Hydrogen Trioxide **Hot Paper**

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A Simple and Efficient Preparation of High-Purity Hydrogen Trioxide (HOOOH)

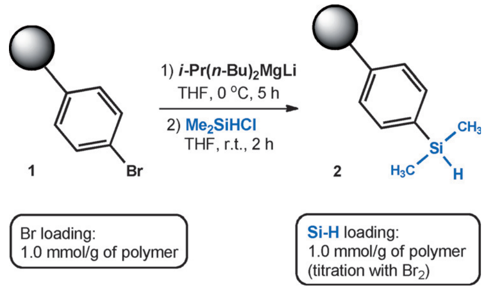
*Gregor Strle and Janez Cerkovnik**

Dedicated to Professor Božo Plesničar on the occasion of his 75th birthday

***Abstract:** A simple and efficient method allows the synthesis of solutions of high-purity hydrogen trioxide (HOOOH), released in the low-temperature methytrioxorhenium(VII) (MTO)-catalyzed transformation of the ozonized polystyrene-supported dimethylphenylsilane. High-purity hydrogen trioxide solutions in diethyl ether, separated from the polymer and free of any reactants and by-products, can be stored at −20°C for weeks. By removing the solvent in vacuo, HOOOH could be isolated in highly pure form or transferred to other solvents, thus significantly extending the research perspectives of HOOOH for novel applications.*

A number of approaches providing relatively highly concentrated solutions of hydrogen trioxide (HOOOH) in various organic solvents have been developed in recent years.[1] Some of the most promising methods are: a) ozone reduction,[2] b) decomposition of hydrotrioxides with retention of the trioxide function,[3] c) reaction of hydrogen peroxide with ozone,[4] d) microwave discharge of an $O_3/O_2/H_2$ gas mixtures at low pressure followed by low-temperature condensation,[5] and d) photoelimination from a metal hydroperoxo-hydroxo complex.[6] However, solutions of HOOOH in various solvents are usually contaminated with a number of by-products, such as oxidation products and HOOH. When first attempting to prepare pure solutions of HOOOH, Wentworth and co-workers ozonized the resin-bound 1,2-diphenylhydrazine in [D$_6$]acetone and [D$_8$]tetrahydrofuran.[4b] The oxidized resin was removed by filtration under argon, and the remaining solutions contained only HOOOH, hydrogen peroxide, and water. Unfortunately, considerable amounts of HOOOH are lost in this way and its concentration is relatively low. More recently, it was discovered that HOOOH is formed nearly quantitatively in the low-temperature methyltrioxorhenium(VII) (MTO)-catalyzed transformation of some silyl hydrotrioxides and 1,3-dioxolanes in various solvents,[7] which represents the first convenient and general method for preparation of HOOOH without the interfering presence of hydrotrioxides (ROOOH) or HOOH. However, the presence of the reaction by-products still remained unsolved.

We describe herein a simple and efficient method for the synthesis of highly pure solutions of HOOOH, released in the low-temperature MTO-catalyzed transformation of the ozonized polystyrene-supported dimethylphenylsilane.[7] In the first step, an efficient metalation of cross-linked 4-bromopolystyrene bead (**1**) was performed by Oshima's trialkylmagnesate complex, $i\mathrm{Pr}(n\mathrm{Bu})_2\mathrm{MgLi}$,[8] to form in situ a Grignard-like polymer,[9] which was then allowed to react with chlorodimethylsilane at room temperature to form nearly quantitatively dimethylphenylsilane-derivatized polystyrene bead (**2**, Scheme 1). This straightforward procedure was employed successfully with different chlorosilanes, as confirmed also by a strong Si−H stretch at 2110 cm^{-1} (ATR-IR analysis; see Figure 1, spectra a) and b)).



Scheme 1. Preparation of dimethylphenylsilane-derivatized polymer bead.

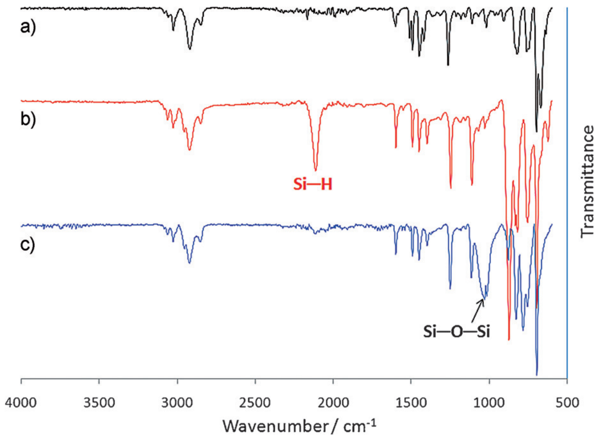


Figure 1. ATR-IR spectra of 4-bromopolystyrene bead (a), dimethylphenylsilane-derivatized polymer bead (b), and polymer bead after ozonization, MTO-catalyzed release of HOOOH and its removal from the solution (c).

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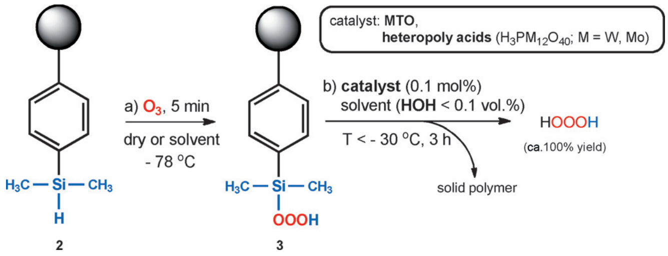


Scheme 2. Ozonation of dimethylphenylsilane-derivatized polystyrene bead **2**, and further efficient catalytic release of hydrogen trioxide from the polymer **3**.

Isolated pure dimethylphenylsilane-derivatized polystyrene bead **2** was further ozonized at −78 °C either as a dry polymer or, more efficiently, as a suspension of polymer in acetone (or any other ozone-resistant solvent as well), to in situ generate silyl hydrotrioxide units (ROOOH, **3**) directly linked to the polymer (Scheme 2, step a). Ozonization was carried out for only 5 min and the solvent was then removed from the polymer suspension containing hydrotrioxide units, in vacuo at −60 °C. It can be assumed that this is the first reported synthesis of a solid polymer with directly attached hydrotrioxide units.

To the isolated solid polymer containing silyl hydrotrioxide units (**3**) any solvent with melting point below −78 °C could be added, without appreciable decomposition of the hydrotrioxide units on the polymer. However, diethyl ether was found to complex the hydrotrioxide units most efficiently, thus increasing their stability. At the same time, diethyl ether was also found to be the most suitable solvent for the efficient catalytic release of HOOOH from the polymer bead (Scheme 2, step b).

HOOOH was released from the polymer **3** into diethyl ether at −30 °C in nearly quantitative yield (based on the amount of derivatized polymer **2**, see also Figure 1, spectrum b and c) when less than 0.1 mol % of MTO was introduced as a catalyst. The solution of HOOOH was filtered from the solid polymer at −78 °C to avoid any decomposition of polyoxide and stored at −20 °C for weeks, typically as 0.05–0.1 M solution. Furthermore, by removing diethyl ether in vacuo, HOOOH could be isolated in highly pure form or transferred in any other solvent. To identify and check the purity, HOOOH was concentrated and dissolved in [D_6]acetone for NMR analysis, which shows a characteristic OOOH ^{1}H NMR absorption at $\delta = 13.53$ ppm (−50 °C) downfield from Me_4Si (Figure 2), and a characteristic IR O−H stretching frequency at 3215 cm^{-1} (−40 °C, Figure 3).

The concentration of HOOOH was determined from a) ^{1}H NMR spectrum by calibration of the residual solvent peak for non-deuterated acetone, and b) the low-temperature oxidation (−40 °C) of triphenylphosphine to triphenylphosphin oxide,[10] monitored by GC-MS analysis.

To demonstrate the versatility of this synthetic methodology, we also tested some other catalysts for HOOOH release from the polymer **3** and found that tungsten and molybdenum heteropoly acids ($H_3PM_{12}O_{40}$; M = W, Mo),[11] used in comparatively small amounts (0.1 mol %), worked almost as well. Furthermore, we also prepared immobilized catalysts on silica and polystyrene as a solid support;[12] however, in this case the release of HOOOH from the polymer **3** was poor.

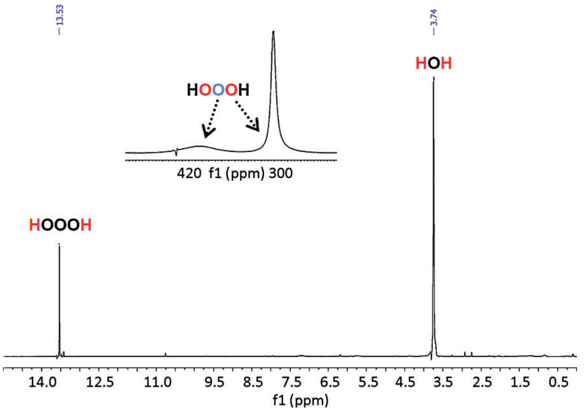


Figure 2. ^{1}H NMR spectrum of highly pure HOOOH in [D_6]acetone at −50 °C released from the ozonized dimethylphenylsilane-derivatized polystyrene **3** (see also the Supporting Information). Inset: ^{17}O NMR spectrum of ^{17}O-enriched HOOOH in [D_6]acetone at −50 °C (for the preparation of ^{17}O-enriched ozone and HOOOH see Ref. [2c] and Ref. [2f]).

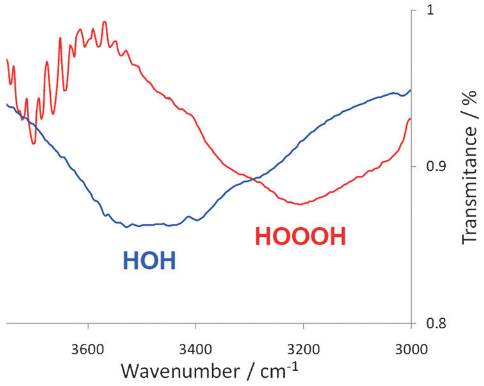
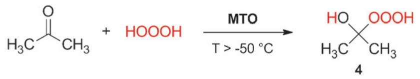


Figure 3. Sections of the low-temperature ATR-IR spectra of HOOOH and HOH (for comparison) in acetone at −40 °C. See also the Supporting Information.

A further experimental observation is noteworthy. Namely, when HOOOH was catalytically released from polymer **3** and dissolved in acetone as a solvent, a relatively fast MTO-catalyzed addition of HOOOH to acetone to form hydroxy-hydrotrioxide, $Me_2C(OH)(OOOH)$, (**4**, Scheme 3) was observed at temperatures above −50 °C, as characterized by the OOOH ^{1}H NMR absorption at $\delta = 13.34$ ppm (−50 °C) (Figure 4).[2c] Although the formation of the hydroxy-hydroperoxide, $Me_2C(OH)(OOH)$, from acetone and HOOH is well established in the peroxide chemistry,[13] our MTO-catalyzed addition of HOOOH to acetone is the first example



Scheme 3. MTO-assisted addition of HOOOH to acetone.

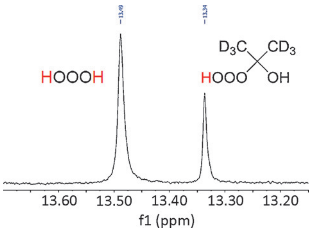


Figure 4. A section of characteristic ^{1}H NMR spectrum after HOOOH addition to [D$_6$]acetone (−50 °C).

of a polyoxide reacting with a carbonyl compound to form a hydroxy-hydrotrioxide intermediate.[2c]

In summary, we have used low-temperature ozonation of dimethylphenylsilane-derivatized polystyrene bead to prepare a solid polymer (**3**) with directly attached hydrotrioxide units. Furthermore, we have successfully released HOOOH from polymer **3** into diethyl ether at −30 °C in a MTO-catalyzed reaction in nearly quantitative yields. HOOOH solutions in diethyl ether could be stored for weeks even at temperatures as high as −20 °C. By evaporating the solvent, HOOOH can be isolated in highly pure form, or it can be dissolved in some other appropriate solvent, thus significantly extending the possibilities of some novel HOOOH applications. The MTO-catalyzed addition of HOOOH to acetone to form the hydroxy-hydrotrioxy intermediate is just one example. The reactions of various organic compounds with highly pure HOOOH as an oxidant are currently under investigation.

Experimental Section

Instrumentation: Low-temperature ^{1}H and ^{17}O NMR spectra were recorded on a Bruker Avance 300 DPX (^{1}H NMR, 300.13 MHz; ^{17}O NMR, 40.70 MHz) and on Varian Unity Inova-600 spectrometers (^{1}H NMR, 600.09 MHz; ^{17}O NMR, 81.37 MHz) with Me$_4$Si and [D$_6$]acetone (^{1}H NMR), and $H_2{}^{17}O$ (^{17}O NMR) as internal standards. ATR-IR spectra were recorded on a Bruker Alpha Platinum and Applied Systems ReactIR 1000 spectrometers. GC-MS analyses were performed on a Hewlett Packard 6890 instrument (HP-5 MS column).

Dimethylphenylsilane-derivatized polymer **2** was prepared by following the procedure of Thomas and co-workers,[9] preparing Oshima's complex (*i*Pr(*n*Bu)$_2$MgLi, 2 equiv) in anhydrous THF (60 mL) at 0 °C under an argon atmosphere. The solution of *i*Pr(*n*Bu)$_2$MgLi was stirred for 30 min to obtain a clear yellow solution. 4-bromopolystyrene cross-linked with 2 % divinylbenzene (**1**, 1 equiv, 1.0 mmol Br loading/g of polymer, ABCR Chemicals) was swollen in anhydrous THF (30 mL per gram of bead) for 15 min at 0 °C under an argon atmosphere and then the preformed *i*Pr-(*n*Bu)$_2$MgLi was added and the resultant mixture slowly stirred for 5 h keeping the temperature at 0 °C. Then chlorodimethylsilane (6 equiv ABCR Chemicals, 98 %) was added and the mixture was agitated and allowed to warm to room temperature over 2 h. Afterwards the derivatized polymer **2** was collected by filtration and washed with stirring in DMF (at 50 °C, 30 min), water and acetone, and dried under reduced pressure. Prepared polymer **2** contains roughly 1 mmol of Si-H units/g of polymer, as determined by titration with standardized bromine solution.[14]

Preparation of HOOOH: In a typical experiment, 100 mg of dimethylphenylsilane-derivatized polystyrene **2** containing 1 mmol of Si-H units/g of polymer was mixed with 2 mL of acetone as solvent, ozonized at −78 °C for 5 min and purged with argon to remove residual ozone afterwards. Acetone was removed from the polymer suspension with vacuum pump at −60 °C and replaced with diethyl ether (2 mL) containing up to 0.1 vol. % of water (always present in the reaction mixture under an experimental condition; for ^{1}H NMR spectra with added H_2O and D_2O see the Supporting Information) and 0.03 mg (0.1 μmol) of MTO as a catalyst. Suspension was stirred at −30 °C for 3 h to release hydrogen trioxide from the ozonized dimethylphenylsilane-derivatized polymer bead **3** and filtered (at −60 °C) to remove HOOOH solution (0.05 M) from the polymer and stored in refrigerator at −20 °C for weeks. The yield of released HOOOH was 95–100 %, based on the amount of starting polymer **2**, and calculated from ^{1}H NMR spectrum of the calibrated residual solvent peak for non-deuterated acetone and added 4-nitroacetophenone as an internal standard. Alternatively, the yield of HOOOH was determined from the low-temperature oxidation (−40 °C) of standardized triphenylphosphine solution in diethyl ether, and produced triphenyphosphin oxide calculated from GC-MS analyzes.[10] For NMR experiments the solvent was removed in vacuo (−50 °C) and replaced with [D$_6$]acetone (1 mL), and transferred to the NMR tube (for a typical NMR spectrum see Figure 2). For other experimental work, the HOOOH solution was concentrated in vacuo (−50 °C) to obtain a white glassy material, sufficiently stable at that temperature to be dissolved in any other solvent.

WARNING: Although we have not had any accidents in handling highly pure HOOOH, care should be exercised in handling of either solid or concentrated solutions of this potentially hazardous compound.

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