\circ}(15) \approx 20-21$ kcal mol^{-1} and $\Delta H^{\circ}(16) \approx 26-27$ kcal mol^{-1}. Therefore, it seems likely that reaction (16) can be ignored in the case of homolytic decomposition of ROOOH. The exothermicity of reaction (17) is equal to the difference between the dissociation energies of the ROOO–H (see Table 7) and X–H bonds. If X = ROO, the reaction (17) can be considered thermally neutral since $\Delta H^{\circ}(17) \approx -5 \pm 3$ kcal mol^{-1}. If X = RO, the reaction (17) is exothermic [$\Delta H^{\circ}(17) \approx 20$ to 25 kcal mol^{-1}].

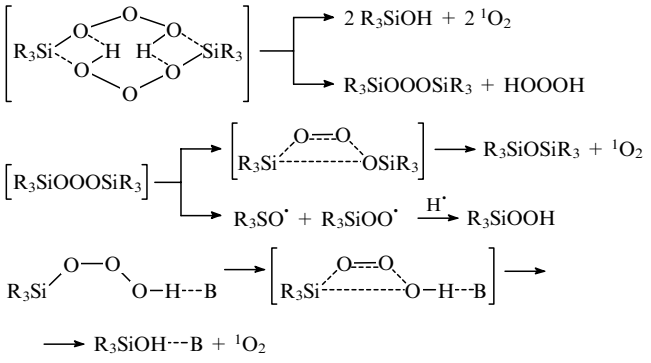
The enthalpy of the reaction of molecular decomposition of ROOOH depends on the chemical nature of both R and products formed but, as a rule, it is much less than zero. For instance, decomposition of cyclohexyl hydrotrioxide into cyclohexanol and singlet molecular oxygen is characterised by $\Delta H^{\circ}(18) = -55$ kcal mol^{-1} and the formation of cyclohexanol and hydrogen peroxide is characterised by $\Delta H^{\circ}(18) = -75.5$ kcal mol^{-1}.

Taking into account the experimental activation energies of thermal decomposition of ROOOH (see Table 16), we can conclude that virtually all mechanisms for the decomposition of ROOOH, *viz.*, reactions (15), (17) and (18), are possible. Large values of the pre-exponential factors for the rate constant of thermal decomposition of several HTO often make the radical mechanism preferable. Solvation of polar transition state can change the log A and E values in the 'compensating' manner. The fact that this dependence holds for almost all compounds ROOOH (see Fig. 1) suggests a common mechanism of the decomposition of HTO with different structures.

Our thermochemical analysis of possible channels of the decomposition of ROOOH is consistent with the experimental results. The particular route of thermal decomposition is determined by the structure of HTO and reaction conditions. This is illustrated below taking different classes of hydrotrioxides as examples.

1. Silane-derived hydrotrioxides

Plesničar *et al.*[33] reported a detailed study of the mechanism of decomposition of silane-derived hydrotrioxides taking dimethylphenylsilyl hydrotrioxide (**20a**) as an example. They determined the kinetic and activation parameters of the reaction (in particular, large negative entropy of activation), revealed a pronounced substituent effect, found that the rate constant for decomposition depends on the solvent polarity and showed that the radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (ionol), has no effect on the kinetics of decomposition. Based on these results, the authors suggested the molecular route as the major channel of decomposition of silane-derived hydrotrioxides.[33]



The formation of dimethylphenylsilyl hydroperoxide at $T > -50$ °C indicates some contribution of the radical reaction to the overall mechanism; however, Plesničar *et al.*[33] concluded that homolytic processes are a minor channel (< 10%) under the conditions investigated.

2. Cumyl hydrotrioxide

Cumyl hydrotrioxide (**8**) is a carbon analogue of dimethylphenylsilyl hydrotrioxide; the kinetics of its decomposition have been studied by ^{1}H NMR spectroscopy.[28,29] It was found that thermal decomposition of **8** at $T > -40$ °C (E_a = 16.0±0.1 kcal mol^{-1} and log A = 10.4±0.1) is substantially retarded in the presence of ionol. Correspondingly, the activation parameters of the reaction change (E_a = 23.9±0.1 kcal mol^{-1} and log A = 16.4±0.1). In the absence of the inhibitor, the reaction results in 2-phenylpropan-2-ol (the major product), acetophenone and cumyl hydroperoxide.

$$PhCMe_2OOOH \longrightarrow PhCMe_2O^{\bullet} + {}^{\bullet}OOH,$$

$$PhCMe_2O^{\bullet} ({}^{\bullet}OOH) + PhCMe_2OOOH \longrightarrow$$
$$\longrightarrow PhCMe_2OH\ (HOOH) + PhCMe_2OO^{\bullet},$$

$$PhCMe_2OO^{\bullet} \longrightarrow PhCMe_2O^{\bullet} + O_2,$$

$$PhCMe_2O^{\bullet} \longrightarrow PhCOMe + Me^{\bullet},$$

$$PhCMe_2O^{\bullet} + PhCHMe_2 \longrightarrow PhCMe_2OH + Ph\dot{C}Me_2,$$

$$Ph\dot{C}Me_2 + O_2 \longrightarrow PhCMe_2OO^{\bullet},$$

$$PhCMe_2OO^{\bullet} + PhCHMe_2 \longrightarrow PhCMe_2OOH + Ph\dot{C}Me_2.$$

In the presence of ionol, induced decomposition is inhibited and 2-phenylpropan-2-ol is virtually the only organic reaction product.[28,29]

$$PhCMe_2O^{\bullet} ({}^{\bullet}OOH) + ArOH \longrightarrow PhCMe_2OH\ (HOOH) + ArO^{\bullet},$$

$$PhCMe_2O^{\bullet} ({}^{\bullet}OOH) + ArO^{\bullet} \longrightarrow \text{non-radical products}.$$

3. Hydrotrioxides derived from oxygen-containing compounds

The kinetic parameters of thermal decomposition of hydrotrioxides derived from oxygen-containing compounds are listed in Table 16 and the reaction products are presented in Table 13.

We will consider the decomposition derived from hydrotrioxides of oxygen-containing compounds taking ethanol-derived hydrotrioxide (**6b**) as an example. Despite the fact that HTO derived from alcohols, ethers, acetals, *etc*., can form intramolecularly hydrogen-bonded structures [based on this, the molecular route of decomposition (Scheme 1, route *a*) was proposed [13]], the experimental results are altogether in better agreement with the radical mechanism for decomposition of ROOOH, the first stage of which involves homolysis of the RO–OOH bond (Scheme 1, route *b*).

Low yields of radicals escaped from the solvent cage are due to self-association of ROOOH and the formation of intermolecular hydrogen bonds (HTO dimers, association with the solvent molecules).[128,129] Yet another factor which stabilises the transition state of the reaction that follows route *b* is an increase in the proton acidity and, hence, strengthening of the hydrogen bond [pK_a(HOOOH) ≈ 9.5,[62] whereas pK_a of the decomposition product, *i.e*., the hydroperoxyl radical, is 4.4 [134]].

The hydrotrioxide **6b** decomposes into acetaldehyde, water, acetic acid and hydrogen peroxide (see Table 13). The first pair of products is formed as a result of disproportionation of the radical pair **A** (Scheme 1, route *c*). The second pair, $MeCO_2H$ and H_2O_2, are formed [76] owing to rotation about the C–O bond in the oxyl radical **A** followed by disproportionation of the radical pair **B** (Scheme 1, route *d*).

The formation of small amounts of organic peroxide products is due to homolytic oxidation reactions which proceed involving free radicals escaped from the solvent cage into the bulk.

4. Factors responsible for the mechanism of thermolysis

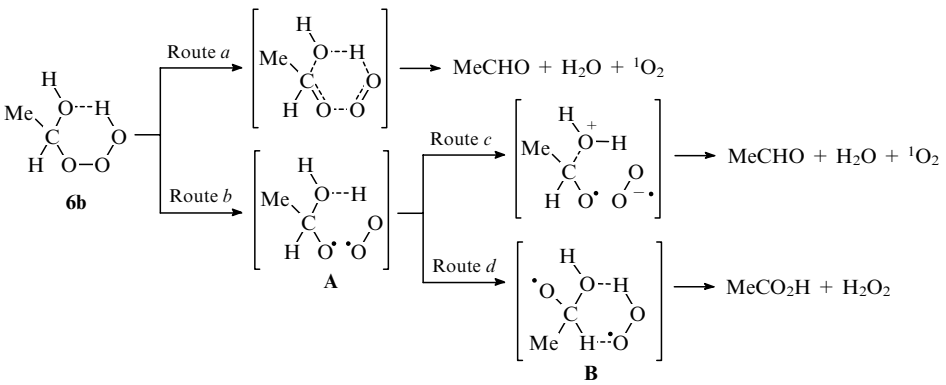
As was shown above, thermal decomposition of ROOOH can follow several pathways. The contribution of each mechanism (radical, induced or molecular decomposition) can vary depending on the experimental conditions. A number of factors determining the direction of decomposition of hydrotrioxides can be distinguished.

1. The nature of the atom bonded to the hydrotrioxide group. The larger the difference between the electronegativities of the X and O atoms in the hydrotrioxide $R^1R^2R^3XOOOH$ the more polar the X–O bond. Because of this, one should expect a larger contribution of the molecular channel of the reaction for silane-derived hydrotrioxides (X = Si). Comparison of the mechanisms for decomposition of hydrotrioxides **8** and **20a** which differ only in the nature of the atom X (see Sections VI.1 and VI.2) confirms this assumption. Koenig *et al.*[36] suggested that in the case of hydrotrioxides derived from organogermanium and organotin compounds (X = Ge, Sn) the molecular mechanism for decomposition is even more pronounced.

2. Temperature. Hydrotrioxides are typical peroxide compounds. By analogy with the latter, the increase in temperature causes a relative increase in the contribution of radical processes characterised by higher activation energies and pre-exponential factors. At low temperatures, polar rearrangements without formation of radical intermediates are more probable. This is confirmed by the results obtained by Plesničar *et al.*[33] who have found that $PhCMe_2OOH$, a typical product of radical transformation, is formed only at relatively high (as regards decomposition of dimethylphenylsilyl hydrotrioxide **20a**) temperatures ($T > -50$ °C) under conditions of fast warmup procedure.

3. Solvent. As was shown in Section V.2, the rate constant for decomposition of hydrotrioxides is affected by both specific and non-specific solvation of HTO and the transition states.[18,26] Polar solvents accelerate the molecular decomposition of ROOOH. For the hydrotrioxide **20a**, the effect of solvent decreases in the order: acetone-d_6 > methyl acetate > dimethyl ether.[33] The solvent polarity has a less pronounced effect on homolysis of the O–O

Scheme 1



bond: hydrotrioxides **3b** and **6k** decompose in acetone, ethyl acetate and diethyl ether with nearly the same rate.[17] Specific interactions (*e.g.*, the formation of hydrogen bonds) cause an increase in the viscosity of HTO solutions and in the degree of association of HTO molecules in solution.

Correspondingly, the amount of radicals escaping from the solvent cage decreases. As a result, the radical mechanism becomes a 'hidden-radical' one, which is virtually indistinguishable from the molecular mechanism under the experimental conditions. We believe that 'hidden-radical' processes make a rather large contribution to the decomposition of HTO of oxygen-containing organic compounds and, hence, the initiating ability of ROOOH is low[129] owing to large cage effect and despite the formally radical type of decomposition.

4. The presence of a heteroatom in the ROOOH molecule. On the one hand, the O atom in α-position relative to the hydrotrioxide group stabilises the positive charge on the carbon atom in the formation of ROOOH (see Section IV.1). On the other hand, this structure of the oxygen-containing compound is extremely favourable for the formation of an intramolecular hydrogen bond. Self-association of ROOOH molecules also decreases the yield of radicals into the bulk, which manifests itself in low initiating ability and the absence of the effect of radical inhibitors on the kinetics of thermal decomposition. This type of HTO decomposes following a non-chain radical route. If the ROOOH molecules contain no heteroatom appropriate for the formation of hydrogen bond, they decompose to give high yields of radicals that initiate an induced decomposition of the HTO.[29]

5. Formation of electronically excited products

As was shown above (Section V.1), decomposition of ROOOH is accompanied by chemiluminescence in the visible and IR spectral regions. The radical mechanism for the decomposition of HTO provides better explanation for the appearance of chemiluminescence in the visible spectral region.

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

$$RO^{\bullet}({}^{\bullet}OOH) + RH\,(SolvH) \longrightarrow R^{\bullet}(Solv^{\bullet}) + ROH\,(HOOH),$$

$$R^{\bullet}(Solv^{\bullet}) + O_2 \longrightarrow ROO^{\bullet}(SolvOO^{\bullet}),$$

$$ROO^{\bullet} + ROO^{\bullet}(SolvOO^{\bullet} + SolvOO^{\bullet}) \longrightarrow \rangle C{=}O^{*} + \ldots$$

Solv — solvent.

Emitters of the chemiluminescence are the excited carbonyl compounds that are formed in the recombination of peroxyl radicals.[138] It is believed that the source of peroxyl radicals is the solvent SolvH (or RH if hydrotrioxides are synthesised in the bulk).

An increase in the cage effect makes the role of free-radical processes less significant and reduces the probability of the formation of triplet excited carbonyl compounds. Indeed, thermal decomposition of hydrotrioxide **6b** proceeds without formation of free radicals[128] and is not accompanied by luminescence in the visible spectral region.

Luminescence in the IR spectral region is caused by singlet oxygen $^1\Delta_g$. The mechanism for its formation has been less studied. The yield of $^1O_2$ determined using polyaromatic acceptors of singlet molecular oxygen was found to be nearly equal for both silane-derived hydrotrioxide **20a** (25% – 60%)[33] which decomposes following the molecular route and the hydrotrioxide **3b** (25% – 45%)[17] which mainly undergoes homolytic decomposition. A drawback of this procedure for the determination of the yield of $^1O_2$ is that the acceptor can be simply oxidised by the hydrotrioxide, which can introduce large errors into the results of measurements. However, the yield of $^1O_2$ in both processes is nearly the same. Thermochemically, the formation of singlet molecular oxygen in the reaction

$$ROOOH \longrightarrow ROH + O_2$$

is quite possible. It is known[69] that the enthalpies of formation of alcohols ROH and corresponding hydroperoxides are related by a simple relationship

$$\Delta_f H^{\circ}(ROOH) = \Delta_f H^{\circ}(ROH) + 19.2 \text{ kcal mol}^{-1}. \quad (19)$$

Taking into account Eqn (11), we get

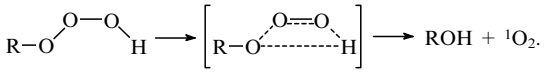
$$\Delta_f H^{\circ}(ROOOH) = \Delta_f H^{\circ}(ROH) + 36.8 \text{ kcal mol}^{-1}. \quad (20)$$

Thus, according to Eqn (20), the thermal effect of the reaction of decomposition of ROOOH into ROH and O_2 molecule (the barrier height is $\sim 10 + 36.8$ kcal mol^{-1}) is sufficient for populating the $^1\Delta_g$ singlet level of molecular oxygen (22.5 kcal mol^{-1}). It is reasonable that singlet molecular oxygen can also be efficiently generated following the radical mechanism to give the same products (however, in this case the activation energy is higher).

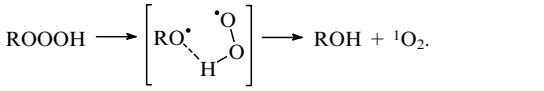
It should be noted that, despite the absence of free radicals and chemiluminescence in the visible spectral region, decomposition of the hydrotrioxide **6b** is accompanied by bright chemiluminescence in the IR spectral region.[16, 18] This indicates the formation of $^1O_2$ in the 'hidden-radical' reactions.

It seems likely that generation of singlet molecular oxygen can proceed by several mechanisms simultaneously.

Route *a* (molecular)



Route *b* ('hidden-radical')



Route *c* (radical-chain)

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

$$RO^{\bullet}({}^{\bullet}OOH) + RH\,(SolvH) \longrightarrow R^{\bullet}(Solv^{\bullet}) + ROH\,(HOOH),$$

$$R^{\bullet}(Solv^{\bullet}) + O_2 \longrightarrow ROO^{\bullet}(SolvOO^{\bullet}),$$

$$ROO^{\bullet} + ROO^{\bullet}(SolvOO^{\bullet} + SolvOO^{\bullet}) \longrightarrow {}^1O_2 + \ldots$$

Undoubtedly, the mechanisms of the formation of singlet molecular oxygen in the thermal decomposition of HTO are still unclear and deserve further investigation.

VII. Organic hydrotrioxides as oxidants

It is well known that peracids and hydroperoxides ROOH (R is alkyl, aryl, acyl) containing active oxygen are highly reactive compounds.[139, 140] Hydrotrioxides containing two active oxygen atoms are highly active oxidants of unsaturated (alkenes, dienes, acenes) and heteroorganic compounds (amines, phosphines, phosphites, sulfides, sulfoxides, sulfur ylides). A salient feature of hydrotrioxides is that both the ROOOH molecule and singlet molecular oxygen generated in the decomposition of ROOOH can act as the oxidants.

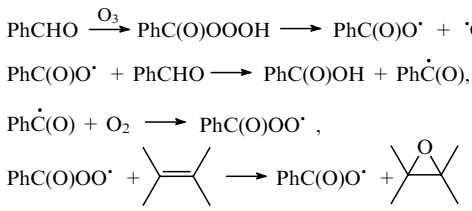
1. Oxidation of unsaturated compounds

Depending on the structure of the substrate, the reactions of ROOOH with unsaturated compounds can result in epoxides, hydroperoxides, endoperoxides, 1,2-dioxetanes (or products of their transformations in the reaction medium).

a. Preparation of epoxides

Epoxidation of alkenes at -50 °C in $CHCl_3$ under the action of ROOOH has been studied taking the reactions of 4-trimethylsilylcyclohexene with hydrotrioxides **1a** and **6f**,**h** as examples (the yields of 4-trimethylsilyl-1,2-epoxycyclohexane calculated with respect to Δ[ROOOH] were ~60%, 13% and 6%, respectively).[141]

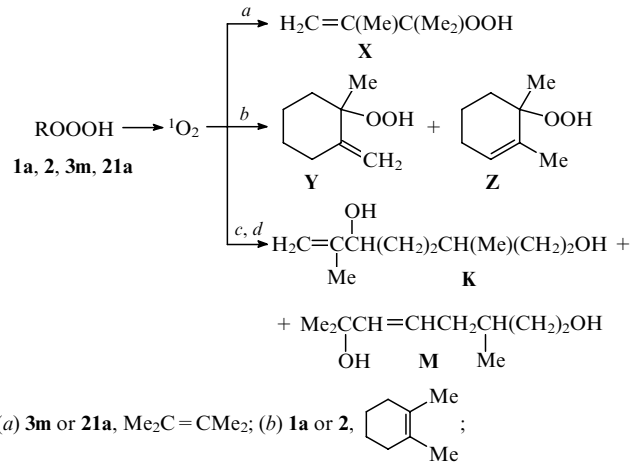
It seems likely that epoxidation by hydrotrioxide **1a** proceeds analogously to the Prilezhaev reaction.[139] In addition, since the radical mechanism contributes largely to the overall decomposition of the hydrotrioxide **1a** (see Table 17), one cannot rule out the contribution of the corresponding channel to the overall reaction of the synthesis of epoxide.[137, 142]



b. Preparation of hydroperoxides

Hydroperoxides can be prepared by oxidation of unsaturated compounds by singlet molecular oxygen generated in the decomposition of hydrotrioxides. Treatment of hydroperoxides with reducing agents results in the corresponding alcohols. This procedure is employed in the synthesis of natural compounds. The oxidation of tetramethylethylene by hydrotrioxides **3m**[13] and **21a**[35] and the oxidation of 1,2-dimethylcyclohexene by hydrotrioxides **1a** and **2** follow this pathway (Scheme 2).[14]

Scheme 2



(*a*) **3m** or **21a**, $Me_2C=CMe_2$; (*b*) **1a** or **2**, ;

(*c*) **21a**, $Me_2CH=CH(CH_2)_2CH(Me)(CH_2)_2OH$; (*d*) $NaBH_4$, EtOH.

The yields of compounds **X**, **Y**, **Z**, **K** and **M** are presented in Table 20. It should be noted that in both cases the oxidation of 1,2-dimethylcyclohexene results in the products **Y** and **Z** in the ratio ~9 : 1, which is typical of the oxidation of this substrate by singlet molecular oxygen.[143] If hydroperoxides obtained upon oxidation of citronellol by hydrotrioxide **21a** are reduced by sodium borohydride (Scheme 2), a 1 : 1 mixture of diols **K** and **M** is formed (see Table 20).[35]

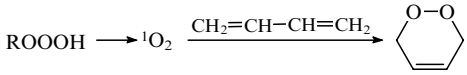
Table 20. The yields of compounds **X**, **Y**, **Z**, **K**, **M**.

Reagent	T /°C	Solvent	Yield (%)				Ref.
			X	**Y**	**Z**	**K**, **M**	
3m	−10 – 5	CH_2Cl_2	61 [a]				13
21a	−78	CH_2Cl_2	40 [b]				35
1a	23	RH	51.3 [a]	51.3 [a]	5.8 [a]		14
2	23	RH		39.7 [a]	3.5 [a]		14
21a	−78	CH_2Cl_2				25 [b, c]	35

[a] Calculated with respect to $\Delta[O_3]$. [b] Calculated with respect to Δ[A]. [c] The ratio **K** : **M** was 1 : 1.

c. Synthesis of endoperoxides

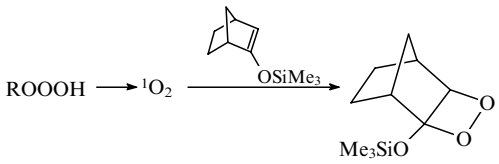
The reaction proceeds by the mechanism of [4 + 2]-cycloaddition of the singlet molecular oxygen generated to conjugated carbo- and heterodienes.



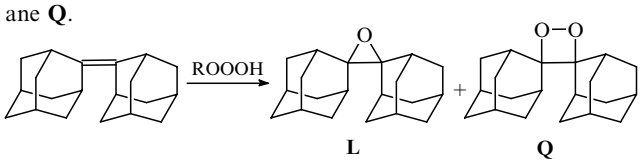
This reaction has been studied in most detail. The corresponding results are presented in Table 21.

d. Synthesis of 1,2-dioxetanes

Oxidation of 2-(trimethylsilyloxy)bicyclo[2.2.1]hept-2-ene into the corresponding dioxetane under the action of hydrotrioxide **21a** (−78 °C, CH_2Cl_2) also follows the mechanism of [2 + 2]-cycloaddition of singlet molecular oxygen evolved in the decomposition of ROOOH to the C = C bond of the substrate. The yield calculated with respect to Δ[A] is 50%.[35]



The reactions of adamantylideneadamantane with hydrotrioxides **1a**, **3m**, **4h** or **6f** in the $RH-CHCl_3$ medium at −78 °C proceed to give a mixture of the epoxide **L** and the 1,2-dioxetane **Q**.



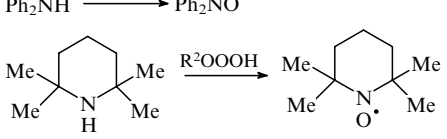
This reaction is an interesting example of dual reactivity of hydrotrioxides. Here, the role of oxidants is played by both the HTO which reacts to give the epoxide **L** and the singlet molecular oxygen which enters into the [2 + 2]-cycloaddition reaction to give the dioxetane **Q**.

Depending on the structure of the hydrotrioxide and composition of the reaction mixture, the reaction can be shifted towards the formation of either the epoxide **L** or the 1,2-dioxetane **Q**. The highest yield of dioxetane **Q** (~85% with respect to Δ[A]) was attained with the hydrotrioxide **4h** taken in the equimolar ratio to the substrate. The most efficient epoxidising agents are hydrotrioxides **1a** and **3m**; if the substrate and oxidant are taken in 1 : 10 ratio, the yield of the epoxide **L** calculated with respect to Δ[A] is 84% for **1a** and 88% for **3m**.[118, 144]

2. Oxidation of nitrogen-containing compounds

a. Secondary amines

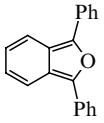
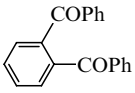
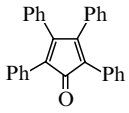
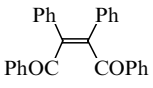
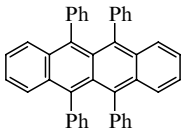
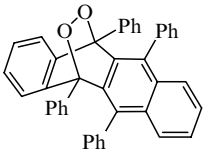
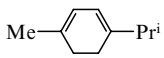
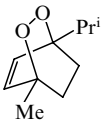
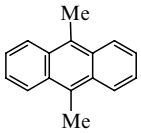
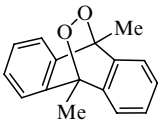
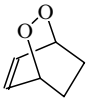
Reactions of hydrotrioxides **1a**, **4h**, **6b**,**f** with diphenylamine or 2,2,6,6-tetramethylpiperidine (−20 °C, the substrate : oxidant ratio is 20 : 1) result in diphenylnitroxyl and 2,2,6,6-tetramethylpiperidin-1-oxyl, respectively.[145]



R^2OOOH = **1a**, **4h**, **6b**,**f**.

The yield of nitroxyl radicals calculated with respect to the hydrotrioxide consumed is low (~2%). This is likely due to either a fast reaction of the radicals with the HTO [129] or amine-catalysed decomposition of the HTO that proceeds concurrently (see Section V.4.a).

Table 21. Oxidation products of conjugated carbo- and heterocyclic dienes by hydrotrioxides.

Substrate	Reaction product	Hydrotrioxide	Temperature /°C	Solvent	Yield (%)	Ref.
		**1a**	−50	$RH-CH_2Cl_2$	96 [a]	14
		2	−70	$RH-Me_2CO$	80 [a]	14
		3a	−23	RH	30 [a]	14
		3b	−40 to −10	Me_2CO	45 [a]	17
				$MeCO_2Et$	–	17
		4f	−50 to −40	$MeCO_2Et$	55 [a]	20
		4h	−50 to −40	RH	54 [a]	20
		5a	−50 to −40	$MeCO_2Et$	46 [a]	20
		5d	−50 to −40	$MeCO_2Et$	85 [a]	20
		6k	−40 to −10	Me_2CO	60 [a]	17
				$MeCO_2Et$	60 [a]	17
		20a	−70 to −40	CD_3COCD_3	65 [a]	33
		21a	−78	CH_2Cl_2	45 [a], 91 [b]	35
		**3m**	−10–5	$RH-CH_2Cl_2$	38 [a]	13
		21a	−78	CH_2Cl_2	62 [b]	35
		**3m**	−10–5	$RH-CH_2Cl_2$	47 [a]	13
		**21a**	−78	CH_2Cl_2	90 [b]	35
		**21a**	−78	CH_2Cl_2	92 [b]	35
		**21a**	−78	CH_2Cl_2	46 [b]	35

[a] Calculated with respect to the amount of ozone [$\Delta(O_3)$] consumed in the synthesis of ROOOH. [b] Calculated with respect to the substrate.

b. Tertiary amines

At −80 to −50 °C, tertiary amines undergo selective oxidation to give the corresponding *N*-oxides.[132, 146]

$$R^1_3N \xrightarrow{R^2OOOH} R^1_3N{\rightarrow}O$$

R^1_3N R^1_3 — pyridine, 2-methylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, quinoline, 7-nitroquinoline;

R^2OOOH = **4h**, **6b**,**f**.

The yields of *N*-oxides calculated with respect to $\Delta[R^2OOOH]$ increase as the ratio $[R^1_3N]_0 : [R^2OOOH]_0$ increases. For instance, the yield of pyridine *N*-oxide in the oxidation of pyridine by the hydrotrioxide **6f** is ~27% if the reagents are taken in ~2 : 1 ratio and 60% if this ratio is 20 : 1. The nature of the HTO has little effect on the yield of *N*-oxides. As the basicity of the amine increases, the ratio $\Delta R^1_3[NO]/\Delta[R^2OOOH]$ decreases, which is due to the amine-catalysed decomposition of the hydrotrioxide (see Section V.4.a).

3. Oxidation of phosphorus-containing compounds

a. Phosphines

At −78 °C, hydrotrioxides **6b**,**f** oxidise triphenylphosphine into triphenylphosphine oxide nearly quantitatively, the reaction being completed during the mixing time of the reactants.[147] As the ratio of the initial concentrations, $[Ph_3P]_0 : [ROOOH]_0$, changes from 1 : 1 to 1 : ⩾ 2, the ratio $\Delta[Ph_3P] : \Delta[ROOOH]$ increases from 1 to 2. The change in the stoichiometric coefficient is thought to be due to the reduction of a hydroperoxide by triphenylphosphine.

$$ROOOH \xrightarrow{Ph_3P} ROOH \xrightarrow{Ph_3P} ROH.$$

Fast and nearly quantitative reduction of HTO with an excess of triphenylphosphine serves as the basis for the method for quantitative determination of HTO by analysing the unconsumed Ph_3P.[147]

Pryor *et al.*[29] used the reaction of Ph_3P with the hydrotrioxide **8** in acetone at −73 °C for identification of the HTO **8**.

b. Phosphites

Hydrotrioxides **1a**, **4a**,**h**, **5a**, **6b**,**d**,**f** oxidise phosphites into the corresponding phosphates (at −78 to −50 °C) in nearly quantitative yields.[148–150]

$$(R^1O)_3P \xrightarrow{R^2OOOH} (R^1O)_3P{=}O$$

R^1 = Me, Et, Pr^i, Bu^n, $CH_2{=}CHCH_2$, Ph, 2-MeC_6H_4;

R^2OOOH = **1a**, **4a**,**h**, **5a**, **6b**,**d**,**f**.

Aromatic phosphites are oxidised somewhat slower than the aliphatic phosphites.[149] The reactivities of phosphites towards the hydrotrioxide **6f** have been studied by the method of competing reactions (at −50 °C in propan-2-ol) with $(EtO)_3P$ as the reference compound:

$$n_r(R^1O)_3P + R^2OOOH \xrightarrow{k_r} n_r(R^1O)_3PO,$$

$$n_0(EtO)_3P + R^2OOOH \xrightarrow{k_0} n_0(EtO)_3PO,$$

where k_r and k_0 are the rate constants for the oxidation of the phosphite under study and triethyl phosphite, respectively, and n_r and n_0 are the stoichiometric coefficients of the corresponding reactions.

If $[R^2OOOH]_0 \ll [(R^1O)_3P] = [(EtO)_3P]_0$ and the stoichiometric coefficients $n_r \approx n_0 \approx 2$, for the relative rate constant we get

$$k_r/k_0 = [(R^1O)_3PO]/[(EtO)_3PO].$$

A correlation was found between the $\log(k_r/k_0)$ value and the sum of the Kabachnik constants ($\Sigma\sigma^{\Phi}$) of the substituents at the phosphorus atom

$$\log(k_r/k_0) = -0.87 - 0.96\,\Sigma\sigma^{\Phi}.$$

At low $[(R^1O)_3P]_0/[R^2OOOH]_0$ ratios, the stoichiometric coefficient $\Delta[(R^1O)_3P]/\Delta[R^2OOOH] \approx 1$. As the phosphite concentration increases, this coefficient also increases approaching a value of 2. It seems likely that here, as in the preceding case, not only the hydrotrioxide but also the hydroperoxide acts as the oxidant. Probably, the reactions of phosphites with hydroperoxides occur during the warmup of the reaction mixtures.

Chemical polarisation of ^{31}P nuclei in $(PhO)_3PO$ observed in the *in situ* reaction of triphenyl phosphite with the hydrotrioxide **6f** carried out in an NMR tube (in propan-2-ol at ~40 °C) indicates the presence of radical species.[149] It is essential that the ^{31}P nuclei in the major product, phosphate, are strongly polarised. This system differs from the phosphite–hydroperoxide system in which the atomic nuclei in the molecules of the minor products are strongly polarised whereas a very weak or even no chemical polarisation is observed for the major product, *viz*., phosphate.[151] The addition of styrene (a free radical acceptor) does not lead to disappearance of chemical polarisation. It thus follows that the polarised phosphate molecules are formed as a result of recombination of the geminate radical pair without exit of the radicals into the bulk.

Taking the oxidation of triphenyl phosphite by hydrotrioxides **1a**, **4h** and **6f** (−26 °C, CH_2Cl_2) as an example, it was found that the reactions are accompanied by chemiluminescence in the visible and IR spectral regions.[144] Maxima in the spectra of chemiluminescence in the visible spectral region are observed at $\lambda = 460 \pm 20$ nm. It is assumed [144] that the emitter of chemiluminescence is the triplet excited phosphate (the phosphorescence spectrum of triphenyl phosphate exhibits a maximum at $\lambda = 465$ nm), as in the case of the oxidation of phosphites by hydroperoxides. The emitter of luminescence in the IR spectral region is the singlet molecular oxygen generated in the thermal decomposition of ROOOH that proceeds in parallel.

4. Oxidation of sulfur-containing compounds

a. Sulfoxides

Oxidation of dimethyl sulfoxide and dibutyl sulfoxide by hydrotrioxides **1**, **3m**, **4h** and **6b**,**f** (−78 to −50 °C, $[R^2OOOH]_0 : [R^1SOR^1]_0 \approx 1-10$, 10–12 h) results in the corresponding sulfones in nearly 100% yields.[152]

$$R^1SOR^1 \xrightarrow{R^2OOOH} R^1SO_2R^1$$

R^1 = Me, Bu^n; R^2OOOH = **1a**, **3m**, **4h**, **6b**,**f**.

The most efficient oxidants are hydrotrioxides **1a** and **6f**. Complete conversion of sulfoxides into sulfones requires a threefold to fivefold excess of these reagents.

The yields of sulfones calculated with respect to $\Delta[R^2OOOH]$ are, as a rule, 5% to 30%; the higher the thermal stability of the HTO the higher the yield of the sulfone. Thus, the oxidation of sulfoxides is accompanied by thermal decomposition of the hydrotrioxide which proceeds concurrently at a rather high rate; singlet molecular oxygen thus formed is inactive in the reaction with sulfoxides under these conditions. Otherwise, one would expect an increase in the yield of sulfones with the increase in the rate of decomposition of such an efficient source of $^1O_2$, as, *e.g*., the hydrotrioxide **6f**.

It was shown [33] that the transfer of oxygen from the hydrotrioxide **20a** to the substrates, $4\text{-}XC_6H_4S(O)Me$ (X = MeO, Me, H, Cl), follows the electrophilic mechanism ($\rho = -1.1$, −78 °C, Me_2CO).

b. Sulfides

Depending on the composition of the initial reaction mixture and the reaction time, sulfides undergo selective oxidation into either sulfoxides or sulfones (at T from −78 to −40 °C).[23, 144, 153]

$$R^1SR^1 \xrightarrow{R^2OOOH} R^1SOR^1,$$

$$R^1SR^1 \xrightarrow{R^2OOOH} R^1SO_2R^1$$

R^1 = Me, Pr^n, Bu^n, n-C_6H_{13}, n-C_7H_{15}; R^2OOOH = **1a**, **4h**, **5a**,**b**, **6b**,**f**,**h**.

The first reaction proceeds at the ratio of the initial concentrations $[R^2OOOH]_0 : [R^1SR^1]_0 \leqslant 1$ (the reaction goes to completion within 15 to 30 min).[144, 153] The yields of sulfoxides calculated with respect to sulfides consumed are close to 100%. If hydrotrioxides **1a** and **6f** are used, the yields calculated with respect to the HTO consumed in the reaction are also close to 100%. On the other hand, if $[\mathbf{6f}]_0 : [R^1SR^1]_0 = 2$, the yields of sulfoxides decrease down to 50%, which indicates that the reaction is accompanied by thermal decomposition of the excess HTO which proceeds concurrently and that $^1O_2$ evolved in the reaction with the sulfide is inactive.

Oxidation of R^1SR^1 into $R^1SO_2R^1$, which seems to proceed *via* the corresponding sulfoxide R^1SOR^1, is observed if the HTO is taken in large excess and the reaction takes a long time. This indicates a relatively low reactivity of sulfoxides towards hydrotrioxides. For instance, a nearly quantitative conversion of dibutyl sulfide into dibutyl sulfone under the action of hydrotrioxides **1a** or **6f** requires that the following conditions be met for the ratios of the initial concentrations, $[\mathbf{1a}]_0 : [R^1SR^1]_0 \geqslant 15$ or $[\mathbf{6f}]_0 : [R^1SR^1]_0 \geqslant 4$; the yields of the sulfones calculated with respect to $\Delta[R^2OOOH]$ were ~7% and 25%, respectively.

The oxidation of sulfides $4\text{-}XC_6H_4SMe$ (X = MeO, Me, H, Cl) by hydrotrioxides **20a**,**b** and **23** in acetone, methyl acetate and n-pentane at −78 °C has been studied.[33, 34] The reactions resulted in the corresponding sulfoxides as the major products (the yields are 70% to 80%); sulfones are not formed in large amounts, since the reactivities of the sulfides are much higher than those of the sulfoxides. The Hammett ρ constants for the oxidation of these aryl methyl sulfides by hydrotrioxides **20a**,**b** and **23** in different solvents are listed in Table 22. An electrophilic nature of the oxidant was revealed.

Table 22. The Hammett ρ constants for the oxidation of aryl methyl sulfides by hydrotrioxides.

Hydrotrioxide	Solvent	ρ	Ref.
20a	Me_2CO	−1.99	33
	$MeCO_2Me$	−1.59	33
	n-C_5H_{14}	−1.65	33
20b	Me_2CO	−1.83	33
	$MeCO_2Me$	−1.77	33
	n-C_5H_{14}	−1.53	33
23	MeCOMe	−1.9	34
	$MeCO_2Me$	−1.9	34

c. Sulfur ylides

Oxidation of the ylide $Me_2\overset{+}{S}-\overset{-}{C}HCO_2Et$ by the excess of the hydrotrioxide **6f** results in a mixture of the oxidation and decomposition products, *viz*., $Me_2S(O)CHCO_2Et$, $EtOC(O)CHO$, Me_2SO and Me_2SO_2, in 2.1 : 4.5 : 1.8 : 1.0 ratio (−78 to −60 °C, $[ROOOH]_0 : [ylide]_0 \approx 4.5$).[154]

* * *

Summing up, mention may be made that hydrotrioxides have found wide use in organic synthesis. They can be used as oxidants, sources of singlet molecular oxygen and initiators of free-radical reactions. Reactions of organic HTO proceed under mild conditions, which extends the possibilities for the synthesis of many valuable compounds. It is hoped that as new experimental information will be available, the use of organic hydrotrioxides will rank high among other synthetic methods.

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