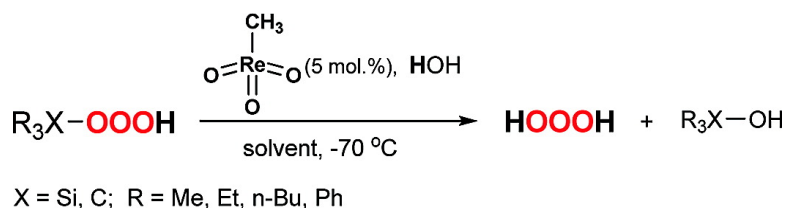## Communication

An Efficient Methyltrioxorhenium(VII)-Catalyzed Transformation of Hydrotrioxides (ROOOH) into Dihydrogen Trioxide (HOOOH)

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An Efficient Methyltrioxorhenium(VII)-Catalyzed Transformation of Hydrotrioxides (ROOOH) into Dihydrogen Trioxide (HOOOH)

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Hydrotrioxides, ROOOH, have already been found to be key intermediates in the reaction of ozone with alcohols, ethers, acetals, hydrocarbons, and organometallic hydrides.[1]

Corey et al. have presented evidence that triethylsilyl hydrotrioxide, Et$_3$SiOOOH, generated by the low-temperature ozonation of triethylsilane, is an excellent source of singlet oxygen (O$_2$($^1\Delta_g$)).[2,3] In an extension of this work, we found that, under certain conditions, HOOOH is also formed (albeit in only relatively modest yields) in the decomposition of some silyl hydrotrioxides in organic oxygen bases as solvents.[1b] All the hydrotrioxides and HOOOH have been well characterized by NMR (^{1}H, ^{29}Si, ^{17}O)[1] and IR[4] spectroscopy. Recently, the structure of HOOOH has finally also been determined by microwave spectroscopy.[5]

We report here that, surprisingly, HOOOH is formed nearly quantitatively in the low-temperature methyltrioxorhenium(VII)[6] (**MTO**)-catalyzed transformation of dimethylphenylsilyl hydrotrioxide in various solvents (acetone-d_6, methyl acetate, *tert*-butyl methyl ether), as confirmed by ^{1}H, and ^{17}O NMR spectroscopy. We found that other silyl hydrotrioxides, as well as some acetal hydrotrioxides investigated so far, react similarly (see Scheme 1, Table 1, and Figures S1−S3 in the Supporting Information (SI)). This type of transformation appears to represent a convenient and general method for the preparation of HOOOH, without the interfering presence of hydrotrioxides (ROOOH) or HOOH.[1,7]

We found that water (always present in the reaction mixture) is consumed as a reaction proceeds and that the reduced amount of HOH notably diminishes the rate of the transformation. In addition, we also observed that the corresponding silanol (alcohol), formed as the byproduct in the **MTO**-catalyzed transformation of ROOOH, could also participate in this reaction (although at a somewhat lower rate), if HOH is not available.

Therefore, we investigated the role of water in these reactions and found that the kinetic solvent isotope effect was negligible, that is, $k_{H2O}/k_{D2O} = 1.1 \pm 0.1$ (Table S1 in SI). All these observations indicate that water is a crucial reaction component, but is not involved in the rate-determining step of this transformation. The reaction rates for the **MTO**-catalyzed transformation of hydrotrioxides into HOOOH are considerably faster than those for the decomposition of hydrotrioxides into the corresponding silanol (alcohol) and singlet oxygen, O$_2$($^1\Delta_g$) (Table S2 in SI). The activation parameters for the catalyzed transformation of hydrotrioxides ($E_a = 9.5 \pm 2.0$ kcal/mol, log $A = 6.5 \pm 1.5$; acetone-d_6, methyl acetate) are slightly lower than those for the uncatalyzed decomposition[1b] (Table S3 in SI).

To shed some light on the mechanism of these transformations, we have undertaken DFT studies on the **MTO**-catalyzed transfor-

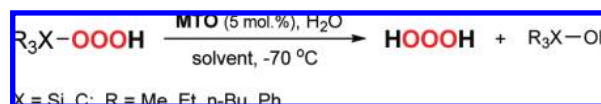**Scheme 1.** **MTO**-Catalyzed Transformation of Various Hydrotrioxides into Dihydrogen Trioxide

Table 1. **MTO**-Catalyzed Transformation of Hydrotrioxides (ROOOH) into Dihydrogen Trioxide (HOOOH) at −70 °C in Acetone-d_6[a]

entry	hydrotrioxide (**ROOOH**)	HOOOH (%)[b]
1	Me, Ph–Si–OOOH, Me	98 (24)[c]
2	Et, Et–Si–OOOH, Et	85 (45)
3	n-Bu, n-Bu–Si–OOOH, n-Bu	70 (2)
4	Ph, Ph–Si–OOOH, Ph	65 (2)
5	Me (Ph) (tetrahydrofuranyl)–OOOH	99 (25)

[a] Concentration of ROOOH: (0.1 ± 0.05) M. Molar ratio ROOOH/**MTO**/H$_2$O = 1.0:0.05:1.0. [b] Yields determined by integration of OOOH absorption of ROOOH and HOOOH in ^{1}H NMR spectra. Standard deviation ≤10%. [c] Values in parenthesis are yields of transformations without added catalyst, **MTO**.

mation of the simplest of silyl hydrotrioxides, that is, H$_3$SiOOOH into HOOOH in the presence of water. Possible starting points for the reaction were investigated using the B3LYP[8] hybrid functional in conjunction with the 6-311++G(d,p) basis set,[9a,b] on all nonmetal atoms, and the SDD quasi-relativistic pseudopotential and associated basis set for Re.[9c] All calculations were run using the Gaussian 03 program.[10]

The simplified H$_3$SiOOOH system was selected to efficiently explore the various mechanistic pathways. However, we have additionally calculated the rate-determining step of the favored mechanism (vida infra) using the dimethylphenylsilyl hydrotrioxide substrate (entry 1, Table 1), and observed only a minor influence on the energetics of the reaction (see SI for details). Therefore, we believe the mechanism outlined in Figure 1 is qualitatively correct for all the substrates tested thus far. A complete computational investigation of all substrates presented in Table 1 will be published subsequently.

The catalytic cycle begins with a concerted reaction between the silyl hydrotrioxide and **MTO**, whereby the Si-OOOH bond is exchanged for a Si−ORe bond and a new Re−OOOH bond is formed.[11] Relative to the separated reactants, the barrier to this
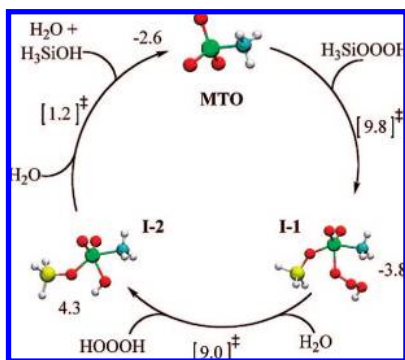
Figure 1. **MTO**-catalyzed mechanism for the production of HOOOH from $H_3SiOOOH$. Values are relative enthalpies (ΔH(298 K)) and are given with respect to the preceding intermediate.

reaction is 9.8 kcal/mol ($\Delta H^{\ddagger}$(298 K)), which is consistent with the experimentally observed value of $E_a = 9.5 \pm 2.0$ kcal/mol. The reaction is exothermic by 3.8 kcal/mol and results in the first intermediate (**I-1**, Figure 1).[12] A reactant complex, which is 6.2 kcal/mol lower in enthalpy relative to the separated reactants can be formed. However, the complex is not directly connected to the TS (i.e., an initial rotation of the reactants from their complex geometry is required to form the TS), and as such we consider the separated reactants as the most meaningful reference state. For further details on the energetics and structures of all calculated reactants, products, and transition states see the SI.

With the addition of water, **I-1** is able to undergo σ-bond metathesis. The water molecule donates a proton to the hydrotrioxide ligand, which breaks the Re−OOOH bond and generates the observed HOOOH. Concomitantly, a new Re−OH bond is formed, resulting in the second intermediate (**I-2**, Figure 1). The barrier to this reaction is 9.0 kcal/mol, relative to the separated reactants. The reaction is thermoneutral ($\Delta H = 0.7$ kcal/mol), with respect to the resulting product complex from this reaction (see SI). However, the dissociation of HOOOH results in an enthalpic penalty of 4.3 kcal/mol.

The final step in the cycle involves the formation of a reactant complex with a second water molecule, which partially offsets the enthalpy loss from the dissociation of HOOOH. The water molecule forms a H-bond with the hydroxide ligand, to generate this complex, which is 4.0 kcal/mol lower in enthalpy than the separated reactants (i.e., **I-2** + HOH).

The second water molecule is catalytic, it substantially lowers the barrier to the hydrogen transfer and is not consumed in the reaction. The barrier is decreased from 18.8 kcal/mol (intramolecular proton transfer in **I-2**) to 1.2 kcal/mol, relative to the separated reactants. The resulting silanol (H_3SiOH) and **MTO** are formed in an exothermic reaction ($\Delta H = -2.6$ kcal/mol).

The rate-limiting step in the catalytic cycle is the initial addition of the silyl hydrotrioxide to the catalyst, which is consistent with the negligible kinetic solvent isotope effect. Furthermore, we have additionally explored a potential role for water in assisting the initial Si−ORe bond-forming step, however this led to an increased barrier, relative to the mechanism presented in Figure 1. Thus, water is unable to play any role in the rate-limiting step of the reaction.

In summary, HOOOH is formed nearly quantitatively in the low-temperature **MTO**-catalyzed transformation of silyl and acetal hydrotrioxides.[13] Further improvements of the method, that is, the use of both the polymer-bound **MTO**[14] and the polymer-bound

silane,[7b] which will hopefully allow the preparation of concentrated solutions of pure HOOOH, are currently under investigation. The suitability of some other catalyst for this purpose is also being explored.

Supporting Information Available: Complete ref 10; additional experimental and computational details, NMR spectra, figure and tables of kinetic data, the structures, Cartesian coordinates and energetic data of all species indicated in the text are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) We have investigated the possibility of an initial interaction between **MTO** and HOH, resulting in two hydroxide ligands, in a mechanism analogous to that outlined in ref 6d (Figure 2) for the HOOH substrate. However, the barrier to forming this complex is 19.5 kcal/mol (23.6 kcal/mol for HOOH) and is not competitive with the reaction between **MTO** and the silyl hydrotrioxide.
(12) A splitting of the CH_3 absorption of **MTO**, observed in the ^1H and ^{13}C NMR spectra of some of the substrates studied (see for example, Figure S4 in Supporting Information), might be tentatively assigned to the intermediates of the type **I-1**.
(13) A possible side reaction, i.e., the catalyst-assisted formation of HOOOH from singlet oxygen ($O_2(^1\Delta_g)$) and water, as recently suggested for the antibody-catalyzed formation of HOOOH,[7a] cannot be completely ruled out. However, our present preliminary evidence, that is, the absence of the ^{17}O-enrichment of HOOOH (by ^{17}O NMR), when ^{17}O enriched (50%) H_2O was added to the reaction mixture before the reaction, does not support this presumption (see Figure S2 in SI).
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