Synthesis and thermal decomposition of hydrotrioxide obtained by ozonization of *exo*-bicyclo[2.2.1]heptan-2-ol

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Low-temperature (−70 °C) ozonization of *exo*-bicyclo[2.2.1]heptan-2-ol in CCl_3F led to a hydrotrioxide, which was identified by ^1H NMR spectroscopy. Kinetics of decomposition of given hydrotrioxide was studied by analysis of the chemiluminescence fading in the IR range of the spectrum and the activation parameters of the process were calculated. Singlet oxygen ($^1\Delta_g$) served as an emitter of eradiation. Yields of $^1O_2$ in a range of temperature from −31.0 to +12.5 °C were determined (at −31 °C the yield was 37.6%). Bicyclo[2.2.1]heptan-2-one was found to be the main product of decomposition of the hydrotrioxide (the yield was 98%).

Key words: hydrotrioxide, singlet oxygen, rate constants, ozonization.

Hydrotrioxides (HTO) are known as unstable intermediates in the low-temperature ozonization of various saturated organic compounds.[1,2] The most important process in decomposition of HTO is the generation of oxygen in a singlet state. Analysis of the methods for determination of the yields of singlet oxygen shows that most methods, which use the $^1O_2$ acceptors, are not effective.[3] There is always a way for the direct interaction of HTO with the acceptors of singlet oxygen, which might give too high yields of $^1O_2$. Unfortunately, the most data on the yields of $^1O_2$ in decomposition of HTO was obtained exactly with the use of acceptors.[2]

By now, there are known eleven literature examples for synthesis of HTO of alcohols with alkyl substituents (Me, Et, Pr, CH_2Cl, CH_2OH, Me_2COH and MeCHOH) as well as HTO with phenyl substituent, namely, 1-hydroxyethyl-1-phenyl-1-hydrotrioxide.[4—7] The kinetic regularities of decomposition were studied for most HTO, however, the yields of singlet oxygen were reliably determined only for three of them.[2]

The highest yield of $^1O_2$ calculated based on the observation data of chemiluminescence (CL) in the IR range of the spectrum[8] was recorded in the decomposition of MeCH(OH)OOOH and varied in a range from 0.9% in $MeNO_2$ to 18% in $CFCl_3$ (+5 °C).[9] Analysis of the solvent effect on the $^1O_2$ yields within the framework of the Koppel—Palm equation shows the yields rise with the increase of the solvent polarity, whereas, the increase in specific solvation leads to the yields decrease. Lowering of the yields of $^1O_2$ with the temperature increase[2] is observed for $Me_2C(OH)OOOH$ and MeCH(OH)OOOH, which can be described within the framework of the Bagdasar'yan equation.[10] It is suggested that formation of $^1O_2$ takes place either as a result of molecular decomposition of HTO or during disproportionation of the radical pair |RO˙ ˙OOH| in the solvent cage. The authors[9] gave preference to the latter suggestion. However, this attitude does not explain why the $^1O_2$ yields change from 15 (−15 °C) to 11% (+18 °C)[9] and why the radical channel part in the decomposition is equal to zero[11] for the thermolysis of MeCH(OH)OOOH, the very object of the analysis.

In the present work we have studied by the chemiluminescence method the decomposition of hydrotrioxide **1**, arising during the low-temperature ozonization of *exo*-bicyclo[2.2.1]heptan-2-ol. The kinetic parameters were determined and the yield of singlet oxygen was calculated.

Experimental

exo-Bicyclo[2.2.1]heptan-2-ol (Aldrich, 98%) was purified by sublimation under low pressure. Dichloromethane was shaken with concentrated sulfuric acid, washed with saturated $NaHCO_3$ solution and water until the neutral reaction persists, dried with $MgSO_4$, and redistilled. Freon 11 (CCl_3F) was saturated with ozone until the blue color steadily persists. After the removal of the excess of ozone, Freon was treated with Na_2CO_3 solution, dried with $MgSO_4$, and redistilled. All the solvents were kept over molecular sieves 4 Å.

NMR spectra were recorded on a Bruker AM-300 spectrometer (standard, Me_4Si; solvents, acetone-d_6, toluene-d_8 and CCl_3F). GLC-analysis was carried out on a Hewlett Packard 5890E SERIES II gas chromatograph with a capillary column HP-5 (cross-linked 5% PH ME Silicon, 30 m × 0.32 mm × 0.25 μm Film). *n*-Decane was used as the

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internal standard. Registration of the IR-chemiluminescence (IR-CL) was performed on a high-sensible photometric installation.[12] The light flows were measured with the help of a FEU-83 photomultiplyer cooled down to −70 °C. When using an IKS-7 light filter, the range of the registration was 1000—1300 nm.

Synthesis of hydrotrioxide 1 from *exo*-bicyclo[2.2.1]heptan-2-ol. A pre-cooled ozone-oxygen mixture was bubbled through the solution of *exo*-bicyclo[2.2.1]heptan-2-ol in CCl_3F (0.22—0.30 mol L^{-1}) kept at −70 °C. It was found by experiment that the optimal time of ozonization to obtain hydrotrioxide in sufficient yield without its further transformation under the action of O_3 is 3 h. After this period, the remaining ozone was removed by bubbling of pre-cooled argon through the solution. The concentration of hydrotrioxide was determined by its reaction with triphenylphosphine.[13] The solutions after ozonization contained 0.21—0.28 mol L^{-1} of the hydrotrioxide. Compound **1** was identified by NMR spectroscopy at −70 °C. In the ^1H NMR spectrum of the hydrotrioxide obtained, there was a characteristic signal of a proton of the O_3H group at δ 13.55 (toluene-d_8—CCl_3F), disappearing after heating up to ~20 °C.

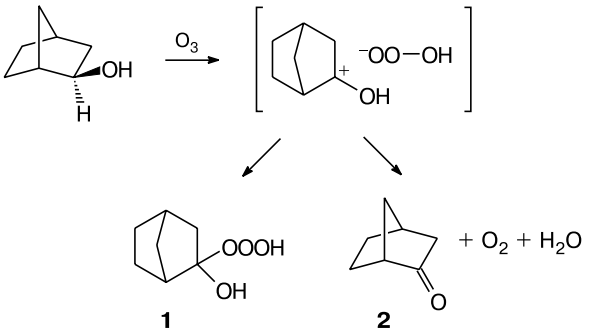
Kinetics of decomposition of hydrotrioxide **1** was studied by analysis of the fading of CL in the IR range of the spectrum. The CH_2Cl_2 (2.5—2.8 mL) was placed into a 10-mL glass reactor kept at constant temperature, then a solution of hydrotrioxide **1** (0.2—0.5 mL, concentration 0.21—0.28 mol L^{-1}) was added with a pre-cooled pipette, and CL was registered. The temperature was varied in the range of −31.0—+12.5 °C. After complete consumption of hydrotrioxide **1**, the solvent was evaporated. The residue, according to the GLC data, contained the starting alcohol (1.5%) and bicyclo[2.2.1]heptan-2-one (**2**) (98%). The product was identified by comparison with authentic samples and by ^{13}C NMR spectroscopy.

Results and Discussion

Ozonization products of *exo*-bicyclo[2.2.1]heptan-2-ol. Bicyclo[2.2.1]heptan-2-one (**2**) is found to be a reaction product of ozone with *exo*-bicyclo[2.2.1]heptan-2-ol and hydrotrioxide **1** was an intermediate in this process. The yield of the ketone after the decomposition of **1** was 98% and the conversion of the substrate was 98%. Compound **2** was formed *via* intermediate **1** by thermal decomposition of the latter with emission of oxygen ($^1O_2$, $^3O_2$) or upon its reaction with ozone. Earlier,[14] it was found that trioxides react with ozone. The stoichiometry of the reaction is evidence of this: 1 mol of the substrate requires 1.2—2 mol of ozone. The control experiments showed that there is no consumption of the trioxide and ozone at −70 °C in the solvent used. It should be noted that, when using CH_2Cl_2 as a solvent for ozonization, the conversion of the substrate does not exceed 15%, with a molar ratio of substrate : O_3 being 1 : 7. The last fact shows that it is unreasonable to use solvents with weak C—H bonds for the low-temperature ozonization. It is due to the formation of oxygen-centered radicals in the reaction of trioxide with ozone[14] and with involvement of the solvent into the process.

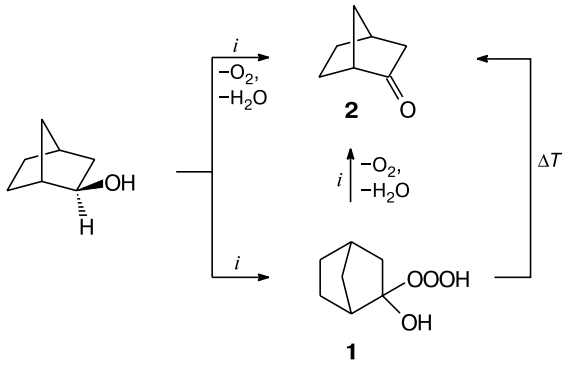
In one of the last publications[15], dealing with the ozonization of acetals, the authors made a conclusion about the ionic character of the reaction of ozone with a C—H bond. According to this mechanism, compounds **1** and **2** might be formed through an ion pair (Scheme 1).

Scheme 1



Phenomenologically in a simplified form, the process can be shown as follows (Scheme 2).

Scheme 2



Reagents and conditions: *i*. O_3, −70 °C.

Consumption of the substrate in the reaction with ozone can take place by two competing ways leading to the ketone or hydrotrioxide. Apart from that, the latter is consumed in the reaction with ozone. All the foregoing accounts for the deviation of stoichiometry of the reaction from the 1 : 1 ratio and the impossibility of obtaining hydrotrioxide **1** in more than 35% yield.

^1H NMR spectrum of hydrotrioxide 1. The spectrum in acetone-d_6 has a set of signals in the range of δ 11.5—13.0 corresponding to the proton of the O_3H group (Fig. 1), whereas in toluene-d_8 there is the only signal at δ 13.55. The dramatic difference in the shape of the signal of the hydrotrioxide proton in these solvents is apparently related to the specific solvation of hydrotrioxide **1** with acetone to form more stable solvate shells, which stabilize

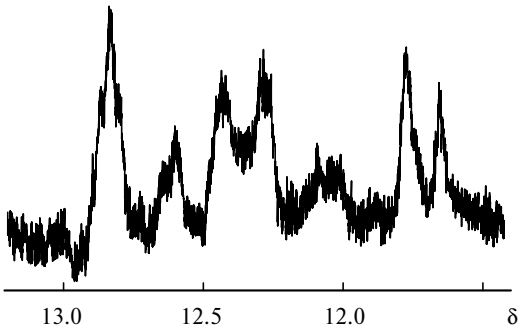
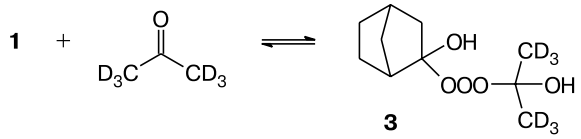


Fig. 1. Signals of proton in the O_3H group in ^1H NMR spectrum of hydrotrioxide **1** in a mixture $CFCl_3$—acetone-d_6 (1 : 1) at −70 °C.

various types of associates of **1**. Moreover, acetone-d_6 can react with compound **1** to yield trioxide **3** (Scheme 3).[16]

Scheme 3



The latter, due to the two OH groups present, can form stable associates with hydrotrioxide **1** causing appearance of new signals of the O_3H group in the spectrum. The presence of only one signal in toluene-d_8 solution can be explained by formation of associates with similar structures and/or by similar electron density on the hydroperoxide proton. In addition, it should be stated that we deal with the individual trioxide and not with the mixture of *exo*- and *endo*-isomers, since the chemical shifts of protons in the O_3H group significantly differ for such isomers.[17,18] It is known[4,6,7] that ozonization of different isomers occurs with retention of configuration, that is why formation of 2-*exo*-hydroxybicyclo[2.2.1]heptyl-2-hydrotrioxide is only possible.

Thermolysis. Thermal decomposition of hydrotrioxide **1** is accompanied by CL in the IR range of the spectrum with the maximum at 1270±20 nm. The change in the solvent (toluene-h_8 to toluene-d_8) leads to the increase in the luminescence intensity. These facts are evidence of the formation in the system of oxygen in a singlet state $^1\Delta_g$.[3] All the kinetic experiments were carried out in CH_2Cl_2, since CL is the most intensive in this solvent. After the addition of the hydrotrioxide solution into the kept at constant temperature reactor, CL is observed the intensity of which reaches the maximum and then exponentially decays. The curve of the IR-CL decay after passing the maximum is well linearized in the coordinates of the first order kinetic equation (Fig. 2).

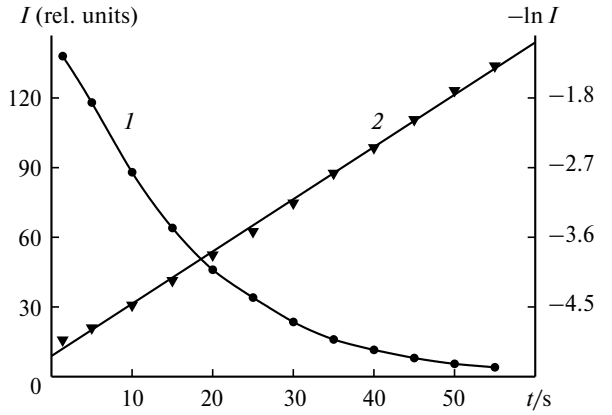


Fig. 2. The typical kinetic curve of the IR-CL fading for decomposition of hydrotrioxide **1** in dichloromethane (*1*) and its semi-logarithmic anamorphose (*2*) (−20 °C; $[\mathbf{1}]_0$ = 0.1 mol L^{-1}).

Table 1. Dependence of the rate constant of decomposition of hydrotrioxide **1** in CH_2Cl_2 (k) and the singlet oxygen yields from the temperature ($[\mathbf{1}]_0$ = 0.1 mol L^{-1})

T/°C	$k \cdot 10^{-2}/s^{-1}$	Yield $^1O_2$ (%)
−31.0	0.8±0.2	37.6
−20.5	1.4±0.1	35.0
−11.5	2.8±0.1	29.2
0	3.3±0.1	24.4
+12.5	6.3±0.3	23.9

The effective rate constants were calculated from the semi-logarithmic anamorphoses of the IR-CL decay curves (Table 1). In addition, the activation parameters of the process were calculated from the data obtained

$$\log k = (2.1\pm0.1) - (6.5\pm0.6)/\theta,$$
$$\theta = 2.3RT \text{ (kcal mol}^{-1}\text{)}.$$

The too low value of the pre-exponential factor may be connected with the highly ordered transition state of the decomposition of **1** to yield $^1O_2$ and/or with the solvation of the transition state by a solvent due to its higher polarity as compared with the starting HTO or its associates. The activation parameters of decomposition of alcohol hydrotrioxides vary within wide limits,[2] and the values for decomposition of compound **1** are near the lower border. The hydrotrioxide **1** is the least stable in comparison with the HTO obtained from alcohols with two alkyl substituents. Thus the rate constant for decomposition of $Me_2C(OH)OOOH$ (see Ref. 6) at −20 °C is equal to $2.8 \cdot 10^{-3}$ s^{-1}, whereas for hydrotrioxide **1** this is 5 times as high, which may be connected with the strained structure of the alkyl fragment in the trioxide under consideration.

The yield of singlet oxygen decreases with the increase in the temperature (see Table 1), which can be explained based on the following suggestions.

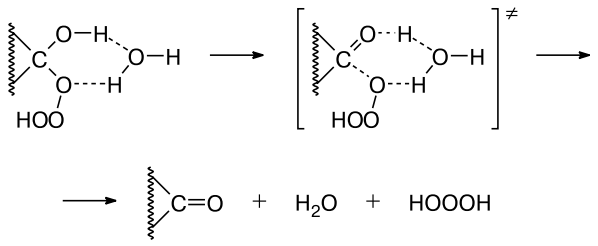
1. Singlet oxygen is formed in the disproportionation of the radical pair |RO˙ ˙OOH| in the solvent cage, the lifetime of which decreases with the temperature increase and, consequently, the yield of $^1O_2$ drops.[9] However, this assumption does not always completely explain all the experimental facts.

2. It cannot be ruled out that the part of the radical processes increases with the increase in temperature, which can lead to the decrease in the yield of singlet oxygen.

3. In the decomposition of HTO, the $^1O_2$ turns out to be in the solvent cage together with the extinguisher (ROH and/or H_2O). It may so happen that with the increase in temperature the decay inside the cage occurs more efficient than in the solution. An example, when the exited state of indole reveals the extraordinary temperature sensitivity concerning its lifetime and quantum yield in aqueous solution,[19,20] can be shown in favour of this suggestion.

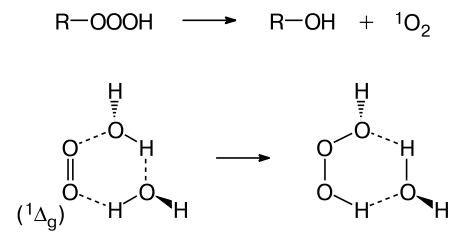
4. In addition, the decomposition of hydrotrioxide **1** with the formation of HOOOH (see Ref. 15) is likely to occur, on decomposition of which the yield of $^1O_2$ can differ from that for **1** (Scheme 4).

Scheme 4



Compound HOOOH is also likely to be formed from $^1O_2$ ($^1\Delta_g$) and two molecules of water[21,22] (Scheme 5).

Scheme 5



This is confirmed by the experimental data on decomposition of silyl- and germylhydrotrioxides in the solvents with varied water contents.[23] This reaction has high energy of activation (29.9 and 33.1 kcal mol^{-1})[15,24] and can contribute to the consumption of singlet oxygen with the increase in the temperature.

In conclusion, the synthesis of hydrotrioxide from *exo*-bicyclo[2.2.1]heptan-2-ol has been accomplished for the first time and its decomposition has been studied by the IR-CL method. In the decomposition of the hydrotrioxide, the yield of $^1O_2$ can be as high as 38%. The use of ozone for the oxidation of *exo*-bicyclo[2.2.1]heptan-2-ol allows one to obtain the corresponding ketone with a high yield (98%).

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