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Formation of hydrotrioxides during ozonation of hydrocarbons on silica gel. Decomposition of hydrotrioxides

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ABSTRACT: Hydrotrioxides (HT), ROOOH, from isopentane, 1,4-dimethylcyclohexane, 1,3-dimethylcyclohexane, decalin and triphenylmethane were synthesized for the first time by low-temperature ozonation of the corresponding hydrocarbons on a silica surface. Thermal decomposition of hydrotrioxides is accompanied by the formation of radicals and by infrared and visible chemiluminescence (CL). In solution the HTs form self-associates and react reversibly with the solvent (acetone) producing Bayer–Villiger type intermediates (unsymmetrical dialkyl trioxides). These reactions cause a complex character of the decomposition kinetics of HTs, as evidenced by monitoring the dependence of CL intensity on time. Activation parameters of thermal decomposition of HTs show a compensation effect (log$A$ vs E_A) which describes well the available experimental and theoretical data for the homolysis of organic trioxides. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: ozone; silica gel; hydrotrioxides; free radicals; chemiluminescence; singlet oxygen; mechanism; hydrogen bonding; association

INTRODUCTION

Hydrotrioxides (HT), ROOOH, were proposed as intermediates in the reaction of ozone with saturated compounds in the early 1960s.[1–4] HTs including a wide range of O- and Si-containing compounds (alcohols, ethers, acetals, aldehydes, silanes, etc.) have been synthesized and examined since then.[5,6] However, the formation of hydrotrioxides on ozonation of hydrocarbons has been proved experimentally only for cumene[7] and for some cyclopropyl-substituted alkanes.[8]

In the mid-1970s, Cohen *et al.*[9] first demonstrated that ozonation of hydrocarbons with tertiary C—H bonds on a silica gel surface (dry ozonation) selectively yields tertiary alcohols. It was proposed that hydrotrioxides are intermediates in this reaction.[10–12] Recently, we have proved experimentally the formation of HT during the ozonation of adamantane on silica.[13] Hence dry ozonation may be considered as a route to hydrotrioxides from hydrocarbons with non-activated C—H bonds.

In this paper we report the synthesis of hydrotrioxides from isopentane, 1,4-dimethylcyclohexane, 1,3-dimethylcyclohexane, decalin and triphenylmethane. The kinetics of the decomposition of HTs were investigated by following the visible and infrared chemiluminescence (CL) which accompanies this process.

EXPERIMENTAL

Reagents

Adamantane, 1,4-dimethylcyclohexane, 1,3-dimethylcyclohexane (Fluka) and acetone-d_6 were used without further purification. Pentane, isopentane, acetone and dichloromethane were purified by common procedures. Decalin was passed through an alumina column and distilled. Triphenylmethane was recrystallized from ethanol. Freon 11 ($CFCl_3$) was saturated with ozone until the stable, deep blue color of ozone persisted. After removing the excess of ozone, the Freon was treated with sodium carbonate solution, dried over anhydrous $MgSO_4$ and distilled. All solvents were additionally dried over 4 Å molecular sieves. *tert*-Butyl hydroperoxide was distilled *in vacuo* (55 °C/43 mmHg). Silica gel (Chemapol, L 40/100, 0.063 –0.2 mm) was precalcinated for 5 h at 250 °C.

Hydrotrioxide synthesis

Adamantane, decalin, 1,4-dimethylcyclohexane, 1,3-dimethylcyclohexane and triphenylmethane were ad-

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sorbed on silica from pentane.[14] Adsorption of isopentane was carried out in sealed ampoules with heating. Samples of silica with adsorbed hydrocarbons (1–3 mmol) were saturated with ozone (1.5–3.0 mmol) at $-70\,^{\circ}$C and kept for 1–3 h at the same temperature. Unreacted ozone was removed by a cooled oxygen stream. Products were eluted with 7–10 ml of precooled acetone-d_6 –Freon 11 (1:1).

Analysis and identification

^{1}H NMR spectra were recorded with a Bruker AM 300 spectrometer equipped with a variable-temperature probe. Hydrotrioxide concentrations were determined using triphenylphosphine.[15] Decomposition products were analyzed by gas–liquid chromatography on a Chrom-5 chromatograph (370×0.3 cm i.d. column, SE-30, 50–300 °C, helium carrier gas, flame ionization detection).

Chemiluminescence

Chemiluminescence in the infrared spectral range was detected with a photometric unit with a cooled FEU 83[16] photomultiplier (the registration range was 1000–1300 nm with a light filter). Visible CL (350–650 nm) was detected with an FEU 148 photomultiplier.

Kinetics of chemiluminescence decay

ROOOH solutions (0.5–0.1 ml, 0.01–0.07 M) were added to the solvent (2.5–2.9 ml) in a thermostated (-7 to $+30\,^{\circ}$C) reactor (10 ml) and CL intensities were recorded after achieving thermal equilibrium (ca 10 s). The temperature in the reactor was controlled by a thermocouple.

Radical intermediates

Equimolar acetone solutions of HT and a spin trap (*N*-phenyl-*tert*-butylnitrone, PBN) were placed in ampoules and electron paramagnetic resonance (EPR) spectra were registered at room temperature using a Radiopan SE/X 2544 spectrometer.

Ab initio calculations

These were performed using the 6–31 G(*p, d*) basis set with full geometry optimization as implemented in the GAMESS package.[17]

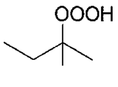
RESULTS AND DISCUSSION

Formation of hydrotrioxides on a silica surface

Hydrotrioxides were synthesized by low-temperature ozonation of hydrocarbons absorbed on silica gel. During supply of ozone on silica with adsorbed substrate a blue color appeared. The period of time between saturation of the sample and removal of unreacted O_3 should be long enough for HT formation in sufficient yield, but not too long to prevent HT decomposition in a secondary reaction with excess of ozone. We found the optimum reaction time to be 1–3 h. For further CL investigations we considered Freon 11 and dichloromethane to be the most favorable solvents because of their inertness, but their eluting capability is poor. Therefore, we used an acetone–Freon 11 mixture as the eluent. Quantitative determination of HT concentrations was performed by treatment of the eluate with a fourfold excess of Ph_3P, then the mixture was warmed to room temperature and unreacted triphenylphosphine was determined by iodometry. The concentration of ROOOH was found to be 0.01–0.13 M. Owing to the high adsorbtivity of silica at low temperatures we were unable to elute HT completely, so the ROOOH yield did not exceed ca 30–60% (with respect to the initial substrate).

By making use of the above procedure we synthesized hydrotrioxides from isopentane, 1,4-dimethylcyclohexane, 1,3-dimethylcyclohexane, decalin, adamantane, and triphenylmethane (**1**–**6**):

$$\mathrm{RH} \xrightarrow[-70^{\circ}\mathrm{C}]{\mathrm{O_3/SiO_2}} \mathrm{ROOOH}$$



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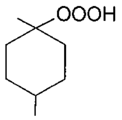

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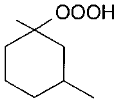

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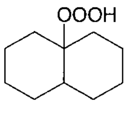

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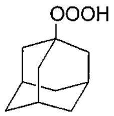

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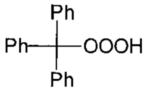

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The low-temperature ^{1}H NMR spectra of the eluates containing ROOOH showed a single peak at ca 13.3 ppm and two signals at ca 4.3 ppm which disappeared after heating to ambient temperature (Fig. 1). An increase in temperature causes upfield shifts of these absorptions (Fig. 1) together with a decrease in their intensity until complete disappearance. Cooling the samples did not lead to any reappearance of the absorption at δ 13.3 and 4.3 ppm. It is well established that the ^{1}H NMR absorption at δ 13 ppm is typical of the hydrotrioxide proton of ROOOH species.[5,6] The nature of the absorption at δ 4.3 ppm will be discussed later. The position of

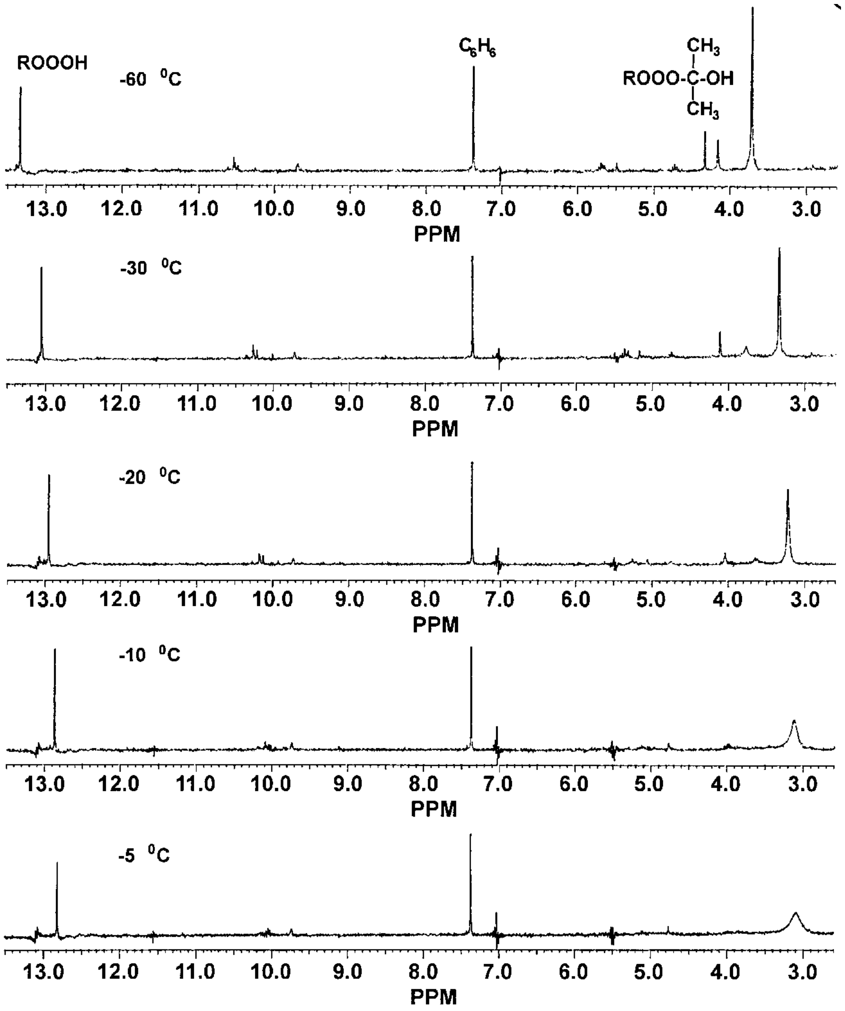


Figure 1. Temperature dependence of the ^{1}H NMR spectra of 1,4-dimethylcyclohexane hydrotrioxide. Acetone-d_6–Freone 11 (1:1), [ROOOH] = 5.1×10^{-2} M, [C_6H_6] = 8.5×10^{-3} M

the signal at 13.3 ± 0.2 ppm (−60 °C) does not depend on the nature of the substituent R. This signal appears as a singlet at any temperature and concentration used in the experiments. In an ethanol-d_6 solution of AdOOOH the absorption at ca 13.3 ppm was not observed.

Hydrotrioxides of alkanes and cycloalkanes synthesized by us have never been obtained by liquid-phase ozonation. In contrast, hydrotrioxides of oxygen-containing compounds,[5,6] alkylaromatic (cumene)[7] and cyclopropyl-substituted hydrocarbons[8] were prepared by ozonation in solution. From our point of view the formation of hydrotrioxides from 'simple' hydrocarbons upon silica-mediated ozonation resulted from the dramatic impact of the surface on the course of the reaction. Several features determine the differences between low-temperature ozonation of hydrocarbons on silica and in solution: the first is the high concentrations of reagents on the surface, which cannot be reached in solution, especially at low temperature. Consequently, ozonation on silica proceeds faster than in solution.[11,13] Second, limited translational motion of adsorbed reagents, intermediates[18] and products reduces the probability of side reactions and, therefore, gives rise to the selectivity of the process. Finally, the silica surface is known to be a highly polar and anisotropic medium, which stabilizes ionic intermediates;[19] in solution such stabilization is possible only in super-acids.[20] As expected earlier,[7,8] [21–23] carbocation stabilization favors HT formation in reactions of ozone with C—H bonds.

In this work we have shown that the formation of hydrotrioxides is a common feature of dry ozonation of branched and cyclic alkanes and alkylaromatic hydrocarbons. Apparently, the formation of triphenylmethyl hydrotrioxide is possible not only at the surface, but also in solution. However, the low solubility of Ph_3CH at ca −70 °C prohibits the synthesis of Ph_3COOOH. Moreover, thermal or photochemical activation of the transient complex $ArH^{\cdot}O_3$ is expected to be necessary for triphenylmethane hydrotrioxide formation in solution as well as for cumene.[7] In the case of dry ozonation the polar silica surface plays a similar activating role.

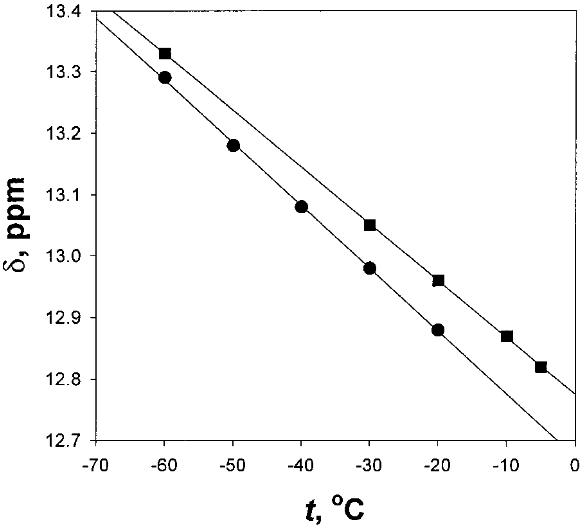
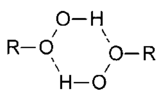


Figure 2. Temperature dependence of ^1H NMR hydrotrioxide proton absorption. (■) Hydrotrioxide of 1,4-dimethylcyclohexane (**2**), 5.1×10^{-2} M; (●) hydrotrioxide of adamantane (**5**), 4.6×10^{-2} M

Association of hydrotrioxides in solution

Under all conditions studied the ^1H NMR signal of the ROOOH proton was represented by a singlet (Fig. 1) which shifts upfield upon warming. Obviously, this behavior of the signal testifies that hydrotrioxides like as hydroperoxides exist in solution in associated form. Indeed, the chemical shift temperature gradients for hydrotrioxides **2** and **5** ($\Delta\delta_{OOOH}/\Delta T = 0.9 \times 10^{-2}$ and 1.0×10^{-2} ppm K^{-1}, Fig. 2) are close to that for hydroperoxides [$\Delta\delta_{OOH}/\Delta T = 1.1 \times 10^{-2}$–$1.7 \times 10^{-2}$ ppm K^{-1} (Ref. 24)]. Unfortunately, there are no experimental data on the structure and relative stability of ROOOH associates. Therefore, we calculated the stabilization energies of cyclic (**9** and **10**) and linear (**11** and **12**) methyl hydrotrioxide dimers using the 6–31 G(*p*, *d*) basis set with full geometry optimization:

Structure	$E_{6\text{–}31G(p,\ d)}$ (hartree)	ΔE (kcal mol^{-1})
CH_3OOH	−189.80757	—
7	−379.62791	8.0
CH_3OOOH	−264.57622	—
9	−529.16690	9.1
10	−529.16291	6.6
11	−529.16068	5.2
12	−529.16021	4.9



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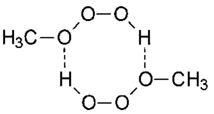
CH_3OOOH

8



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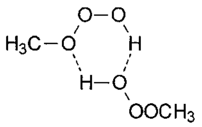

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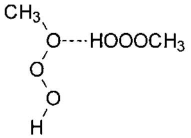

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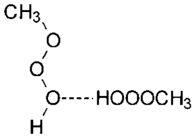

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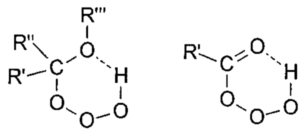
It can be seen that the cyclic octatomic dimer **9** is the most stable of the methyl hydrotrioxide associates. These results are in accordance with RHF/6–31G calculations reported early by Koller *et al.*[25] [14.2 kcal mol^{-1} (1 kcal = 4.184 kJ)]. However, the absolute values obtained by us are more accurate owing to inclusion of polarization *p* and *d* functions in the basis set during geometry optimization. For example, our result for methyl hydroperoxide cyclic dimer (**8**) (8.0 kcal mol^{-1}) is in good accordance with the experimental values (6.5–7.7 kcal mol^{-1}).[26] Obviously, at low temperature hydrotrioxides preferably exist as cyclic dimers (**9**). With increasing temperature, the molecular mobility increases leading to other associated forms (**10–12**), which results, as for hydroperoxides,[26] in an upfield shift of the hydrotrioxide proton signal.

In the light of the data discussed above, we can reconsider the reasons for splitting of the ROOOH proton signal in the ^1H NMR spectra of hydrotrioxides obtained from the low-temperature ozonation of alcohols, ethers and acetals.[27–30] This splitting was previously assigned to the presence of two hydrotrioxide forms with OOOH bonded either intramolecularly or intermolecularly **9–12**:



The different hydrogen bonds or the different conformations of associates were considered to lead to distinct NMR signals.[28] Our results and also data reported for cumyl[7] and dimethylphenylsilyl hydrotrioxides,[31] which are unable to form intramolecular hydrogen bonds, strongly support the explanation of ROOOH proton signal splitting as being due to intramolecular hydrogen bonds.

Chemiluminescence kinetics on thermal decomposition of hydrotrioxides in solution

Thermal decomposition of HTs **1–6** was found to be accompanied by infrared and visible CL. Most of the infrared runs were performed in CH_2Cl_2, since the most intense CL was observed in this solvent. The decay kinetics of CL depend on the initial concentration of HT, $[ROOOH]_0$, and on the nature of the solvent. The shapes of the kinetic curves of visible and infrared CL decay are different. Addition of *tert*-butyl hydroperoxide (0.1 M)

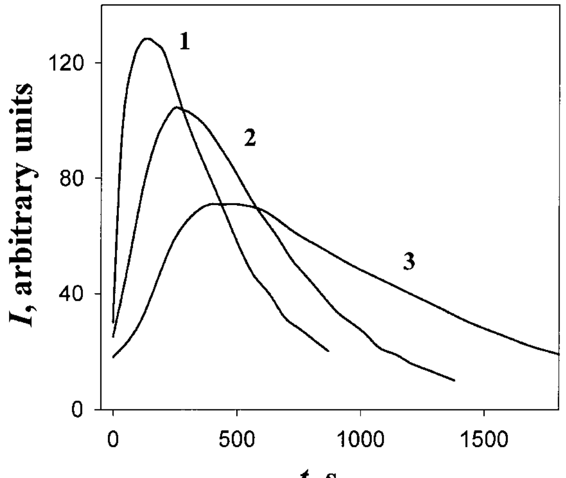


Figure 3. Kinetics of infrared chemiluminescence on decomposition of isopentyl hydrotrioxide in CH_2Cl_2: (1) 18; (2) 12; (3) 7 °C

led to a considerable (more than one order of magnitude) decrease in CL intensity in both spectral ranges.

Infrared chemiluminescence. Infrared CL kinetic curves for the decomposition HTs **1–5** have similar shapes (Fig. 3). After addition of the HT solution to the thermostated reactor, the CL intensity increases, reaches a maximum and then decreases according to an exponential law. The lower the temperature the longer is the time to achieve the maximum (Fig. 3). During the decomposition of HT **6**, a maximum on kinetic curve was not observed, and only an exponential decay of CL intensity took place in this case.

This curious behavior of CL intensity with time cannot arise as a result of thermal instability caused by addition of the cold (−70 °C) ROOOH solution, since the thermal equilibrium is adjusted in ca 10 s. In a typical run the time required to reach maximum CL intensity was 100–500 s. The CL decay followed first-order kinetics. From the temperature dependence of the rate constant k_{IR} the activation parameters of the process were calculated (Table 1). The rate constant k_{IR} increases with increasing initial concentration, $[ROOOH]_0$.

The kinetic curves of infrared CL from decomposition of hydrotrioxides **1, 2, 4** and **5** have a shape typical of reactions with intermediate product formation (Fig. 3). Obviously, this behavior of CL intensity is caused by the transformation of one unstable species in to another when the cold (−70 °C) hydrotrioxide solution is added to the solvent which is at a substantially higher temperature (−5 to +30 °C).

Let us assume that hydrotrioxides in solution at low temperatures are present in a form A. When the solution is heated or diluted the form *A* decomposes irreversibly:

$$A \longrightarrow h\nu(vis) + \ldots \tag{1}$$

or reversibly transforms into form B:

$$A \rightleftharpoons B \tag{2}$$

The hydrotrioxide in form B also undergoes thermal decomposition:

$$B \longrightarrow h\nu(ir, vis) + \ldots \tag{3}$$

The slow rise of CL intensity (Fig. 3) indicates that other unstable compounds are present in solution besides associates of hydrotrioxides. This suggestion is confirmed by the presence of high-field ^{1}H NMR signals at δ 3–4 ppm which irreversibly disappear upon heating. These signals are not due to another type of hydrotri-

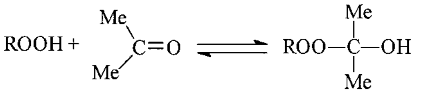
Table 1. Activation parameters for infrared (*ir*) and visible (*vis*) chemiluminescence decay on thermal decomposition of hydrotrioxides of hydrocarbons

ROOOH	$[ROOOH]_0$ (10^{-3} M)	Solvent, method	$k(10^{-3}\ s^{-1})^a$	Log A (s^{-1})	E_A (kcal mol^{-1})
1	3.2	CH_2Cl_2, *ir*	1.4	11.5 ± 1.2	18.6 ± 1.6
1	5.7	CH_2Cl_2, *vis*	2.4	6.8 ± 0.6	12.2 ± 0.8
2	5.8	CH_2Cl_2, *ir*	6.4	7.0 ± 0.6	11.9 ± 0.7
2	7.8	CH_2Cl_2, *vis*	8.1	7.1 ± 0.4	11.9 ± 0.6
2[c]	7.8	Acetone, *vis*	32.6	6.7 ± 0.9	10.6 ± 1.2
2[d]	7.8	Acetone, *vis*	3.4	5.1 ± 1.8	9.8 ± 2.3
4	6.5	CH_2Cl_2, *ir*	4.1	9.2 ± 0.9	15.0 ± 1.2
4	4.0	CH_2Cl_2, *vis*	7.0	10.2 ± 0.7	16.0 ± 1.0
5	6.4	CH_2Cl_2, *ir*	8.2	9.5 ± 0.9	15.0 ± 0.9
5[b]	2.1	CH_2Cl_2, *ir*	6.0	14.0 ± 1.4	21.0 ± 1.9
5	3.7	CH_2Cl_2, *vis*	10.6	9.3 ± 0.7	14.6 ± 0.9
5	2.3	Acetone, *vis*	5.8	12.9 ± 1.4	19.6 ± 1.9
6	7.4	CH_2Cl_2, *ir*	53.5	9.0 ± 0.9	13.3 ± 1.3

[a] Calculated at 10 °C.
[b] ROOOH was eluted with Freon 11–ethanol-d_6
[c] First part ($k_{VIS}{}^{i}$).
[d] Second part ($k_{VIS}{}^{ii}$).

oxide, e.g. a secondary hydrotrioxide, since OOOH always gives absorption near δ 13 ppm. Moreover, low-temperature ozonation of hydrocarbons on a silica surface proceeds selectively and affords the tertiary alcohols as predominant (>98%) products.[9] We presume that this additional intermediate is formed by the reaction of hydrotrioxide with the solvent acetone.

Hydrogen peroxide[32] and alkyl hydroperoxides[33,34] are known to react readily with aliphatic and alicyclic ketones giving α-oxyhydroperoxides and α-oxyperoxides (**13**), respectively, even without acid or base catalyst:



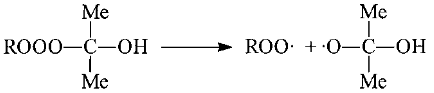
$$\mathrm{ROOH} + \mathrm{Me_2C{=}O} \rightleftharpoons \mathrm{ROO{-}C(Me)_2{-}OH} \qquad (4)$$

13

Apparently, a similar reaction takes place in a solution of ROOOH in acetone, affording 2-alkyltrioxy-2-oxypropane (**14**). Reaction (4) proceeds as a nucleophilic addition at a rate dependent on hydroperoxide acidity, and therefore on the degree of activation of the ketone carbonyl group by protons, rather on the reactivity of the hydroperoxide itself.[33] Hence more acidic hydrotrioxides would react with ketones more readily.

The values of the forward and backward reaction constants (5.3×10^{-4} l mol^{-1} s^{-1} and 1.2×10^{-3} s^{-1}, respectively) and the value of the equilibrium constant (2.9 l mol^{-1}) for the reaction of tetralyl hydroperoxide with acetone (20 °C)[33] suggest that the reaction equilibrium adjusts slowly and a significant part of the hydroperoxide is transformed into 2-tetralylperoxy-2-oxypropane. Based on the data on the equilibrium constants for the reaction of cyclohexyl hydroperoxide with cyclohexanone at -60 °C (3.8×10^3 l mol^{-1}) and 25 °C (6.6 l mol^{-1}),[34] one must assume that hydroperoxide (10^{-2} M) in neat ketone would exist preferably as adduct **13** at low temperature. After 10-fold dilution and warming of the solution to ambient temperature the content of adduct would decrease to ca 10%.

We therefore attributed the hydrotrioxide (monomer, cyclic or linear dimer) to form B that gives NMR absorption at δ 13.3 ppm. Adduct **14** corresponds to form A and represents, in essence, an unsymmetrical dialkyl trioxide. Apparently, the absorptions at δ 3–4 ppm arise from the intermolecular and intramolecular hydrogen-bonded proton of the hydroxy group of adduct **14**. Dialkyl trioxides are less stable than hydrotrioxides[35] and decompose through homolysis of an OO—O bond with formation of alkoxy and peroxy radicals.[36] The hydroxyl group in the adduct **14** destabilizes the adjacent O—OO bond even more:

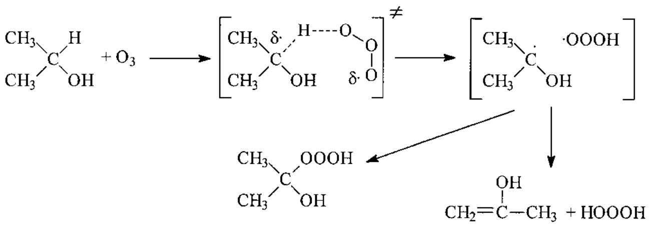


$$\mathrm{ROOO{-}C(Me)_2{-}OH} \longrightarrow \mathrm{ROO\cdot} + \mathrm{\cdot O{-}C(Me)_2{-}OH}$$

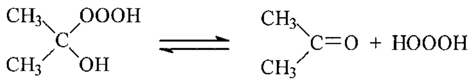
14

Owing to irreversible decomposition [reaction (1)] and adjustment of equilibrium (2) upon heating and dilution, adduct **14** (δ 3–4 ppm) is exhausted more rapidly than hydrotrioxide (δ 13 ppm), which is clearly confirmed by the ^{1}H NMR data (Fig. 1).

Recently, Plesničar *et al.*[37] showed that low-temperature ozonation of isopropyl alcohol affords significant amounts of hydrogen trioxide in addition to hydrotrioxide ROOOH (H_2O_3:ROOOH = 0.6:1). The following scheme was proposed to explain H_2O_3 formation:



According to this scheme, abstraction of a hydrogen atom from the methyl group of 2-hydroxypropyl radical by HO_3 with formation of H_2O_3 proceeds at almost the same rate as recombination of trioxyl and alkyl radicals which leads to ROOOH. Taking into account that HO_3 is very labile[23] and decomposes with a rate constant 1.1×10^5 s^{-1} even in acidic solution,[38] one can suggest another route leading to H_2O_3. We consider that the initial reaction of alcohol with ozone affords only hydrotrioxide, which further transforms reversibly into hydrogen trioxide and acetone:



$$\mathrm{(CH_3)_2C(OOOH)OH} \rightleftharpoons \mathrm{(CH_3)_2C{=}O} + \mathrm{HOOOH}$$

With these data in hand, we can explain the regularities of the CL kinetics. The kinetic features of the infrared CL upon decomposition of hydrotrioxides **1–5** become clear if one assumes that CL emitters are formed in reaction (3) but not in reaction (1). Thus, the infrared CL reflects accumulation and depletion of associates *B*. The top of the kinetic curves corresponds to the moment when *A* has almost disappeared and the concentration of *B* has reached a maximum. After the maximum the infrared CL kinetics represent the decomposition of a hydrotrioxide in form *B*. The equilibrium adjusts more rapidly and the maximum appears after a shorter period of time as the temperature is increased (Fig. 3). Perhaps the absence of a maximum in the infrared CL kinetic curve upon decomposition of triphenylmethane hydrotrioxide (**6**) is accounted for by a sterically hindered and therefore slower backward reaction (2) resulting in a negligible proportion of adduct **14**.

Visible chemiluminescence. In acetone, the visible CL on adamantyl hydrotrioxide (**5**) decomposition decayed according to an exponential law, whereas for other HTs the CL decay was described by a biexponential law. In the case of HT **2** we succeeded in evolving biexponential

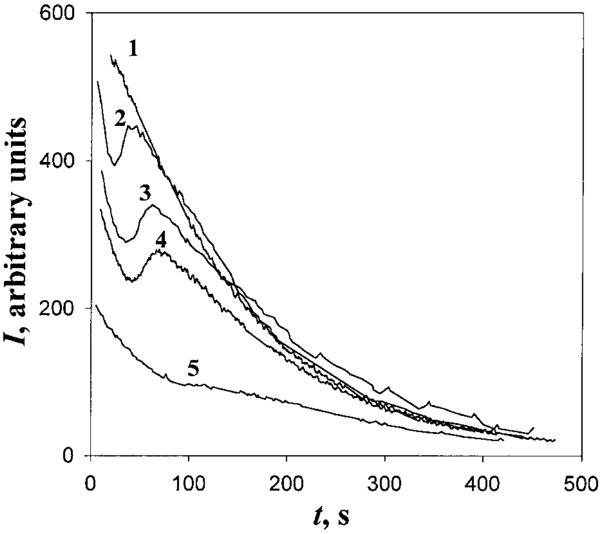


Figure 4. Kinetics of visible chemiluminescence on decomposition of adamantyl hydrotrioxide in CH_2Cl_2 at 12 °C; (1) 7.1×10^{-3}; (2) 2.5×10^{-3}; (3) 2.1×10^{-3}; (4) 1.5×10^{-3}; (5) 0.4×10^{-3} M

components and determining rate constants $k_{VIS}{}^{i}$ (first part) and $k_{VIS}{}^{ii}$ (second part) and their activation parameters (Table 1). For HTs **1** and **6** the first component was very fast and close to the response constant of the CL set-up, so it was impossible to calculate $k_{VIS}{}^{i}$.

In dichlormethane, the kinetic curves of CL intensity for all ROOOH studied had a common appearance: a fast first and slower second regions (Fig. 4). There are no differences in the spectra of the first and second parts of CL curve. When the initial concentration of the HT was increased a small maximum appeared between the first and second parts of the kinetic curve (Fig. 4). The most dramatic effect was observed for HTs **5** and **1;** the maximum was less pronounced for other ROOOH and was not observed for HT **6**. The kinetic curves of the CL decay follow an exponential law. The dependences of k_{VIS} on temperature and the initial concentration of ROOOH are presented in Tables 1 and 2.

Kinetic curves of visible CL can readily be explained if one assumes that both reactions (1) and (3) produce light emitters. The first rapid region represents adduct *A* depletion in reactions (1) and (2). The next slow region corresponds to full conversion of *A* into *B* and represents the decomposition kinetics of the latter. Depending on the reaction conditions (e.g. temperature, solvent, initial hydrotrioxide concentration and radiation quantum yield of emitters), the maximum in the kinetic curves may be more or less expressed or absent (Fig. 4).

Table 2. Concentration dependence of rate constant of infrared chemiluminescence decay upon thermal decomposition of adamantyl hydrotrioxide in CH_2Cl_2 (+5 °C)

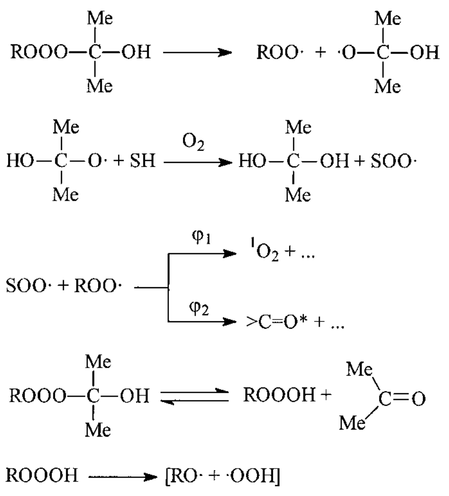
$[ROOOH]_0$ (10^{-3} M)	k (10^{-3} s^{-1})
8.2	10.0
4.9	7.0
3.3	5.9
2.7	5.0
2.2	4.9
1.6	3.7
1.1	3.2
0.5	2.4

Mechanism of decomposition of hydrotrioxides

CL in the visible and infrared regions upon decomposition of hydrotrioxides is a well-known phenomenon.[39,40] Infrared CL arises from radiation relaxation of singlet molecular oxygen $^1\Delta_g\ O_2$,[41,42] which forms directly from ROOOH or from the disproportionation of peroxy radicals. The latter process also gives emitters of visible CL. The peroxyls are formed either directly from ROOOH or through involvment of a solvent in the radical process.

The radical spin adducts produced by the decomposition of the hydrotrioxides **3** and **5** in the presence of the spin trap PBN indicate the generation of free radicals during the thermolysis of hydrocarbon hydrotrioxides. We assigned the EPR signal consisting of triplets of doublets ($a_N = 1.33$ mT, $a_H{}^{\beta} = 0.20$ mT) to an adduct of PBN with an alkoxy radical which is formed directly upon the hydrotrioxide decomposition (form *A* and *B*) or on rearrangement of the PBN adduct with a peroxy radical.[28,43] In the case of adamantyl hydrotrioxide an additional weak triplet signal ($a_N = 0.79$ mT) appeared. It was assigned to benzoyl *tert*-butylnitroxide produced by direct oxidation of PBN by hydrotrioxide.[28,31]

The yield of radicals during the decomposition of HTs varies from zero (ethanol hydrotrioxide[44]) to almost quantitative (cumyl hydrotrioxide[7]). It is believed that in most cases the decomposition proceeds through a concerted mechanism with a small fraction along a radical path.[45] Visible CL is not observed if the radical path is not distinguished.[44] Hence the behavior of visible and infrared CL can be explained according to the scheme below (SH denotes a solvent molecule):



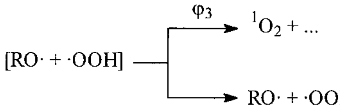
$$\mathrm{ROOO{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{{-}OH} \longrightarrow \mathrm{ROO\cdot} + \mathrm{\cdot O{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{{-}OH} \qquad (5)$$

$$\mathrm{HO{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{{-}O\cdot} + \mathrm{SH} \xrightarrow{O_2} \mathrm{HO{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{{-}OH} + \mathrm{SOO\cdot} \qquad (6)$$

$$\mathrm{SOO\cdot} + \mathrm{ROO\cdot} \begin{cases} \xrightarrow{\varphi_1} {}^{1}O_2 + \ldots \\ \xrightarrow{\varphi_2} >C{=}O^{*} + \ldots \end{cases} \qquad (7)$$

$$\mathrm{ROOO{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{{-}OH} \rightleftharpoons \mathrm{ROOH} + \mathrm{(Me)_2C{=}O} \qquad (8)$$

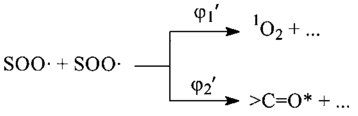
$$\mathrm{ROOOH} \longrightarrow [\mathrm{RO\cdot} + \mathrm{\cdot OOH}] \qquad (9)$$



(10)

$$RO\cdot + ROOOH \longrightarrow ROH + RO\cdot + O_2 \tag{11}$$

$$RO\cdot + SH \xrightarrow{O_2} ROH + SOO\cdot \tag{12}$$



(13)

At low temperatures in acetone solution the trioxide exists preferably as the adduct **14**. Injection of a portion of this solution in to a 'hot' (-5 to $+30\,°C$) solvent accelerates the forward reaction (8), affording monomers, linear dimers and cyclic dimers of the hydrotrioxide. Simultaneously, the fast homolytic decomposition of adduct **14** (form *A*) takes place [reaction (5)]. In the presence of molecular oxygen alkoxyls formed in this reaction react with solvent SH affording peroxy radicals, predominantly $Cl_2CHOO^\cdot$ and $CH_3COCH_2OO^\cdot$. Disproportionation of peroxyls leads to formation of singlet molecular oxygen and excited carbonyls (Cl_2CO and CH_3COCHO). We consider that homolysis of **14** is an effective radical initiation process. In a recent paper[36] we have shown that almost all radicals formed during the decomposition of di(*tert*-butyl) trioxide escape the solvent cage.

Hydrotrioxide ROOOH (form *B*) decomposes according to reaction (9). The radical pair [$RO^\cdot$ $^\cdot OOH$] either disproportionates in the solvent cage giving molecular singlet oxygen with efficiency φ_3 or escapes the cage [reaction (10)]. Free radicals induce hydrotrioxide decomposition [reaction (11)] and also generate peroxyls from the solvent [reaction (12)]. As mentioned above, disproportionation of peroxyls leads to $^1O_2$ and excited carbonyl compounds.

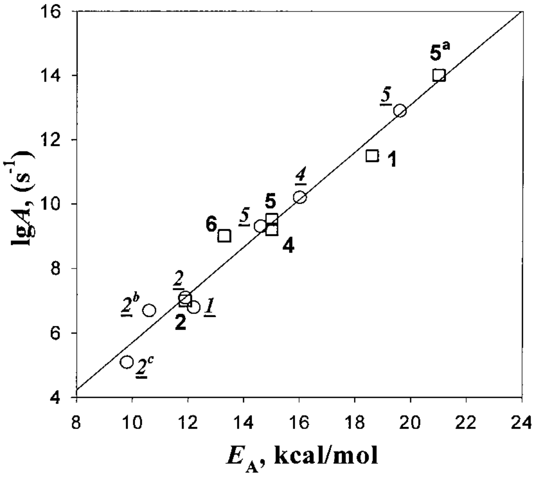


Figure 5. Compensation dependence of the activation parameters of infrared and visible chemiluminescence decay on thermal decomposition of hydrocarbon hydrotrioxides. (□) Infrared CL; (○) visible CL (*underlined*); for alphabetical indices, see Table 1

One can consider that singlet oxygen is generated more efficiently in the cage than from peroxyls which escaped the cage, $\varphi_3 \gg \varphi_1, \varphi_1'$. Actually, hydrotrioxides generate singlet oxygen with high efficiency,[40,41] while disproportionation of peroxyls usually gives small yields of $^1O_2$.[46] At the same time, the formation of excited carbonyls in reactions (7) and (13) proceeds with comparable efficiencies, $\varphi_2 \approx \varphi_2'$. Such ratios of quantum yields explain the absence of infrared CL in the first stage of the HT decomposition and the two regions in the kinetic curves of visible CL.

The important role of radicals in the generation of CL emitters is confirmed by dramatic (more than 10-fold) attenuation of visible and infrared CL in the presence of *tert*-butyl hydroperoxide (Bu^tOOH). Addition of Bu^tOOH to the hydrotrioxide solution leads to fast ($k_{14} = 2.5 \times 10^8\,l\,mol^{-1}s^{-1}$)[47] exchange of alkoxy and hydroperoxy radicals that escaped the solvent cage on *tert*-butylperoxyls[35,48]:

$$RO^\cdot + Bu^tOOH \longrightarrow ROH + Bu^tOO^\cdot \tag{14}$$

The concentration of Bu^tOOH (0.1 M) is high enough to associate effectively with hydrotrioxide and thus to play the role of a cage for the radical pair [$RO^\cdot$ $^\cdot OOH$]:

$$[RO^\cdot + {}^\cdot OOH] + Bu^tOOH \longrightarrow ROH + Bu^tOO^\cdot + HOO^\cdot \tag{15}$$

Disproportionation of *tert*-butylperoxyls in non-polar solvents does not lead to the formation of visible and infrared CL emitters.[35,46] Since quenching of CL emitters by hydroperoxide is negligible, the only explanation for the CL attenuation is the exchange of radicals according to reactions (14) and (15). Residual CL arises from incomplete capture of $RO^\cdot$ and $HOO^\cdot$ radicals by hydroperoxide.

Therefore, the second part in the kinetic curves of visible and infrared CL reflects the thermal decomposition of hydrotrioxide in the form *B*. In addition to the equilibrium [reaction (2) or (8)], the kinetics of the CL decay can also be complicated by induced decomposition of hydrotrioxide. Thus, the rate constants observed are effective values that reflect their dependence on the initial concentration of hydrotrioxide (Table 2). Hence the activation parameters are also effective values. It can be seen for the activation parameters presented in Table 1 that a linear dependence (compensation effect) between the logarithm of the *A* factor and the activation energy of the CL decay is observed (Fig. 5):

$$\log A = (-1.66 \pm 0.55) + (0.74 \pm 0.04)E_A$$

This dependence indicates a common mechanism for the decomposition of the hydrotrioxides studied. Moreover, the activation parameters for the decomposition of various ROOOH do not depend on the nature of the substituent R, but only on the initial hydrotrioxide concentration. Quantum chemical calculations also indicate that the RO—OOH bond dissociation energy is independent of the nature of R.[22,49]

The experimental and theoretical values of the activation parameters obtained earlier for the thermal decomposition of organic trioxides obey satisfactorily the compensation dependence depicted in Fig. 5: log $A = 16.4\ \mathrm{s}^{-1}$, $E_A = 23.9\ \mathrm{kcal\ mol}^{-1}$ (Ref. 7) (cumene hydrotrioxide), log $A = 17$, $E_A = 23$ (Ref. 50) and log $A = 14.5$, $E_A = 20.8$ (Ref. 35) [di(*tert*-butyl) trioxide], log $A = 16$, $E_A = 23$ (Ref. 51) (theoretical estimation). This testifies to a common mechanism for the trioxide decomposition, which proceeds via homolytic cleavage of the $R^1O—OR^2$ bond.

CONCLUSIONS

The formation of hydrotrioxides in the reaction of ozone with C—H bonds appears to proceed through ionic intermediates. This mechanism can be realized only if stabilization of the ionic intermediates by a heteroatom or aryl or cyclopropyl group is possible. The silica surface acts as a stabilizer of this kind, and therefore hydrotrioxides of inactivated hydrocarbons unavailable from ozonation in solution can be synthesized on the silica surface.

The thermal decomposition of the hydrotrioxides studied is accompanied by radical formation and by infrared and visible CL. Hydrotrioxides of hydrocarbons self-associate in solution and react reversibly with the solvent acetone. This reaction results in a complex character of the kinetics of CL decay. The nature of the alkyl substituent R does not affect the rate constant for ROOOH decomposition.

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