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The Quantum Yield of Singlet Oxygen in Thermal Degradation of Alcohol Hydrotrioxides

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Abstract—The yield of singlet oxygen ($^1O_2$) in the decomposition of a number of hydrotrioxides of alcohols (cyclobutanol, cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, L-menthol, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol, heptan-4-ol, propanol-2, and 1-cyclopropylethanol) has been determined using the IR chemiluminescence technique. It has been shown that cyclopentanol, 1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol and 1-cyclopropylethanol hydrotrioxides are efficient sources of singlet oxygen; the yield of $^1O_2$ reaches up to 58%.

Keywords: singlet oxygen, hydrotrioxides, chemiluminescence

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INTRODUCTION

Singlet oxygen $^1O_2$ ($^1\Delta g$), molecular oxygen in the lowest electronically excited state, is formed in photochemical and chemical processes. Its role is important and diverse, ranging from that in chemical synthesis and polymer degradation to a signaling molecule in the cells of living organisms. Thus, the interest of researchers in methods for obtaining singlet oxygen and its properties has not been lost over more than the last 50 years [1, 2]. Among the chemical sources, the most effective and practical ones are systems involving peroxides (hydrogen peroxide, phosphite ozonides, and hydrotrioxides). Information on hydrotrioxides (ROOOH) as a source of singlet oxygen is contradictory and, as a rule, is based on the determination of the $^1O_2$ yield using the scavenging technique. The results obtained by this method are unreliable [3], possibly, because of the occurrence of the hydrotrioxide reaction with a scavenger. The measurement of singlet oxygen phosphorescence at 1270 nm is the most reliable and convenient method for studying $^1O_2$ reactions, including the determination of its yield of in the decomposition of hydrotrioxides [3].

It was previously shown that the yield of singlet oxygen in the degradation of alcohol hydrotrioxides, as determined by measuring chemiluminescence (**CL**) at 1270 nm in methylene dichloride, was 2.5, 13, or 8% for methanol, ethanol, or 2-propanol hydrotrioxide, respectively [3]. Later we found out that the degradation of a hydrotrioxide bearing a carbocyclic substituent (2-*exo*-hydroxybicyclo[2.2.1]heptyl-2) produced $^1O_2$ in CH_2Cl_2 in as high a yield as 38% [4].

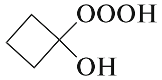
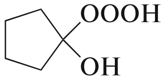
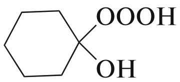
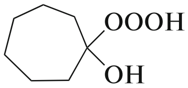
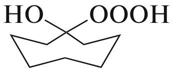
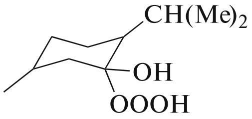
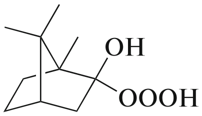
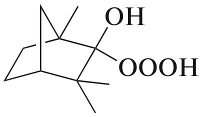
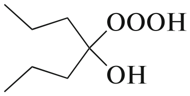
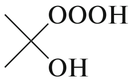
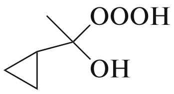
In this study, we determined the yield of singlet oxygen in the decomposition of a number of hydrotrioxides of secondary alcohols with the aim of searching for efficient chemical sources of singlet oxygen.

EXPERIMENTAL

Hydrotrioxides were synthesized by ozonation of alcohols at a low temperature in a solvent according to the standard procedure [5]. The following alcohols were chosen as the starting compounds: cyclobutanol (**1**), cyclopentanol (**2**), cyclohexanol (**3**), cycloheptanol (**4**), cyclooctanol (**5**), L-menthol (**6**), 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**7**), 1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol (**8**), heptan-4-ol (**9**), propanol-2 (**10**), and 1-cyclopropylethanol (**11**). The ^1H NMR spectra of hydrotrioxides **1a**–**11a** are identical to those reported earlier [5]. The concentration of hydrotrioxides was determined according to the standard procedure with triphenylphosphine [6].

The yield of singlet oxygen in the thermolysis of hydrotrioxides was determined using the IR chemiluminescence technique. The wavelength range of singlet oxygen emission was isolated using an IKS-7 visible light cut-off filter ($\lambda > 900$ nm). The chemiluminescence measurement unit was calibrated using a source with a known singlet oxygen yield (Φ), triphenyl phosphite ozonide, for which $\Phi = 1.0$ [7]. All experiments on the determination of the yield of singlet oxygen were carried out maintaining constant parameters, such as the reactor volume and geometry, the total volume of the reaction mixture, the voltage applied to a photomultiplier tube (FEU-83), and its

Table 1. The yield of singlet oxygen in thermolysis of hydrotrioxides **1a**–**11a** (solvent, *t*-BuOMe)

ROOOH		$[ROOOH]_0$, mol/L	*T*, K	Φ_0, %
	**1a**	0.15	288	32 ± 3
			273	34 ± 3
			263	35 ± 3
	**2a**	0.14	288	40 ± 4
			273	44 ± 4
			263	58 ± 4
	**3a**	0.17	288	15 ± 2
			273	18 ± 2
			263	23 ± 2
	**4a**	0.14	288	17 ± 3
			273	29 ± 3
			263	35 ± 3
	**5a**	0.13	288	21 ± 3
			273	37 ± 3
			263	51 ± 5
	**6a**	0.03	283	14 ± 2
			263	24 ± 3
	**7a**	0.03	283	21 ± 3
			273	22 ± 3
			263	25 ± 3
	**8a**	0.04	283	47 ± 5
			273	50 ± 5
			263	51 ± 4
	**9a**	0.1	288	18 ± 2
			273	22 ± 3
			263	31 ± 3
	**10a**	0.2	263	35 ± 3
	**11a**	0.1	288	30 ± 3
			273	45 ± 4
			263	56 ± 5

temperature (183 K). The yield of singlet oxygen was calculated as described in [8]. Methyl *tert*-butyl ether (*t*-BuOMe) was used as a solvent, because the synthesis of hydrotrioxides in it proceeds rapidly and with a high yield [3, 5].

RESULTS AND DISCUSSION

The yield of singlet oxygen was calculated (Table 1) from CL decay rate curves (Fig. 1) measured during the degradation of hydrotrioxides **1a**–**10a**. For these hydrotrioxides, the yield of singlet oxygen decreases with increasing degradation temperature, a change that can be explained by an increase in the contribution of the radical chain reaction route. As temperature increases, the rate of decomposition of a hydrotrioxide into radicals increases, which leads to an increase in its consumption in the radical chain process [5]. The formation of singlet oxygen in that case can result only from combination of peroxide radicals. The yield of singlet oxygen by the combination of peroxide radicals bearing alkyl substituents does not exceed 8% [9]. The contribution of this route in the thermal degradation of hydrotrioxides **la**, **7a**, and **8a** is apparently minimal, and there is an insignificant effect of temperature on the yield of $^1O_2$. In addition, during the thermolysis of hydrotrioxides, singlet oxygen can be present in the solvent cage along with a quencher, the parent alcohol and/or H_2O. Perhaps, quenching in the cage proceeds more efficiently with increasing temperature and leads to a decrease in the yield of singlet oxygen.

The yield of singlet oxygen in the degradation of aliphatic secondary alcohols **9a** and **10a** in *t*-BuOMe is ~30%. The introduction of the highly strained cyclopropyl substituent significantly increases the yield of $^1O_2$, $\Phi = 56\%$ in thermolysis of **11a**.

The degradation of hydrotrioxides of secondary alcohols with the –OOOH group located on the cyclic moiety in **1a**–**8a** leads to the formation of singlet oxygen with a yield of 23–58% (−10°C). Three types of strain are known for cycloalkanes. The highest yield of singlet oxygen is observed for hydrotrioxides **2a**, **5a**, and **8a** characterized mainly by Pitzer strain. The energies of this strain per CH_2– group in the cyclopentane–cyclooctane series are 1.3, 0.0, 0.9, and 1.2, respectively [10]. Indeed, for compounds **2a**, **4a**, and **5a** with five, seven, and eight-membered cycles, respectively, the yield of singlet oxygen increases to 58% relative to that with **3a** and **6a** (23%, −10°C). The degradation of hydrotrioxide **1a** is characterized by a lower $^1O_2$ yield than in the cases of **2a** and **5a**, which is probably due to the presence of Bayer strain in the cyclobutane moiety (a significant change in the C–C–C bond angle).

Bicyclic hydrotrioxides **7a** and **8a** are similar in Pitzer strain and differ in steric strain. In the case of isomer **8a**, the steric strain due to the methyl groups in the 3-position will be lower than for **7a**, in where they are in the 7-position [11]. The yield of singlet oxygen in the thermolysis of **8a** and **7a** is 51 and 25%, respectively.

Thus, the increase in the yield of singlet oxygen can be associated with an increase in Pitzer strain and a decrease in Bayer and steric strains in the cyclic moieties of hydrotrioxides.

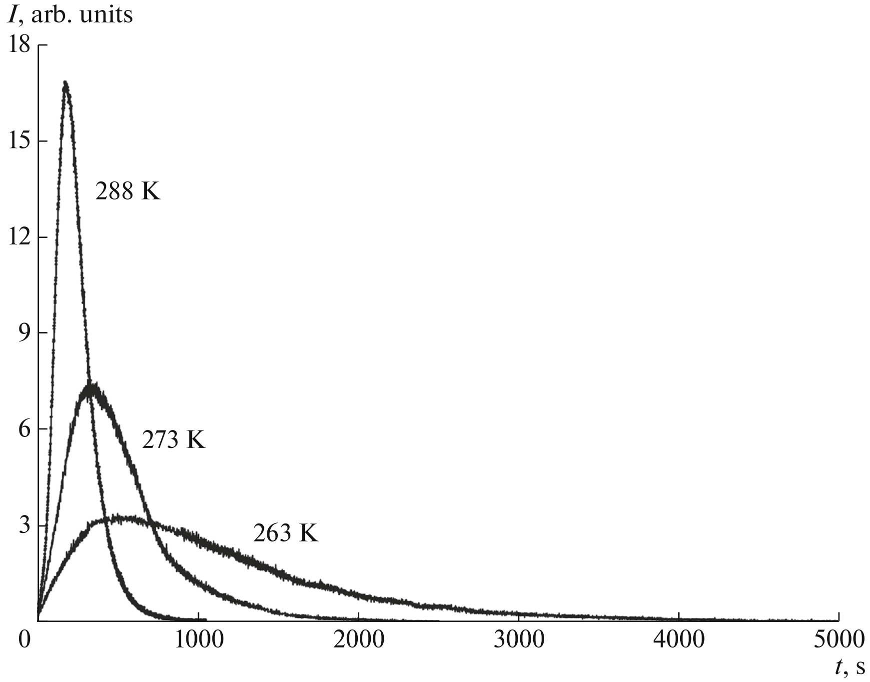


Fig. 1. Decay rate curves of IR chemiluminescence during the degradation of 1-hydroxycyclopentylhydrotrioxide (0.14 mol/L) in *t*-BuOMe at temperatures of 288, 273, and 263 K.

CONCLUSIONS

The yield of singlet oxygen in the degradation of the specified hydrotrioxides of secondary alcohols has been found, using the IR chemiluminescence method, to be significantly higher than that for the compounds studied previously. In the series examined, 1,3,3-trimethyl-2-hydroxybicyclo[2.2.1]heptyl-2-hydrotrioxide, 1-hydroxycyclopentylhydrotrioxide, and 1-cyclopropylethylhydrotioxide are the best sources of singlet oxygen.

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