UV–vis spectrophotometer, both thermostated and equipped with computerized data acqusition and analysis. All pH measurements were performed with an Orion Research 611 digital pH meter calibrated for 50% Me$_2$SO–50% water (v/v) with buffers described by Hallē et al.[32]

The kinetics of the conversion of 7-CH to 4-OCH$_2$CH$_2$SH in acidic solution (Scheme III) was followed by HPLC by using a reverse-phase ODS Hypersil (4.6 × 100 mm) column and a Hewlett-Packard 1090M LC instrument. This instrument is equipped with a diode array detector which allows recording of the spectra of each eluting species. The peak area corresponding to 7-CH was measured as a function of time at 230 nm; the retention time of this peak was 5.4 min at 40 °C, 1.5 mL/min in 50% acetonitrile–50% water. A plot of ln (peak area) vs time was linear over at least 2.5 half-lives and its slope was equated with k_{obsd}[11].

All other HPLC experiments were performed under the same conditions.

Supplementary Material Available: Tables S1–S6 containing pseudo-first-order rate constants (k_{obsd}) for the hydrolysis of Ph(LG)=CPh(NO$_2$) and the reaction of 7⁻ and 4-(OMe,OMe)⁻ with acid (9 pages). Ordering information is given on any current masthead page.

Chemistry of Hydrotrioxides.[1] Preparation, Characterization, and Reactivity of Dimethylphenylsilyl Hydrotrioxides. Hydrogen Trioxide (HOOOH), a Reactive Intermediate in Their Thermal Decomposition?

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Abstract: The preparation and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic characterization of dimethylphenylsilyl hydrotrioxides (**2**), produced by the low temperature (−78 °C) ozonation of dimethylphenylsilanes (**1**) in acetone-d_6, methyl acetate, and dimethyl ether, is reported. ^{1}H NMR spectroscopic evidence for the involvement of a transient polyoxide, tentatively assigned to hydrogen trioxide (HOOOH), in the decomposition of **2** is given. All attempts to characterize both types of hydrotrioxides by ^{17}O NMR spectroscopy failed. The calculated relatively strong binding energy for the intermolecularly hydrogen-bonded cyclic dimer of HOOOH (BE = 7.7 kcal/mol, 6-31G**//6-31G) support the belief that self-association is, similarly to previously studied hydrotrioxides, H$_3$SiOOOH and CH$_3$OOOH, the characteristic structural feature of this species. Kinetic and activation parameters for the decomposition of **2**, i.e., large negative activation entropies, a rather significant substituent effect on the decomposition of **2a** in methyl acetate (Hammett ρ value 1.2 ± 0.1) as well as the observed dependence of the rate of the decomposition of **2a** on solvent polarity, indicate the importance of polar decomposition pathways. The results of ESR spin trapping experiments are, together with product studies, discussed in terms of possible contributions of homolytic processes to the overall mechanism of the decomposition of **2**. The negative Hammett ρ values for the oxidation of phenyl methyl sulfides to sulfoxides and the latter to the corresponding sulfones with **2** as well as the reactivity order 4-XPhSMe ≫ 4-XPhSOMe indicate an electrophilic nature of the oxidant.

Introduction

Considerable interest has been devoted in recent years to the studies of ozonation of various saturated organic substrates.[2] Although the involvement of hydrotrioxides, ROOOH, in the reaction of ozone with C–H bonds has already been documented,[3,4] there have been no reports in the literature on the spectroscopic characterization of silyl hydrotrioxides.[5] However, these polyoxides have already been proposed as transient intermediates in the reaction of ozone with various silanes.[6] Very recently, triethylsilyl hydrotrioxide has been shown to be an excellent source of ^{1}O$_2$[7] as well as an efficient reagent for direct conversion of electron-rich olefins to 1,2-dioxetanes and for the conversion of unactivated olefins to oxidatively fragmented carbonyl products.[8] As a part of our continuous interest in polyoxides, we wish to report the preparation, characterization, and thermal decomposition of dimethylphenylsilyl hydrotrioxides. Evidence for the involvement of still another polyoxide species, tentatively assigned to hydrogen trioxide (HOOOH), in the decomposition of these hydrotrioxides is given. Ab initio calculations have been carried out to predict the equilibrium structures of monomeric and cyclic dimeric HOOOH. The importance of polar decomposition pathways in the decomposition of these polyoxides is stressed. Attempts have

Table I. Selected ^{1}H, ^{13}C, and ^{29}Si NMR Chemical Shifts (δ) of Dimethylphenylsilyl Hydrotrioxide and Some Other Organosilicon Analogues in Acetone-d_6 at −78 °C[a]

| X | ^{1}H NMR | | ^{13}C NMR | | ^{29}Si NMR |
	δCH$_3$	δSi–X	δCH$_3$	δC(1)	δSi
H	0.30	4.40	−1.1	140.6	−16.95
OH	0.32	4.5–5.5	3.1	143.5	3.30
OOH	0.43	11.2	2.8	139.6	14.31
OOOH	0.55	13.96[c,d]	2.7	138.5	17.31
		13.76 (−50 °C)			
OSi(CH$_3$)$_2$Ph	0.33		3.9	143.1	−0.96
OOSi(CH$_3$)$_2$Ph	0.40		2.8	139.5	16.6

[a] Values in parts per million downfield from the internal standard Me$_4$Si. [b] Area ratio of peaks δSi–X:δCH$_3$ (X = H, OH, OOH, OOOH) was in all cases 1:6. [c] δOOOH, methyl acetate, 13.62; ethyl acetate, 13.64; dimethyl ether, 13.40. [d] δOOOH, 4-CH$_3$PhSi-(CH$_3$)$_2$O$_3$H, 13.78; 4-CH$_3$OPhSi(CH$_3$)$_2$O$_3$H, 13.78; 4-ClPhSi-(CH$_3$)$_2$O$_3$H, 13.70.

also been made to elucidate possible contributions of homolytic processes to the overall decomposition mechanism of **2**. We also

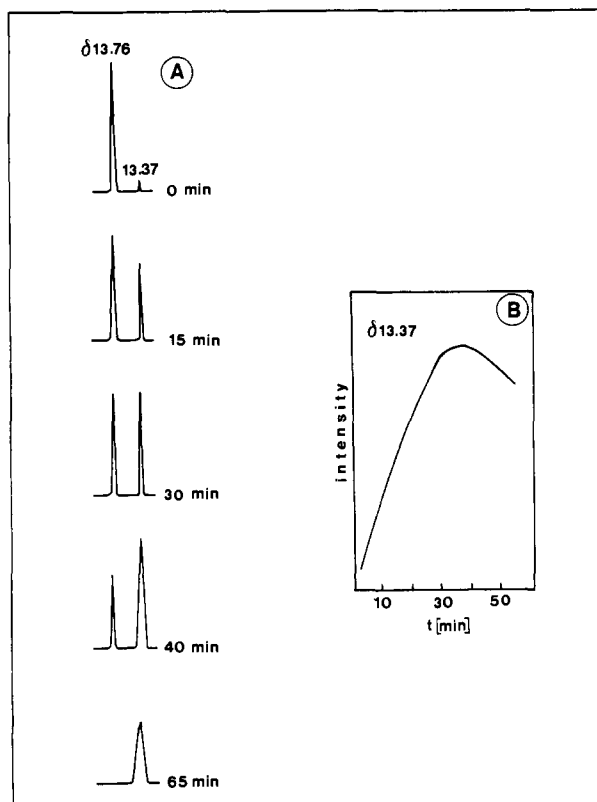[†] University of Ljubljana.
[‡] "Boris Kidrič" Institute.

Figure 1. Segments of ^{1}H NMR spectra of dimethylphenylsilyl hydrotrioxide, **2a** (0.5 M): (A) The disappearance of the OOOH absorption at δ 13.76 ppm as a function of time. After 65 min, the CH$_3$ and ^{29}Si NMR absorptions of **2a** completely disappeared. (B) A change in the intensity (in relative arbitrary units) of a signal at δ 13.37 ppm as a function of time in acetone-d_6 at −60 °C.

present evidence that the silyl hydrotrioxides under investigation oxidize sulfides to sulfoxides and the latter to sulfones as electrophilic oxidants.

Results and Discussion

NMR Spectra. Ozonation of **1** (0.6 ± 0.2 M) with ozone-oxygen or ozone-nitrogen mixtures in acetone-d_6, methyl acetate,

(1) For the previous paper in this series, see: (a) Koller, J.; Hodošček, M.; Plesničar, B. *J. Am. Chem. Soc.* **1990**, *112*, 2124. (b) Preliminary accounts for a part of the present work were presented at the International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidations, Tsukuba, Japan, July 1987 (Abstract M-27) and at the 9th IUPAC Conference on Physical Organic Chemistry, Regensburg, West Germany, August 1988 (Abstract C-29).

(2) For reviews, see: (a) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, 1982; Vol. II. (b) Keinan, E.; Varkony, H. T. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 19.

(3) For a review, see: Plesničar, B. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 16.

(4) (a) Murray, R. W.; Lumma, W. C., Jr.; Lin, W.-P. *J. Am. Chem. Soc.* **1970**, *92*, 3205; **1976**, *98*, 1880. (b) Kovač, F.; Plesničar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677. (c) Shafikov, N. Ya.; Sadykov, R. A.; Shereshovets, V. V.; Panasenko, A. A.; Komissarov, V. D. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1923. (d) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614. (e) Pryor, W. A.; Prier, D. G.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883. (e) Zarth, M.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2429. (f) Kuramshin, E. M.; Kulak, L. G.; Zlotskii, S. S.; Rakhmankulov, D. L. *Zh. Org. Khim.* **1986**, *22*, 1986. (g) Plesničar, B.; Kovač, F.; Schara, M. *J. Am. Chem. Soc.* **1988**, *110*, 214.
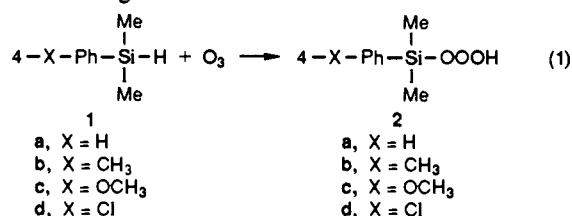
(5) When the preliminary results of this study were already reported,[1b] we became aware of a report on the ^{1}H NMR characterization of tri-*n*-butylsilyl hydrotrioxide (δOOOH = 14 ppm, neat in the parent silane at −78 °C). Tarunin, B. I.; Tarunina, V. N.; Kurskii, Yu, A. *Zh. Obshch. Khim.* **1988**, *58*, 1060.

(6) (a) Spialter, L.; Pazdernik, L.; Bernstein, S.; Swansiger, W. A.; Buell, G. R.; Freeburger, M. E. *Adv. Chem. Ser.* **1972**, *112*, 65. (b) Oulette, R. J.; Marks, D. L. *J. Organomet. Chem.* **1968**, *11*, 407.

(7) Corey, E. J.; Mehrotra, M. M.; Khan, A. U. *J. Am. Chem. Soc.* **1986**, *108*, 2472.

(8) (a) Posner, G. H.; Wetzberg, M.; Nelson, W. M.; Murr, B. L.; Seliger, H. H. *J. Am. Chem. Soc.* **1987**, *109*, 278. (b) Posner, G. H.; Webb, K. S.; Nelson, W. M.; Kishimoto, T.; Seliger, H. H. *J. Org. Chem.* **1989**, *54*, 3252.

or dimethyl ether at −78 °C produced the corresponding hydrotrioxide, characterized by the OOOH ^{1}H NMR absorption at δ 13.4 ± 0.5 ppm downfield from Me$_4$Si, in yields of 80–90%. The ^{1}H, ^{13}C, and ^{29}Si NMR data of **2** are together with those of some other silicon analogues collected in Table I.

$$4-X-Ph-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-H + O_3 \longrightarrow 4-X-Ph-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OOOH \quad (1)$$

1	**2**
a, X = H	a, X = H
b, X = CH$_3$	b, X = CH$_3$
c, X = OCH$_3$	c, X = OCH$_3$
d, X = Cl	d, X = Cl

As already reported, the absorption at δ 13.6 ± 0.5 ppm is typical of an ROOOH species.[3,4] Although it was possible to investigate the concentration dependence of the OOOH absorption of **2** only in a relatively narrow concentration range (0.1–0.7 M), it was nevertheless evident that its position did not change much with dilution (<0.10 ppm). It is interesting to note that at low concentrations of **2a** in acetone-d_6 and methyl acetate (<0.2 M), the OOOH absorptions shifted downfield. The temperature variation studies revealed a small but definitive upfield shift of this absorption with increasing temperature (δ OOOH = 0.4–0.5 ppm, from −80 to −40 °C). Recent ab initio calculations on the cyclic dimeric form of H$_3$SiOOOH and CH$_3$OOOH indicate strong intermolecular hydrogen bonds in these entities (7–8 kcal/mol).[1a] We, therefore believe that, in analogy with hydroperoxides and hydrotrioxides of benzylic ethers and alcohols studied previously,[4g] **2** exists in solutions of oxygen bases investigated in the self-associated cyclic dimeric and/or polymeric form which is in equilibrium with the opened hydrotrioxide–oxygen base adduct. It is quite possible that the cyclic dimeric form is additionally solvated with the oxygen base, B. Such highly ordered entities would be particularly marked at very low temperatures.

$$R_3SiOOOH \cdot \cdot \textcircled{B} \quad (2)$$
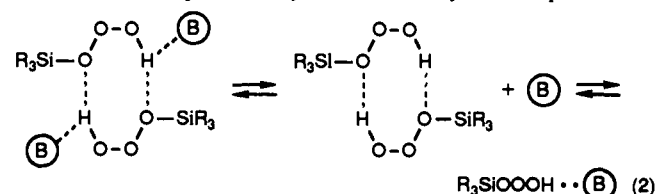
In solvents of low basicity the dimeric (or polymeric) form is most probably the predominant one, while stronger bases, for example *N,N*-dimethylacetamide (DMAA), disrupt the intermolecular hydrogen bonds in the dimers thus shifting the equilibrium of the above equation to the right. Namely, a considerable downfield shift of the OOOH absorption was observed when DMAA was added to solutions of **2** in acetone and methyl acetate, respectively.

The interchange between all the forms of **2** must be very fast since we were not able to observe any appreciable exchange broadening of the OOOH absorption even at the lowest temperatures investigated (−100 °C, dimethyl ether). It should, however, be pointed out that the observed OOOH chemical shift reflects both the "complexation effect" and the "donor-anisotropy effect" of the carbonyl oxygen bases (methyl acetate and acetone).

A significant deshielding of the δ ^{29}Si chemical shift, when going from dimethylphenylsilyl hydroperoxide to the corresponding hydrotrioxide **2a**, additionally supports the structural assignment. We were, unfortunately, unsuccessful in obtaining ^{17}O NMR spectra of either the hydrotrioxide **2a** or the corresponding hydroperoxide derivative at any concentration (<0.8 M) or temperature examined (−80 to −40 °C). Apparently, such identification will require preparation of highly ^{17}O-enriched hydrotrioxides (prohibitively expensive for our purposes).

Products from the Decomposition of the Hydrotrioxides. Hydrotrioxides **2** decomposed in the temperature range −70 to −40 °C to produce among other product singlet oxygen (^{1}O$_2$).

A detailed study of the decomposition products of **2a** in acetone-d_6 (0.5 ± 0.2 M) by GC/MS method revealed dimethylphenylsilanol (90 ± 3%, yield/mol of **2**) and dimethylphenyl-

Table II. Kinetic and Activation Parameters for the Decomposition of Dimethylphenylsilyl Hydrotrioxide, **2a** (0.4–0.7 M) and Temperature Dependence of the OOOH Absorption

solvent	temp, °C	δOOOH, ppm	$10^4 k_1,^a$ s^{-1}	E_a, kcal/mol	log A	$(\Delta S^\ddagger)$, eu
$(CD_3)_2CO$	−80	(13.96)	0.55	4.7	1.0	(−58)
	−75	(13.93)	0.60			
	−70	(13.85)	0.70			
	−65	(13.79)	1.20			
	−60	(13.76)	1.31	9.5	5.5	(−35)
	−50	(13.69)	1.91			
	−45	(13.60)	2.52			
	−40	(13.56)	3.70			
	−30	(13.48)	10.7^b			
	−20		17.1			
CH_3CO_2C- H_3	−70	(13.60)	0.43	10.0	5.9	(−33)
	−60	(13.41)	0.46			
			$(3 \pm 1)^c$			
	−50	(13.32)	1.1			
	−40	(13.24)	2.7			
	−30	(13.10)	8.4			
	−20		17.0			
$(CH_3)_2O$	−60	(13.25)	0.20	12.6	8.2	(−23)
	−50	(13.20)	0.80			
	−40	(13.13)	1.45			
	−30	(13.09)	7.30			

^{a}Unless stated otherwise, standard deviations are ±8%. ^{b}For comparison, the kinetic and activation parameters for the decomposition of cumyl hydrotrioxide (0.4 M in acetone-d_6) are k_1(−33 °C) = 0.70 × 10^{-4} s^{-1}, E_a = 16.0 kcal/mol, log A = 10.4. In the presence of 2,6-di-*tert*-butyl-4-methylphenol, the decomposition of the hydrotrioxide is retarded and the activation parameters become E_a = 23.9 kcal/mol and log A = 16.4, in agreement with thermochemical predictions for the homolytic scission of the RO–OOH bond (ref 1d). ^{c}In the presence of CH_3OH (molar ratio, **2a**/CH_3OH = 1:4).

disiloxane (8 ± 2%). Dimethylphenylsilyl hydroperoxide (5 ± 2%) was detected by ^{1}H and ^{29}Si NMR spectroscopy in the decomposition mixture below −45 °C. This hydroperoxide, which was otherwise reasonably stable at room temperature when prepared by an independent route, decomposed quite rapidly in the decomposition mixture at temperatures above −45 °C. Hydrogen peroxide (9 ± 2% yield by iodometry; TLC identification[4b]) was also detected in the decomposition mixture after warmup procedure. Singlet oxygen, $^1O_2$, was determined by typical singlet oxygen acceptors, i.e., 1,3-diphenylisobenzofuran (yield, 65 ± 5%) and tetraphenylcyclopentadienone (25 ± 5%).[4g]

It was obvious from ^{1}H NMR spectra that besides the decomposition products already mentioned, still another transient intermediate was formed during the decomposition of **2a** in acetone-d_6. Namely, the disappearance of OOOH and CH_3 absorptions was accompanied by a simultaneous appearance of another low field absorption at δ 13.2 ± 0.1 ppm (Figure 1). It is interesting to mention that somewhat lower concentrations of this intermediate were detected in the decomposition of **2a** in methyl acetate and dimethyl ether. However, when CH_3OH was added to solutions of **2a** in methyl acetate, significantly higher yields of this unstable intermediate were formed. A downfield shift of the OOOH absorption was observed in this case. At the same time, dimethylphenylmethoxysilane was detected in the decomposition mixture. When **1a** was ozonized in CH_3OH as solvent, yields of dimethylphenylmethoxysilane up to 60% (per mol of **2a**) were detected. A relatively fast decomposition of **2a** in this solvent was observed.

Since the OOOH absorptions evidently belonged to a species with exchangeable protons (relatively fast exchange of the hydrogen atom with deuterium after treating solutions of **2a**, after partial decomposition, with CH_3OD at −50 °C), it was, in the absence of any other resonance that could be attributed to an organic intermediate, tentatively assigned to hydrogen trioxide (HOOOH). It is interesting to mention that this absorption began to disappear appreciably at around −50 °C, i.e., approximately the same temperature as that reported by Giguere et al.[9] for the decomposition of HOOOH. Namely, these authors studied IR
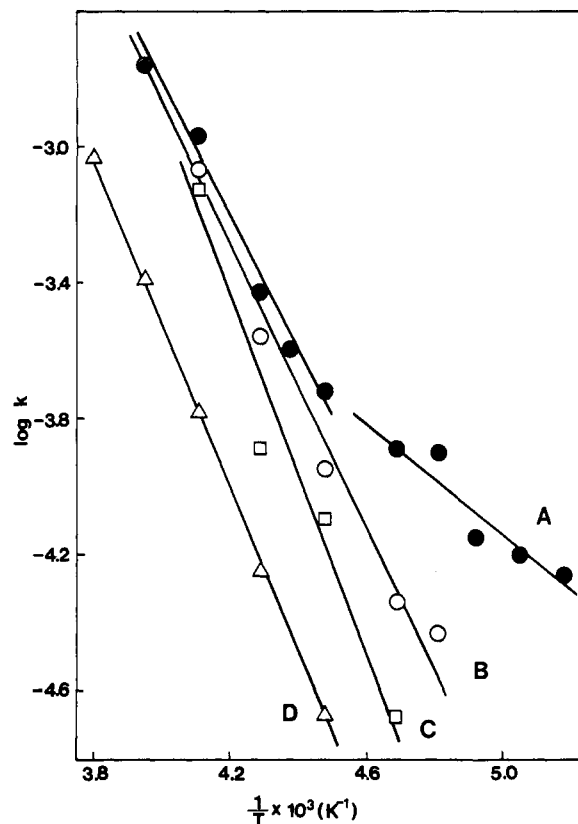

Figure 2. The Arrhenius plot of log k vs $1/T$ for the decomposition of dimethylphenylsilyl hydrotrioxide, **2a**, in (A) acetone-d_6 (●), (B) methyl acetate (○), and (C) dimethyl ether (□). (D) The Arrhenius plot for the disappearance of the upfield OOOH absorption, tentatively assigned to HOOOH in acetone-d_6 (△).

spectra of the products obtained after the condensation of the effluent of deuterated water/hydrogen peroxide mixture having been subjected to electric discharge. An absorption at 760 cm^{-1}, assigned to DOOOD, disappeared with a half-life of approximately 5 h, corresponding to an apparent first-order rate constant of about 3.8 × 10^{-5} s^{-1} at −65 °C). However, the maximum concentration of this species in the matrix material was only around 5%.[10]

Assuming that the hydrotrioxide species is HOOOH, the maximum yield of this polyoxide was estimated to be 15 ± 5%. Again, all attempts to obtain ^{17}O NMR spectra of this species failed.[11]

The observation of the appearance of the upfield OOOH absorption was also made by studying the decomposition of trimethylsilyl hydrotrioxide (($CH_3)_3SiOOOH$), obtained by the low-temperature ozonation of trimethylsilane in acetone-d_6 in 80–90% yield (δ OOOH, 13.64 ppm, acetone-d_6 (0.6 M) at −80 °C; after partial decomposition of this hydrotrioxide, the upfield OOOH absorption appeared at δ 13.34 ppm (−80 °C)).

Kinetic Studies. The kinetics of decomposition of **2** was measured by following the decay of CH_3 and OOOH absorptions and was found to obey first-order kinetics over at least 1–2 half-lives in all solvents investigated. Both absorptions decayed by approximately the same rate. The kinetic and activation parameters for the decomposition of **2a** in various solvents are summarized in Table II.

As evident from Figure 2, the Arrhenius plot of log k vs $1/T$ is nonlinear ("concave upward") for the decomposition of **2a** in acetone-d_6. Thus, the activation parameters were obtained from the slopes of approximately linear portions of this plot. Although there were some indications that such a curvature of the Arrhenius plot might also be present in the case of the decomposition of **2a** in methyl acetate and dimethyl ether, we were unable to verify this. Namely, all attempts to measure the kinetics of the decomposition of **2a** in these solvents with a reasonable degree of accuracy below −65 °C failed. Although we can only speculate

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Table III. Kinetic and Activation Parameters for the Decay of the OOOH Absorption Tentatively Assigned to Hydrogen Trioxide and Temperature Dependence of the OOOH Absorption

temp, °C	δOOOH, ppm	$10^4 k_1$,^{a} s^{-1}	E_a, kcal/mol	log A ($\Delta S^{\ddagger}$, eu)
−70	13.46			
−60	13.37			
−50	13.29	0.20	11.0	6.1
−40	13.16	0.56		(−32)
−30	13.08 (12.73)	1.6 (1.3)^b		
−20		4.0		
−10		9.3		

^{a} Standard deviations, ±10%. ^{b} In dimethyl ether (±15%).

about the origin of this phenomenon at the present time, we believe that it might be due to the fact that the second hydrotrioxide, tentatively assigned to HOOOH, began to decompose appreciably at about −60 to −50 °C (the formation of water?).

The substituent effect on the decomposition of **2** in methyl acetate at −50 °C was investigated, and it was found that the electron-withdrawing group accelerates decomposition, while electron-donating groups retard it. The relative rates of decomposition were p-Cl, 2.91; H, 1.00; p-CH$_3$, 0.77; p-CH$_3$O, 0.60. The resulting Hammett ρ value vs σ is 1.2 ± 0.1 It is interesting to note that comparable ρ values were obtained for the decomposition of hydrotrioxides of substituted benzylic ethers and benzaldehyde dimethyl acetals in diethyl ether.[4b,8]

The effect of solvent on the decomposition of **2a** was examined. We found that the rate of decomposition of **2a** is sensitive to solvent polarity, the rate increasing with the solvent polarity (k_{rel} = 6.3, 2.3, and 1.0 for acetone-d_6 (E_T = 42.2), methyl acetate (E_T = 40.0), and dimethyl ether (E_T = 35), respectively). As already mentioned, the decomposition of **2a** in CH$_3$OH proceeded very fast (see also Table II).
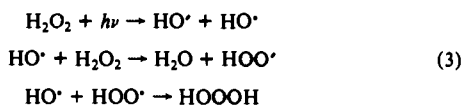
In order to test the hypothesis that the decomposition of **2** might be an induced decomposition, we studied the kinetics of the decomposition of **2a** in the presence of 2,6-di-*tert*-butyl-4-methylphenol. We found that this radical inhibitor had no measurable effect on the rate of the decomposition of **2** in acetone-d_6 or methyl acetate.

We succeeded in measuring (after complete disappearance of **2a**, as evidenced by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy) the kinetics of the decay of the upfield OOOH absorption. The kinetic and activation parameters for its decay in acetone-d_6 are collected in Table III (Figure 2).

(9) Giguere, P. A.; Herman, K. *Can. J. Chem.* 1971, 49, 2242. (b) Arnau, J. L.; Giguere, P. A. *J. Chem. Phys.* 1974, 60, 270. (c) Giguere, P. A. *Chemistry* (ACS, Washington), 1975, 48, 21. For a discussion of this work, see: Tso, T.-L.; Lee, E. K. *J. Phys. Chem.* 1985, 89, 1618. Patrick, R.; Barker, J. R.; Golden, D. M. *J. Phys. Chem.* 1984, 88, 128.

(10) Hydrogen trioxide, HOOOH, has also been proposed as a transient intermediate in the oxygenation of alkanes with ozone in superacid media (Olah, G. A.; Yoneda, N.; Parker, D. G. *J. Am. Chem. Soc.* 1976, 98, 5261. Yoneda, N.; Olah, G. A. *J. Am. Chem. Soc.* 1977, 99, 3113) and in the pulse radiolysis of air-saturated perchloric acid solutions (Bielski, H. J.; Schwartz, H. A. *J. Phys. Chem.* 1968, 72, 3836).

(11) UV irradiation (300-W lamp) of H$_2$O$_2$ in methyl acetate (5–6 M), 80–99% H$_2$O$_2$ (by weight) at −80 °C, produced an oxygen-rich intermediate, characterized by an ^{1}H NMR absorption at ca. δ 14.5 ± 1.0 ppm, downfield from Me$_4$Si. This polyoxide, tentatively assigned to HOOOH, decomposed in the temperature range from −60 to −30 °C to produce ^{1}O$_2$. The presence of small amounts of water in H$_2$O$_2$ appeared to assist in the formation and/or stabilization of the hydrotrioxide, sharpened the OOOH absorption, and shifted its position downfield. The maximum yields of HOOOH (8 ± 2%, per mole of H$_2$O$_2$) were obtained by using 85% H$_2$O$_2$. The following homolytic processes are most probably involved in the formation of this polyoxide:

$$H_2O_2 + h\nu \rightarrow HO^{\bullet} + HO^{\bullet}$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HOO^{\bullet} \qquad (3)$$

$$HO^{\bullet} + HOO^{\bullet} \rightarrow HOOOH$$

Further studies of this reaction are in progress. For a recent discussion of the reactions involved in the photolysis of H$_2$O$_2$ in the gas phase, see: Stephens, S. L.; Birks, J. W.; Glinski, R. J. *J. Phys. Chem.* 1989, 93, 8385. See, also: Mozurkewich, M. *J. Phys. Chem.* 1986, 90, 2216; DeMore, W. B. *J. Phys. Chem.* 1982, 86, 121. Sridharan, U. C.; Qiu, I. X.; Kaufman, F. *J. Phys. Chem.* 1984, 88, 1281. Nangia, P. S.; Benson, S. W. *J. Phys. Chem.* 1979, 83, 1138. Benson, S. W. *Oxid. Commun.* 1982, 2, 169.
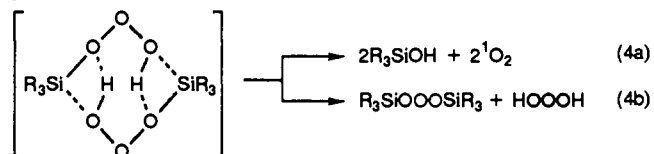
Scheme I
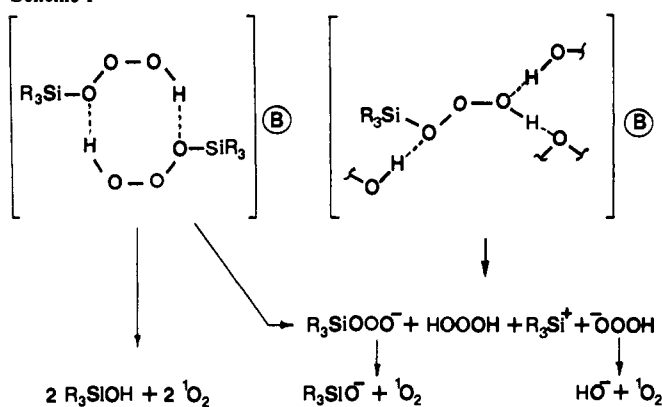
Although the activation parameters for the decomposition of both hydrotrioxide species are very similar, it is, nevertheless, evident that the upfield OOOH absorption, tentatively assigned to HOOOH, decayed about 10 times slower than that of **2a** (acetone-d_6).

Mechanisms for the Decomposition of the Hydrotrioxides. Dimethylphenylsilyl Hydrotrioxides. Although we do not know at the present time whether activation parameters, deduced from the observed rates are for one reaction pathway or represent the activation parameters for the decomposition which is proceeding by several simultaneous first-order processes, we nevertheless believe that (a) large negative entropies of activation, (b) a rather significant substituent effect on the decomposition of **2a** in methyl acetate, and (c) the observed dependence of the rate of decomposition of **2a** on solvent polarity, indicate a predominantly "polar" decomposition mechanism. This is in contrast to the observations made by studying the decomposition of cumyl hydrotrioxide, the carbon analogue of **2** in acetone-d_6 as solvent. Namely, this hydrotrioxide has been shown to decompose exclusively according to radical mechanisms.[4d]

Some mechanistic possibilities involving solvated dimeric and/or polymeric intermolecularly hydrogen-bonded forms of the hydrotrioxide are shown in Scheme I.

In view of the expected greater acidity of organosilicon hydrotrioxides compared to carbon analogues,[12] proton transfer from one hydrotrioxide molecule to another should be thermodynamically favorable. Although the formation of silicenium ions[13a] in this type of reactions is not unexpected in view of the pronounced ionic character of the Si–O bonds,[13b] the possibility of the involvement of the intermediates and/or transition states with pentacoordinated silicon, such as shown below, appears also plausible.
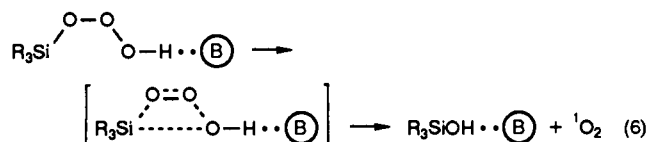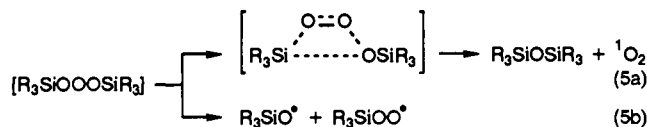

$$2R_3SiOH + 2\,^1O_2 \qquad (4a)$$
$$R_3SiOOOSiR_3 + HOOOH \qquad (4b)$$

A concerted two-proton transfer leading to the silanol and $^1O_2$ (eq 4a) is similar to the one already shown in Scheme I, while

(12) (a) Silanols are more acidic than the corresponding alcohols. For example: Et$_3$SiOH, pK_a = 13.6 (Arm, H.; Hochstrasser, K.; Schindler, P. W. *Chimia* 1974, 28, 237); Me$_3$COH, pK_a = 17 (Bruice, T. C.; Noar, J. B.; Ball, S. S.; Venkataraman, U. V. *J. Am. Chem. Soc.* 1983, 105, 2452); Me$_3$COOH, pK_a = 12.8 (Everett, A. J.; Minkoff, G. J. *Trans. Faraday Soc.* 1953, 49, 410). (b) Theoretical acidity, estimated as the energy difference between the neutral hydrotrioxide or hydroperoxide molecule and the corresponding anions, ΔE_{eq}(kcal/mol), and calculated at the RHF 6-31++G//6-31++G level of sophistication (complete geometry optimization) reveals the following order of acidity: HOOOH (352.3) > H$_3$SiOOOH (353.3)[1a] > MeOOOH (358.3)[1a] > H$_3$SiOOH (365.3)[1a] > MeOOH (371.4).[1a]

(13) (a) For a recent discussion on the silicenium ions, see: Olah, G. A.; Heiliger, L.; Li, X.-Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1990, 112, 5991. Lambert, J. B.; Schulz, W. J.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* 1988, 110, 2201. (b) For a recent theoretical study on the polarity of the Si–O bond, see: Gronert, S.; Glaser, R.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1989, 111, 3111, and references cited therein.

the transfer of only one proton would, together with the formation of the Si–O bond, result in the formation of disilyl trioxide and hydrogen trioxide (eq 4b). While the existence of dialkyl trioxides (ROOOR, R = *t*-Bu, CF$_3$) is well documented,[14] there have been no reports in the literature on the spectroscopic evidence for the silicon analogues. Such species, if formed during the decomposition of **2**, would break down quickly either in a heterolytic (eq 5a) or homolytic process (eq 5b). An analogous heterolytic

$$[R_3SiOOOSiR_3] \longrightarrow \left[R_3Si \overset{O\overset{\cdots}{-}O}{\cdots\cdots\cdots} OSiR_3 \right] \longrightarrow R_3SiOSiR_3 + {}^1O_2 \quad (5a)$$

$$\longrightarrow R_3SiO^\bullet + R_3SiOO^\bullet \quad (5b)$$

$$R_3Si \overset{O-O}{\underset{}{\diagup\diagdown}} O-H\cdots\circledB \longrightarrow$$

$$\left[R_3Si \overset{O\overset{\cdots}{-}O}{\cdots\cdots\cdots} O-H\cdots\circledB \right] \longrightarrow R_3SiOH\cdots\circledB + {}^1O_2 \quad (6)$$
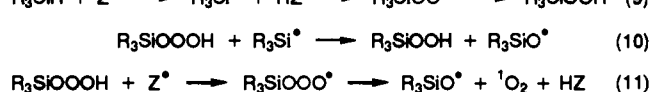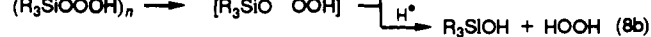
decomposition pathway is also available for the monomeric silyl hydrotrioxide (complexed with the oxygen base) (eq 6). It should be pointed out that the intramolecular coordination between silicon and oxygen, already proposed to be the driving force in the decomposition of organosilicon peroxides,[15] is in accordance with the ab initio calculations showing a substantial accumulation of negative charge on the terminal oxygen atoms in silyl hydrotrioxide.[1a]

The formation of structures with pentacoordinated silicon would seem to explain both the observed substituent effect on the decomposition of **2** as well as the formation of dimethylphenylmethoxysilane and the observed higher yields of HOOOH in the presence of CH$_3$OH.

$$R_3Si \overset{O-O-O-H\cdots}{\underset{\overset{|}{\underset{CH_3}{O}}}{\diagup\diagdown\text{H}}} \longrightarrow R_3SiOCH_3 + HOOOH \quad (7)$$
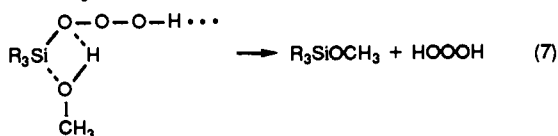
It is not possible on the basis of the above mentioned kinetic results to exclude completely the possibility of radical contributions to the overall decomposition mechanism, especially at temperatures above –50 °C (fast warmup procedure).[16] Although experiments with added radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol showed no reduction of the decomposition rates, the possibility still exists that the oxygenated products, i.e., dimethylphenylsilyl hydrotrioxide,[4g] dimethylphenylsilyl hydroperoxide,[17a] dimethylphenylsilanol,[17b] or oxygen,[17c] are better traps for silyl and/or silyloxyl radicals than the phenol.

Some mechanistic possibilities involving homolytic decomposition pathways which are consistent with the results of product studies are shown below.

$$(R_3SiOOOH)_n \longrightarrow [R_3SiO^{\bullet\,\bullet}OOH] \overset{}{\underset{H^\bullet}{\Bigg\langle}} \begin{array}{l} \longrightarrow R_3SiOH + {}^1O_2 \quad (8a) \\ \longrightarrow R_3SiOH + HOOH \quad (8b) \end{array}$$

$$R_3SiH + Z^\bullet \longrightarrow R_3Si^\bullet + HZ \overset{O_2}{\longrightarrow} R_3SiOO^\bullet \overset{H^\bullet}{\longrightarrow} R_3SiOOH \quad (9)$$

$$R_3SiOOOH + R_3Si^\bullet \longrightarrow R_3SiOOH + R_3SiO^\bullet \quad (10)$$

$$R_3SiOOOH + Z^\bullet \longrightarrow R_3SiOOO^\bullet \longrightarrow R_3SiO^\bullet + {}^1O_2 + HZ \quad (11)$$

The formation of dimethylphenylsilyl hydroperoxide in the decomposition of **2a** at low temperatures deserves further dis-

(14) (a) Bartlett, P. D.; Lahav, M. *Isr. J. Chem.* **1972**, *10*, 101. (b) Hohorst, F. A.; DesMarteau, D. D.; Anderson, L. R.; Gould, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 3866.

(15) Yablokov, V. A. *Usp. Khim.* **1980**, *49*, 1711, and references cited therein.

(16) For a review on radical reactions of silanes, see: Wilt, J. W. In *Reactive Intermediates*; Abramovitch, R. A. Ed.; Plenum: New York, 1983; Vol. 3, pp 113–197.

(17) (a) Curtice, J.; Gilman, H.; Hammond, G. S. *J. Am. Chem. Soc.* **1957**, *79*, 4754. (b) Cornett, B. J.; Choo, K. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1980**, *102*, 377. (c) Bennett, J. E.; Howard, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 8244.

Table IV. Equilibrium Geometries and Total Energies for Hydrogen Trioxide Monomer, Dimer, and Hydrotrioxide Anion and Binding Energies for the Hydrogen Trioxide Dimer[a-c]

bond lengths (Å) and angles (deg)	$H_1-O_2-O_3-O_4-H_5$ 6-31G	$H_1-O_2-O_3-O_4^-$ 6-31++G	$(HOOOH)_2$ 6-31G
H_1-O_2	0.958 (0.972)[d]	0.958	0.957
O_2-O_3	1.432 (1.439)[d]	1.479	1.435
O_3-O_4	1.432 (1.439)[d]	1.494	1.430
O_4-H_5	0.958 (0.972)[d]		0.967
$O_2\cdots H_5$			1.841
$\angle H_1-O_2-O_3$	104.1 (100.2)[d]	100.1	105.3
$\angle O_2-O_3-O_4$	106.5 (106.3)[d]	104.2	106.5
$\angle O_3-O_4-H_5$	104.1 (100.2)[d]		103.6
$\angle O_4-H_5\cdots O_2$			161.0
$\angle O_3-O_2\cdots H_5-O_4$			34.3
$\angle H_1-O_2-O_3-O_4, \Psi_1$	83.9 (78.1)[d]	0.0	80.4
$\angle H_5-O_4-O_3-O_2, \Psi_2$	83.9 (78.1)[d]		82.8
6-31++G//6-31G	–225.45286		
6-31++G//6-31++G		–224.89147	
6-31G//6-31G	–225.44304		–450.90760 (–11.0)
6-31G**//6-31G	–225.54026		–451.09287 (–7.75)

[a] Total energies in hartrees (binding energies in kcal/mol). [b] HO$_3^-$, 6-31++G**: $R(H_1-O_2) = 0.949$ Å, $R(O_2-O_3) = 1.420$ Å, $R(O_3-O_4) = 1.402$ Å, $\angle H_1-O_2-O_3 = 97.6°$, $\angle O_2-O_3-O_4 = 105.1°$, $\Psi = 0°$ (–224.95815). [c] The calculated HOOO dihedral angle Ψ in HO$_3$ radical is 90° (Blint, R. J.; Newton, M. D. *J. Chem. Phys.* **1973**, *59*, 6220. Dupuis, M.; Fitzgerald, G.; Hammond, B.; Lester, W. A.; Schaefer, III, H. F. *J. Chem. Phys.* **1986**, *84*, 2691). [d] Reference 24.
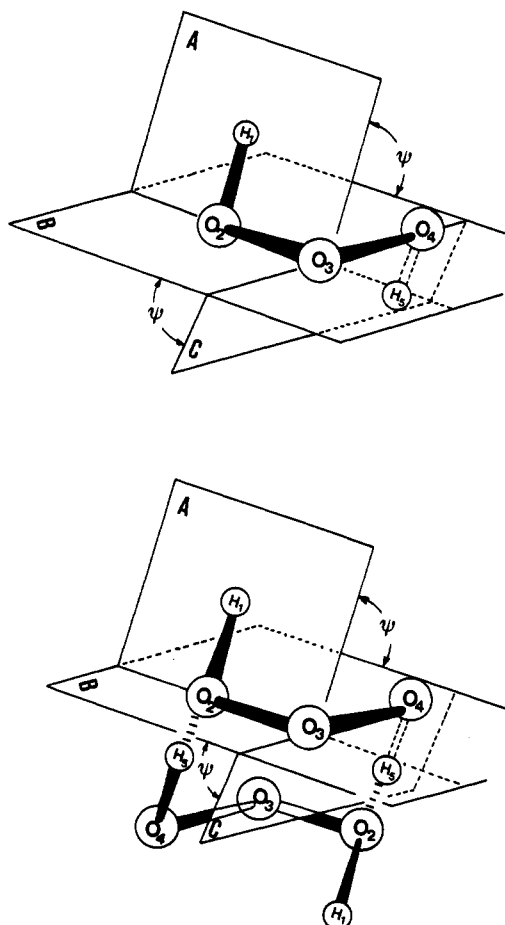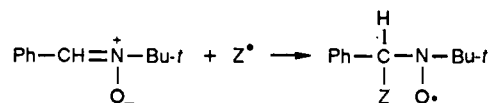

Figure 3. Geometrical representation (atomic numbering scheme) of monomeric and dimeric HOOOH: H_1, O_2, and O_3 in plane A and O_2, O_3, and O_4 in plane B.

cussion. Since in all samples of **2a** used small amounts of the parent silane remained present (<5%), the possibility existed that any reactive radical, **7**, present in the system (for example, silyloxyl radical formed according to eqs 8, 10, and 11) would abstract a hydrogen atom from the silane (eq 9). The silyl radicals thus

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formed would be expected to react easily with oxygen to form silylperoxyl radicals (and the hydroperoxide, eq 9). Still another possibility is that silyl radicals, if formed in these reactions, attack the middle oxygen atom in the hydrotrioxide in an S_H2 process (eq 10) to form the silyl hydroperoxide.[4g,16]
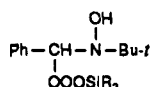
Although it is difficult to quantify all the possible radical processes presumably involved in the decomposition of **2**, we nevertheless believe that they are only minor (<10%) under the conditions investigated.[18,19]

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(18) Nonradical processes also play an important role in the decomposition of other organosilicon peroxides. For a review, see: Alexandrov, Yu. A. *J. Organomet. Chem.* **1982**, *238*, 1.

(19) Since we were not able to observe by "direct" ESR any radical during the decomposition of **2a**, we have undertaken a low-temperature study of the decomposition of this polyoxide in the presence of phenyl-*N-tert*-butylnitrone (PBN), a well-known spin trap (spin-trapping technique).[20]

$$Ph-CH\!\!=\!\!\overset{+}{N}-Bu\text{-}t \;+\; Z^{\bullet} \;\longrightarrow\; Ph-\overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle O\bullet}{\displaystyle |}}{C}}-\overset{\underset{\displaystyle |}{\displaystyle |}}{\underset{\displaystyle Z}{N}}-Bu\text{-}t$$

Unfortunately, these studies were complicated by the fact that **2a** oxidized PBN. Namely, when **2a** was used in excess of PBN (molar ratio, **2a**:PBN = 5-10:1) some benzaldehyde and 2-methyl-2-nitropropane were found in the decomposition mixture (<1% yield, based on PBN) after warmup to room temperature. We have found no evidence, however, for the formation of 2-methyl-2-nitrosopropane (NtB) in these reactions. Mixing a degassed sample of **2a** (50-100 mM) with PBN in methyl acetate (molar ratio, **2a**/PBN = 1:3-5) at -78 °C, an ESR spectrum consisting of three rather broad lines (A_N = 12.1 ± 0.1 G) was observed. Similar observations were made when acetone was used as solvent (A_N = 12.2 ± 0.1 G). The ESR signal exhibited no proton hyperfine splitting until the sample was warmed up to about -20 to -10 (in 10° increments) when it transformed into another triplet of doublets. The same ESR spectrum was obtained when the sample was warmed up quickly to about -20 °C and then cooled back down (A_N = 12.9 ± 0.1 G, A_{β}^H = 1.9 ± 0.1 G, -20 °C). The signal obtained at higher temperatures was the same as that obtained by photolyzing bis(dimethylphenylsilyl) peroxide in the presence of PBN (A_N = 12.9 ± 0.1 G, A_{β}^H = 1.7 ± 1.0 G, -80 °C, A_N = 13.0 ± 0.1 G, A_{β}^H = 1.9 ± 0.1 G, 20 °C, in methyl acetate or acetone) and was thus tentatively assigned to the dimethylphenylsilyloxyl radical spin adduct. This spin adduct was stable for several hours at room temperature.[21] We cannot at the present time unambiguously identify the spin adduct obtained at -78 °C. Its ESR characteristics are consistent with either a peroxyl (or a mixture of peroxyl and oxyl radical adducts) or a benzoyloxyl radical adduct of PBN. Since the spin adduct decomposed at higher temperatures (-40 to -30 °C), as would be expected of a peroxyl radical adduct, we prefer the former possibility. Namely, an ESR signal consisting of three rather broad lines (A_N = 11.8 ± 0.1 G, -84 °C), which completely disappeared at <-30 °C, was observed when di-*tert*-butyl peroxide (DTBP) was photolyzed in the presence of **1a** and PBN (**1a**/PBN/DTBP = 10:3:1, **1a** (50 mM)) in solutions of methyl acetate saturated with oxygen.[22,23] At the same time, benzoyloxyl radical adduct obtained by mixing (dibenzoyloxy)iodobenzene with PBN or by photolyzing dibenzoyl peroxide in the presence of PBN and which has very similar ESR characteristics (A_N = 11.7 G, A_{β}^H = 1.2 G, -80 °C; A_N = 11.7 G, A_{β}^H = 1.4 G, 20 °C, methyl acetate) is stable at room temperature. It is interesting to mention also the results of spin trapping experiments in methylene chloride. When **2a** (50-100 mM) was mixed with PBN (**2a**/PBN = 1:3-5) at -78 °C, a triplet of doublets with A_N = 12.1 ± 0.1 G and A_{β}^H = 1.2 ± 0.1 G was observed. This spin adduct had the same ESR characteristics as the radical adduct prepared independently by photolyzing di-*tert*-butyl peroxide in the presence of **1a** and PBN in methylene chloride saturated with oxygen (A_N = 12.0 ± 0.1 G, A_{β}^H = 1.1 ± 0.1 G, -80 °C) and was thus tentatively assigned to the silylperoxyl radical adduct. The signal disappeared completely during the slow warmup procedure (<-30 °C). On the other hand, benzoyloxyl radical adduct of PBN (A_N = 11.9 G, A_{β}^H = 1.0 G, at -80 °C) is very stable in this solvent at 20 °C. When the molar ratio **2a**/PBN was 3-5:1 or larger, either a triplet of doublets (A_N = 12.2 ± 0.1 G, A_{β}^H = 1.3 ± 0.1 G, -80 °C) and a triplet with A_N = 7.6 G or the latter triplet alone were observed in the ESR spectrum. The former signal, tentatively assigned to silylperoxyl radical spin adducts, disappeared slowly when the temperature was raised, while the triplet, ascribed to benzoyl *tert*-butyl nitroxide (PBNO$_x$), i.e., the oxidized form of PBN, remained in the spectrum.[24] It should be pointed out, however, that, besides the oxidation of the spin trap by the hydrotrioxide, PBN itself may induce decomposition of these polyoxides to produce radicals,[4g] either by forming trioxidic hydroxylamine (particularly in more polar solvents) with subsequent homolytic scission (and/or oxidation) of the latter or interacting with the hydrotrioxide in a nonspecific manner.[4g] Therefore, the spin trapping technique is of only limited value for the evaluation of possible radical contributions to the overall mechanistic decomposition scheme of these species.

$$Ph-\overset{\overset{\displaystyle OH}{\displaystyle |}}{\underset{\underset{\displaystyle OOOSiR_3}{\displaystyle |}}{CH}}-N-Bu\text{-}t$$

Table V. Net Atomic Charges (e)[a]

	6-31G**//6-31G		6-31++G**//6-31++G**
atom	H_1-O_2- $O_3-O_4-H_5$	$(HOOOH)_2$	$H_1-O_2-O_3-O_4^-$
H_1	0.374	0.383 (+0.009)[b]	0.331
O_2	-0.330	-0.383 (-0.053)[b]	-0.523
O_3	-0.087	-0.077 (+0.010)[b]	-0.014
O_4	-0.330	-0.351 (-0.020)[b]	-0.793
H_5	0.374	0.427 (+0.153)[b]	

[a] The term net atomic charge is defined as $Z - n$ (6-31G**//6-31G or 6-31++G**//6-31++G**) where Z is the atomic number and n is the net electronic density of an atom. [b] The losses and gains of charge (e) after complexation. The calculated electric dipole moment of HOOO anion: μ = 2.18 D (6-31++G//6-31++G) and 2.33 D (6-31++G**//6-31++G**).

A Theoretical Study of the Hydrogen Trioxide Dimer Interaction. Since the NMR spectroscopic behavior (temperature and concentration dependence studies, a downfield shift of the OOOH absorption after the addition of DMAA) as well as the kinetic and activation parameters for the decay of both OOOH absorptions were very similar, we hypothesized that the structure as well as the decomposition mechanism for these two hydrotrioxide species must be also similar. In order to test this presumption, we have undertaken an ab initio MO study of the monomeric and dimeric hydrogen trioxide. This is to the best of our knowledge the first theoretical study of the association of this species.

The parameters of equilibrium geometries of the monomeric and dimeric HOOOH are, together with the corresponding equilibrium energies, summarized in Table IV. The schematic representation of the geometry of the monomeric and dimeric entities are shown in Figure 3.

It is evident from Table IV that the geometry parameters for HOOOH, obtained at the 6-31G level of sophistication, are very similar to those obtained previously by Cremer[25a] and Jackels et al.[25b] at higher levels of theory (MP-2/6-31G*). It was already stated that this is due to the fact that, in trioxides (ROOOR, R = alkyl or H), the rotational potential is much steeper compared to that in peroxides and thus less sensitive to the basis set effect.[1a] Therefore, it appears unlikely that further refinement of the geometry of the HOOOH dimer at still higher levels of theory (prohibitively expensive for our purposes), including correlation effects, would result in major changes of the geometry of this assembly.

The Mulliken population analysis for HOOOH shows, similar to the results of theoretical studies on other hydrotrioxides,[1a,25]

(20) (a) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. (b) Janzen, E. G. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1980; Vol. IV, Chapter 4.

(21) Similar ESR characteristics were reported for other alkoxyl radical spin adducts of PBN. See, for example: (a) Niki, E.; Yokoi, S.; Tsuchiya, J.; Kamiya, Y. *J. Am. Chem. Soc.* **1983**, *105*, 1498. (b) Pryor, W. A.; Prier, D. G.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883.

(22) (a) For peroxyl spin adducts of PBN, see: Meritt, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713. Ohto, N.; Niki, E.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1770. Howard, J. A.; Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176. Janzen, E. G.; Nutter, D. E.; Davis, E. R.; Blackburn, B. J. *Can. J. Chem.* **1978**, *56*, 2237. Zubarev, V. E.; Belevskii, V. N.; Yarkov, S. P. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1392. (b) Somewhat lower A_N values for the spin adduct tentatively assigned to silylperoxyl radical spin adducts of PBN, compared to A_N values for the corresponding alkylperoxyl derivatives, might reflect a difference in the conformation of the two types of nitroxides.

(23) Dimethylphenylsilyl radicals, generated in this way, are not trapped efficiently either by oxygen or acetone (Sakurai, H.; Hosomi, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1551) under conditions investigated. Namely, they were detected as the corresponding spin adducts of PBN after warmup to room temperature (A_N = 14.0 G, A^H = 5.7 G). For silyl radical adducts of PBN, see: (a) Adeleke, B. B.; Wong, S.-K.; Wan, J. K. S. *Can. J. Chem.* **1974**, *52*, 2901. (b) Chandra, H.; Davidson, M. T.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. II* **1982**, 1353.

(24) (a) Janzen, E. G. In *Creation and Detection of the Excited State*; Ware, W. R., Ed.; Marcel Dekker: New York, 1976; Chapter 3. (b) Pryor, W. A.; Govindan, C. K. *J. Org. Chem.* **1981**, *46*, 4679.
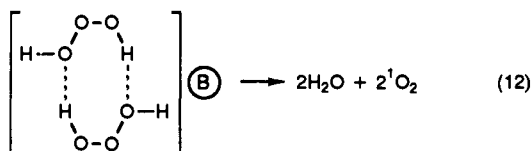
(25) (a) Cremer, D. *J. Chem. Phys.* **1978**, *69*, 4456. See, also: Cremer, D. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 1. (b) Jackels, C. F.; Phillips, D. H. *J. Chem. Phys.* **1986**, *84*, 5013.

a considerable accumulation of charge on both terminal oxygen atoms with only little charge accumulated on the central oxygen. The results are very similar to those by Jackels et al.[25b] by using 6-31G**/CI (O_1, O_3, −0.31 e; O_2, −0.07 e; H, −0.35 e). When going from the monomeric to dimeric entity, the acceptor oxygen atom, as expected, gains charge, while the hydrogen atoms lose it (Table V).

The calculated dipole moment of HOOOH (6-31G**//6-31G, μ = 1.13 D) is in close agreement with the net moment of 1.26 D, calculated at the CI level.[23b]

The hydrogen bond distance O–H⋯O in the dimeric HOOOH is somewhat longer compared to that in the dimeric $H_3SiOOOH$ (1.734 Å) and approximately the same as R_{HB} in $(CH_3OOOH)_2$ (1.823 Å).[1a] The binding energies, BE, in the cyclic dimers of all these polyoxides are also very similar (7–8 kcal/mol).

It seems, thus, on the basis of all the above mentioned results, safe to conclude that self-association is the main structural feature of HOOOH and that its decomposition must be very similar to that of silane hydrotrioxides under investigation. Assuming cyclic dimeric structures as the predominant ones in solvents of low basicity, it seems reasonable to propose the following mechanistic schemes for the decomposition of this polyoxide.

$$\left[\begin{array}{c} O-O \\ H-O \quad\quad H \\ \vdots \quad\quad \vdots \\ H \quad\quad O-H \\ O-O \end{array} \right] \textcircled{B} \longrightarrow 2H_2O + 2\,{}^1O_2 \qquad (12)$$

The intramolecular transfer of the proton (H_1) to the terminal oxygen atom (O_4) in the complexed monomeric form, (HOOO-H)B, to yield ${}^1O_2$, and H_2O appears also plausible. It should be pointed out that such a process is also available for the decomposition of the hydrotrioxide anion, HOOO⁻ (Scheme I). Namely, the results of our ab initio studies indicate that the anion is most likely stabilized by an intramolecular hydrogen bonding (R-(H_1⋯O_4) = 2.07 Å, Ψ = 0°(6-31++G), and $R(H_1$⋯O_4) = 1.96 Å, Ψ = 0°(6-31++G**)), see Table IV). This appears to be the main reason for the relatively high acidity of HOOOH as compared to other hydrotrioxides and hydroperoxides investigated (see ref 19).

The Oxidation of Sulfides and Sulfoxides. The remarkable reactivity of triethylsilyl hydrotrioxide with various olefins has already been reported.[8] During our earlier studies of the reactivity of 2 and hydrotrioxides of benzylic ethers and alcohols,[4a] we have found that these polyoxides oxidize simple dialkyl sulfides (dimethyl and diethyl sulfides) to the corresponding sulfoxides and the latter to sulfones. In order to find out the nature of the oxidizing species in these reactions, we have now studied oxidation of a series of substituted phenyl methyl sulfides and sulfoxides.

Deozonized solutions of 2 in various solvents (0.2 M) at −78 °C oxidized phenyl methyl sulfides to sulfoxides in yields ranging from 70 to 80%. Practically no sulfone was formed in these reactions. When phenyl methyl sulfoxides were allowed to react with 2 only relatively small amounts of the corresponding sulfones were obtained (5 ± 1%). The oxidations, which were carried out in the presence of excess of the sulfides/sulfoxides (molar ratio, 2:sulfide/sulfoxides = 1:5), proceeded very fast. Similar observations were made by studying the oxidation of diphenyl sulfide, although in this case the yields of the sulfoxide were somewhat lower (30 ± 10%). Control experiments with DABCO, an efficient singlet oxygen quencher, showed no effect on these oxidations.

A series of competitive kinetics experiments with para-substituted phenyl methyl sulfides and sulfoxides gave the relative reactivities and the Hammett ρ values summarized in Table VI.[26]
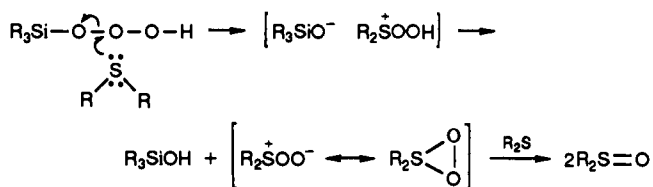
The negative Hammett ρ values and the reactivity order PhSMe ≫ PhSOMe indicate an electrophilic O-transfer from 2 to the sulfide and sulfoxide. It is interesting to note that 2a reacted with thianthrene 5-oxide, introduced by Adam et al.[27] as a chemical

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(26) The Hammett ρ value of −1.6 was reported for the oxidation of phenyl methyl sulfides with singlet oxygen in methanol (Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765).

Table VI. Relative Rates and the Hammett ρ Values for the Oxidation of Phenyl Methyl Sulfides and Sulfoxides with Dimethylphenylsilyl Hydrotrioxides (2)

hydro-trioxide	substrate	solvent	k_X/k_H		Hammett ρ value
2a	4-XPhSMe	$(CH_3)_2CO$	4-MeO	3.93	−1.99 (r = 0.997)
			4-Me	2.06	
			H	1.00	
			4-Cl	0.37	
		$CH_3CO_2CH_3$	4-MeO	2.94	−1.59 (r = 0.998)
			4-Me	2.05	
			H	1.00	
			4-Cl	0.47	
		$CH_3(CH_2)_2CH_3$	4-MeO	2.36	−1.65 (r = 0.970)
			4-Me	1.18	
			H	1.00	
			4-Cl	0.29	
2b		$(CH_3)_2CO$	4-MeO	3.36	−1.83 (r = 0.999)
			4-Me	2.11	
			H	1.00	
			4-Cl	0.41	
		$CH_3CO_2CH_3$	4-MeO	3.48	−1.77 (r = 0.997)
			4-Me	2.14	
			H	1.00	
			4-Cl	0.44	
		$CH_3(CH_2)_3CH_3$	4-MeO	2.56	−1.53 (r = 0.999)
			4-Me	1.88	
			H	1.00	
			4-Cl	0.44	
2a	4-XPhSOMe	$(CH_3)_2CO$	4-MeO	2.87	−1.10 (r = 0.939)
			4-Me	2.28	
			H	1.00	
			4-Cl	0.87	

probe for differentiating between the electrophilic versus nucleophilic nature of various oxidants, as an "electrophilic" oxygen transfer reagent in methyl acetate or methylene chloride (X_{Nu} = 0.11 ± 0.02; for comparison, X_{Nu} for the reaction with O_3 (C-H_2Cl_2) is 0.17[27a]) but as a "nucleophilic" oxidant (X_{Nu} = 0.63 ± 0.5) in acetone at −78 °C (total yield of the products was 4 ± 2% in all solvents investigated). Similar observations were also made by studying the oxidation of this probe with 2b. Although a discrepancy between the X_{Nu} and the Hammett ρ values for the reaction of sulfides and sulfoxides with dioxiranes[27c] and dialkylperoxonium ions[28] has already been reported, the observation that such a discrepancy may be caused by a change of the solvent (polarity?) appears to be novel.[29] The oxidation of the probe by the hydrotrioxide species (tentatively assigned to HOOOH), formed in appreciable amounts during the decomposition of 2 in acetone-d_6 even at −78 °C, might be another complicating factor in the determination of X_{Nu} values.

While alternative explanations for the oxidation of the sulfides and sulfoxides with 2 may be possible (for example, single-electron-transfer processes), we believe that all the above mentioned results can best be accommodated by the mechanism which involves the rate-determining nucleophilic attack of the sulfide/sulfoxide on the middle oxygen atom in the hydrotrioxide according to the following mechanistic scheme.[30]

$$R_3Si-O-O-O-H \longrightarrow [R_3SiO^- \quad R_2\overset{+}{S}OOH] \longrightarrow$$

$$R_3SiOH + [R_2\overset{+}{S}OO^- \longleftrightarrow R_2S\overset{O}{\underset{O}{\diagdown}}] \xrightarrow{R_2S} 2R_2S=O$$

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(27) (a) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1980**, *102*, 7241. (b) Adam, W.; Durr, H.; Haas, W.; Lohray, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 101. (c) Adam, W.; Chan, Y.-Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800.

(28) Bloodworth, A. J.; Melvin, T.; Mitchell, J. C. *J. Org. Chem.* **1988**, *53*, 1078.

(29) For comments on the use of this probe, see: Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.

(30) For a discussion on some of the intermediates proposed to be involved in these reactions, see: (a) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478, and references cited therein. (b) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085.

Namely, the results of ab initio MO studies unambiguosly showed that the middle oxygen atom is most likely the "electrophilic" center in silyl hydrotrioxides (for example, H_3-SiO_3H, O^1, -0.484; O^2, -0.079; O^3, -0.321 e $(6-31G**//6-31G))$.[1a]

Experimental Section

Instrumentation. Low-temperature ^1H and ^{13}C NMR spectra were recorded with a JEOL PS 100 spectrometer. Initial ^{17}O measurements were carried out on a Varian XL300 NMR spectrometer equipped with a 5-mm broad band probe. Additional ^{17}O and ^{29}Si NMR work was carried out on a Bruker 500-MHz NMR spectrometer equipped with a 10-mm broad band probe. Gas chromatography was performed on a Varian 1800 and Perkin-Elmer Sigma 3B + Sigma 10B gas chromatographs. GC/MS was performed on a Model Hewlett Packard 5970. HPLC was performed on a Milton Roy 3100 and Shimadzu LC-4 chromatographs.

Materials. All solvents were the purest commercially available products and were (except of acetone-d_6) rigorously dried and distilled according to the literature procedures before use. Their purity was checked by GC/MS. Acetone-d_6 (100.0 atom %, Aldrich) was used as received. Dimethylphenylsilane (Petrarch) was distilled before use, while Me_3SiH (Petrarch) was used as received. Substituted dimethylphenylsilanes, dimethylphenyldisiloxane, and dimethylphenylmethoxysilane were prepared according to the literature procedures.[31] All these compounds were checked by NMR and GC/MS and were found to be >99% pure.

Dimethylphenylsilyl hydroperoxide was synthesized from the corresponding silylamine according to the procedure by Dannley et al.[32] All attempts to purify this moderately stable (20 °C), as yet not reported hydroperoxide (90% pure by iodometry and NMR), either by vacuum distillation or by column chromatography (<10 °C), failed. Dimethylphenylsilanol was found to be the only impurity in the crude hydroperoxide. Bis(dimethylphenylsilyl) peroxide was prepared according to the literature procedure[33] and was found to be >98% pure by iodometry and NMR.

The spin trap PBN was used as received from Aldrich. 2,6-Di-*tert*-butyl-4-methylphenol (Aldrich) was recrystallized from ethanol before use. Phenyl methyl sulfides were, except for the *p*-chloro-substituted derivative, which was prepared from the corresponding thiophenol, commercial products (Aldrich). All the sulfides were distilled before use (>99% pure). The oxidation of the sulfides to sulfoxides or sulfones was performed by using 3-chloroperoxybenzoic acid. All the sulfoxides and sulfones were purified either by distillation in vacuum (sulfoxides) or by column chromatography and recrystallization before use (>99%). Thianthrene 5-oxide, thianthrene 5,5-dioxide, thianthrene, 5,10-dioxide, and thianthrene 5,5,10-trioxide were gifts from Prof. W. Adam and were also prepared by the literature procedures.[34]

Ozonation Procedure. Ozone–oxygen mixtures delivered at a rate 0.2–0.3 mmol of ozone min^{-1} were produced by flowing oxygen through a Welsbach T-816 ozonator. Ozone–nitrogen mixtures were obtained as already described.[4a] The concentration of ozone in the gas streams was measured according to the literature procedure.[35]

Product Analysis. Decomposition products of **2a** were determined by a combination of techniques. All products, except hydrogen peroxide and dimethylphenylsilyl hydroperoxide, were determined by GC(SE 30)/MS, by using calibrated internal standards and known reference materials. All products were also collected and identified by NMR. Dimethylphenylsilyl hydroperoxide was detected in the decomposition mixture by ^1H, ^{13}C, and ^{29}Si NMR (-70 to -55 °C). Hydrogen peroxide was determined as already described previously.[4a]

Singlet oxygen (Δ^1O_2) was determined by adding the acceptor (2-fold excess per mol of the hydrotrioxide) to the deozonized solution of **2a** in the dark at -78 °C, and the reaction mixture was allowed to warm up slowly to room temperature. The amount of singlet oxygen available to

react with 1,3-diphenylisobenzofuran and tetraphenylcyclopentadienone was determined by measuring the decrease in absorbance at 405 and 510 nm, respectively. The corresponding reaction products, i.e., *o*-dibenzoylbenzene and (*Z*)-1,2-dibenzoylstilbene, were also isolated on silica gel chromatography columns. Their identity was checked by spectral and chromatographic (HPLC) comparison with authentic samples available from the previous studies.[4b] Control experiments showed that neither dimethylphenylsilyl hydroperoxide nor hydrogen peroxide reacted with the singlet oxygen acceptors under the conditions investigated.

ESR Spin Trapping. ESR spectra were recorded on a Varian E9 X-band 9.7-GHz spectrometer with a cavity equipped with a quartz Dewar insert for low-temperature work. Spin trapping experiments were performed as already described.[4a]

Kinetic Studies. Kinetic measurements of the decomposition of **2a** (0.5–0.7 M) were performed by following the decay of the OOOH and CH_3 absorptions by ^1H NMR, using Me_4Si as internal standard.[4a] Kinetic and activation parameters were obtained by standard procedures.

Oxidation of Para-Substituted Phenyl Methyl Sulfides with Dimethylphenylsilyl Hydrotrioxides. The hydrotrioxide (10 mM) was mixed with phenyl methyl sulfide (50 mM) and either *p*-chlorophenyl methyl sulfide (50 mM), *p*-methoxyphenyl methyl sulfide, or *p*-methylphenyl methyl sulfide in the appropriate solvent at -78 °C. The reaction mixture was allowed to stand for 1 h (at -78 °C), then warmed up to room temperature, and concentrated at reduced pressure. The extent of the competition reactions was determined by GC (Supelco SPB-1 capillary column). The relative rates, k_X/k_H, were calculated by using the integrated rate equation: $k_X/k_H = (\log [(A - X)/A])/(\log [(B - Y)/B])$ where A and B are the amounts of sulfides at the beginning of the reaction and X and Y are the amounts of sulfoxides at the end of the reaction. A similar procedure was used for the oxidation of phenyl methyl sulfoxides (HPLC, Supelco S5-ODS2, acetonitrile/water = 23:77, vol %).

Oxidation of Thianthrene 5-Oxide with Dimethylphenylsilyl Hydrotrioxide. The hydrotrioxide (0.05 mM) was mixed with thianthrene 5-oxide (0.05 mM) in the appropriate solvent at -78 °C. The reaction mixture was allowed to warm up to room temperature after 1 h and was then concentrated at reduced pressure. The reaction products, i.e., thianthrene 5,5-dioxide, thianthrene 5,10-dioxide, and thianthrene 5,5,10-trioxide were determined by HPLC (Supelco RP-8, acetonitrile/water = 30:70, vol %). The X_{Nu} values were calculated according to the method of Adam.[27]

Methods of Calculation. The calculations were carried out within the closed-shell LCAO-SCF approximation with 6-31G basis set.[36a] The equilibrium energies of the HOOOH monomer and dimer were also calculated with 6-31G**, which has polarization (d-type) functions on non-hydrogen atoms and p-type functions on hydrogen.[36b] The geometry optimization of the anion was carried out with 6-31++G and 6-31++-G** basis sets, which include diffuse orbitals to accommodate the negative charge.[36c]

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