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Reactivity of Alkyl versus Silyl Peroxides. The Consequences of 1,2-Silicon Bridging on the Epoxidation of Alkenes with Silyl Hydroperoxides and Bis(trialkylsilyl)peroxides

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The bond dissociation energies for a series of silyl peroxides have been calculated at the G2 and CBS-Q levels of theory. A comparison is made with the O−O BDE of the corresponding dialkyl peroxides, and the effect of the O−O bond strength on the activation barrier for oxygen atom transfer is discussed. The O−O bond dissociation enthalpies (ΔH_{298}) for bis (trimethylsilyl) peroxide (**1**) and trimethylsilyl hydroperoxide (**2**) are 54.8 and 53.1 kcal/mol, respectively at the G2 (MP2) and CBS-Q levels of theory. The O−O bond dissociation energies computed at G2 and G2(MP2) levels for bis(*tert*-butyl) peroxide and *tert*-butyl hydroperoxide are 45.2 and 48.3 kcal/mol, respectively. The barrier height for 1,2-methyl migration from silicon to oxygen in trimethylsilyl hydroperoxide is 47.9 kcal/mol (MP4//MP2/6-31G*). The activation energy for the oxidation of trimethylamine to its *N*-oxide by bis(trimethylsilyl) peroxide is 28.2 kcal/mol (B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d)). 1,2-Silicon bridging in the transition state for oxygen atom transfer to a nucleophilic amine results in a significant reduction in the barrier height. The barrier for the epoxidation of *E*-2-butene with bis(dimethyl(trifluoromethyl))silyl peroxide is 25.8 kcal/mol; a reduction of 7.5 kcal/mol relative to epoxidation with **1**. The activation energy calculated for the epoxidation of *E*-2-butene with $F_3SiOOSiF_3$ is reduced to only 2.2 kcal/mol reflecting the inductive effect of the electronegative fluorine atoms.

Introduction

One of the first systematic studies on the reactivity of silyl peroxides invoked neighboring group participation by the silyl group to assist in the heterolysis of the O−O bond.[1] More recently additional examples of the use of silyl peroxides such as bis(trimethylsilyl) peroxide (BTSP) have been utilized in oxidative processes including those that employ a metal catalyst.[2] A particularly useful oxidation procedure uses BTSP as a source of anhydrous H_2O_2 in the presence of methyltrioxorhenium as the catalyst.[3] The propensity of a peroxo oxidizing reagent to donate an oxygen atom may in principle be a function of its O−O bond dissociation energy (BDE)[4a] if the reaction proceeds by a homolytic pathway. An understanding of the energetics of the O−O bond in the silyl peroxides is germane to our rationalizing the mechanism of oxygen atom transfer. However, for a great many reactions that involve heterolytic O−O bond cleavage, there is no apparent relationship between the O−O BDE and the relative reactivity of the peroxide.[4] The high reactivity of peroxides has traditionally been ascribed to the weakness of the O−O bond linkage and hence the ease with which it is homolytically cleaved. One of the most blatant examples to the contrary is the relative reactivity of peroxyacetic acid and trifluoroperoxyacetic acid. Both peroxides have essentially the same O−O BDE (48.3 and 48.9 kcal/mol),[4a] but the latter oxidizing agent is orders of magnitude more reactive,[5] suggesting the intervention of a heterolytic O−O bond cleavage that takes advantage of the greater stability of the trifluoroacetate anion as a leaving group.

Methodology

There are several general theoretical procedures available to obtain thermodynamical data within chemical accuracy (ca. 2 kcal/mol). The Gaussian-2 (G2) theory introduced by Pople and co-workers[6a] was shown to have a mean absolute deviation over a set of 125 experimental atomization energies of 1.2 kcal/mol. The limited ap-

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plicability computationally of the G2 theory with molecules having more than six heavy (nonhydrogen) atoms comes with the use of fourth-order Møller–Plesset calculations along with various large basis sets up to 6-311G(2df,p). The G2(MP2) procedure, which limits basis set corrections to second-order Møller–Plesset perturbation theory, was developed to allow the treatment of larger systems such as those described in this study.[6b] The G2(MP2) procedure replicates the set of 125 experimental energies with a mean absolute deviation of 1.58 kcal/mol. The CBS-Q method[7] is equally reliable for calculating the BDE of peroxides.[4a] The CBS-Q method has a lesser disk and CPU time requirement than G2 calculations on molecules of the same size. Both theoretical procedures are based upon geometries optimized at MP2/6-31G(d) levels. At 0 K the G2(MP2) enthalpy is obtained by addition of the following components:

$$\text{QCISD(T)/6-311G}^{**} + \text{MP2/6-311+G(3df,2p)} - \text{MP2/6-311G}^{**} + \text{ZPE} + \text{HLC} \quad (1)$$

In the above equation, ZPE is the zero point vibrational energy, and HLC is a high level correction that provides energies with the best fit to the set of experimental data. The ZPE and the thermal corrections to the enthalpies are routinely obtained by the scaling of HF/6-31G(d) frequencies by 0.8929; whereas the HLC contribution is given by $\text{HLC} = (-4.81\text{n}_\beta - 0.19\text{n}_\alpha) \times 10^{-3}$ au, where n_β and n_α are the number of β and α valence electrons.

Molecular orbital calculations were carried out using the Gaussian 98 program system[8a] utilizing gradient geometry optimization.[8b] The thermodynamical analysis at 298 K was carried out using the rigid rotor and harmonic oscillator approximations. For the study of the reactions of O-transfer from silyl peroxides, we located both minima and TSs at the MP2/6-31G(d) level of theory and characterized them by frequency calculations at the HF/6-31G(d) level. Single point MP4(SDTQ) calculations were performed on selected molecules to improve the activation barriers. The larger fully methylated systems were optimized at the B3LYP level of theory[8e–h] with the 6-31G(d) and 6-31+G(d,p) basis sets, and in some cases single point calculations are done with the 6-311+G(3df,2p) basis set. We have previously demonstrated[4] that this DFT method gives adequate geometries for the structures involved in these oxidation procedures. The activation energies for alkene epoxidation are typically underestimated by 5–6 kcal/mol relative to the recommended procedure[4b] that utilizes single point QCISD(T)/6-31G* energies with B3LYP/6-31G* optimized geometries.

Results and Discussion

(a) The Energetics of Oxygen–Oxygen Bond Cleavage. In the present study we examine initially the relationship between the reactivity of alkyl versus silyl peroxides and their O–O bond dissociation energies. Most of the experimental work has been carried out with bis(trimethylsilyl) peroxide(**1**) and an X-ray geometry determination of this structure has been reported.[9] The MP2/6-31G* optimized geometry is in quite good agreement with experimental data (Figure 1) especially when it is taken into account that these geometries refer to different physical states.

The most significant deviation in geometry is the Si–O–O–Si dihedral angle, and this is most likely a consequence of crystal packing forces. Because of the relatively long Si–O and Si–C bond lengths (1.72 and 1.87 Å), the trimethylsilyl (TMS) group actually presents less of a steric presence than a *tert*-butyl group despite the apparent size of the TMS group.

We summarized the calculated O–O bond dissociation energies (BDE) for different alkyl and silyl peroxides (Table 1).

In general, the ΔE (the difference in total energies between the peroxide and its oxygen radical fragments derived from homolytic O–O bond cleavage) computed at the MP2/6-31G* level are on average 6–7 kcal/mol higher than the ΔH_0 (enthalpy of dissociation at 0 K) calculated by the G2(MP2) method. Upon the basis of the decreasing O–O BDE (ΔH_{298}) for HO–OH, CH_3O–OH, and CH_3O–OCH_3 (Table 1), a methyl group increases the stability of an oxygen radical (relative to HO•) by a little more than 5 kcal/mol. When a *tert*-butyl substituent is compared to a methyl group, the relative stability of the alkoxy radical produced upon O–O bond cleavage in the hydroperoxide is increased by an additional 2–3 kcal/mol. One may also deduce from this summary of computed O–O bond dissociation energies (ΔH_{298}) for hydroperoxides that the relative stability of a trimethylsilyl oxygen radical ($(CH_3)_3SiO•$) is 4.8 kcal/mol *less* than a *tert*-butoxy radical ($(CH_3)_3CO•$). The calculated entropies for O–O bond dissociation are notably higher than the experimental ΔS_0 values reported that range from 11 to 14 cal/(mol K).[10] However, in many instances the experimental entropies do not correspond to simple first-order homolysis but involve thermal rearrangement attending O–O bond rupture (see below).

The O–H BDE (ΔH_{298}) of CH_3O–H, $(CH_3)_3CO$–H, and $(CH_3)_3SiO$–H are also consistent with this order of oxygen radical stability where the energy requirements for homolytic O–H cleavage of $(CH_3)SiO$–H is 12.2 kcal/mol greater than that of $(CH_3)_3CO$–H (Table 2).

These data suggest that a silyl peroxide should be less reactive than the corresponding alkyl peroxide if the

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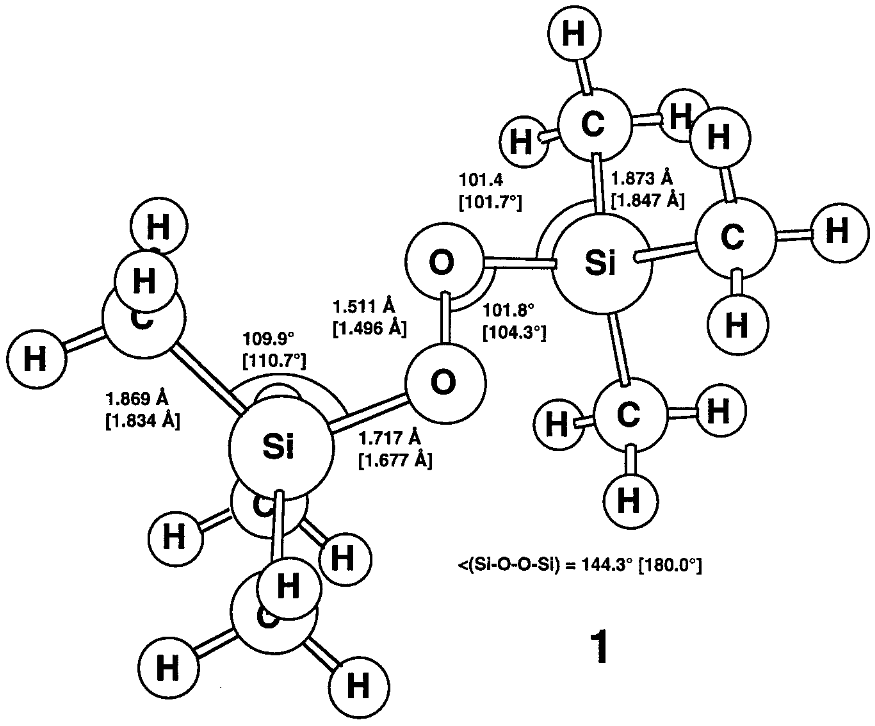

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Figure 1. Optimized geometry for bis(trimethylsilyl) peroxide (**1**) at the MP2/6-31G* level. X-ray experimental values are in brackets (ref 9).

Table 1. Calculated O−O Bond Dissociation Thermodynamical Data. Values in Parentheses Are Based on G2 or CBS-Q Results. Values in Brackets AreEstimated According to the Expression BDE(X−Y) = (1/2)(BDE(X−X) + BDE(Y−Y)) for Unsymmetrical Molecules and BDE(X−X) = 2BDE(X−H)-BDE(H−H) for Symmetrical Molecules

	ΔE (kcal/mol)[a]		ΔH_0 (kcal/mol)		$\Delta H_{298.15}$ (kcal/mol)		$\Delta G_{298.15}$ (kcal/mol)		$\Delta S_{298.15}$(cal/(mol K))
	MP2(full)/6-31G(d)		G2MP2		G2MP2		G2MP2		HF/6-31G(d)
HO−OH	55.54		49.87	(48.92)[b]	51.40	(50.45)[b]	42.21		30.83
CH_3O-OH	52.36	[52.66]	44.86	(43.78)[b] [44.92]	46.04	(44.96)[b] [46.04]			
CH_3O-OCH_3	49.78		39.98	(38.72)[b]	40.68	(39.43)[b]			
$(CH_3)_3CO-OH$	53.89	[54.33]	47.13		48.30		37.39		36.58
$(CH_3)_3CO-OC(CH_3)_3$	53.13			[44.39]		[45.20]		[32.58]	
$(CH_3)_3CO-OCH_3$		[51.5]							
$H_3SiO-OH$	57.82	[58.15]	51.26	[52.07]	52.46	[53.42]	42.02	[42.05]	35.00
$H_3SiO-OSiH_3$	60.76		54.27		55.45		41.90		45.43
$(CH_3)_3SiO-OH$	57.86		52.10		53.10		42.51		35.54
$(CH_3)_3SiO-OC(CH_3)_3$		[57.6]							
$(CH_3)_3SiO-OSi(CH_3)_3$	62.05	(56.71)[c] [60.18]		(56.24)[c] [54.33]		(56.83)[c] [54.8]		[42.81]	

[a] These differences in total energy, ΔE, are without ZPE. All other values are by convention with ZPE. [b] Values taken from ref 4a. [c] Values calculated by the CBS-Q method.

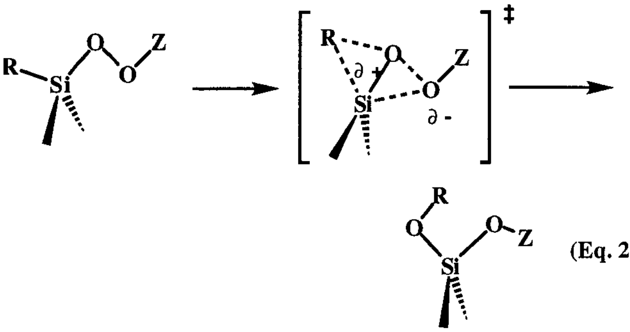
oxidative reaction involves a simple first-order homolytic O−O bond cleavage process. The fact that silyl peroxides are in general more reactive oxygen donors than alkyl peroxides is then consistent with an O−O bond cleavage that is more heterolytic in nature and requires 1,2-silicon bridging to assist with the O−O bond heterolysis. Indeed, the increasing electron affinity (EA) of oxygen radicals, $CH_3O\cdot$, $(CH_3)_3CO\cdot$, and $(CH_3)_3SiO\cdot$ (Table 2) suggests that the silyloxy anion would be a better leaving group based upon the stability of the developing oxyanion in the TS than its corresponding alkyl-substituted oxygen analogues. The proton affinities (PA) of this series of oxyanions are also in accord with this trend suggesting a greater stability of the larger more polarizable TMS oxyanion. A comparison of the EA and PA data (Table 2, column 4th) suggests that the relative energy of the TMS oxygen anion is 26.2 and 14.0 kcal/mol more stable than the corresponding *tert*-butyl oxygen anion. Upon the basis of the acidity of the parent alcohol (Me_3SiOH $pK_a = 10$; Me_3COH $pK_a = 17$),[1] the TMS oxyanion should be a much better leaving group in this type of S_N2 nucleophilic displacement at oxygen. The intrinsic capacity of the TMS group to stabilize an adjacent negative charge is consistent not only with a favorable heterolytic O−O bond rupture but is also suggestive of the potential for 1,2-silicon bridging in the transition state (TS) for oxygen atom transfer.

(b) The Role of 1,2-Silicon Bridging in O−O Bond Thermolysis. The kinetics of the thermal decomposition of simple silyl peroxides have been studied.[11] These data suggest that trialkylsilyl alkyl peroxides are more stable than their corresponding dialkyl peroxides consistent with the relative stability of the $(CH_3)_3SiO\cdot$ and $(CH_3)_3CO\cdot$ oxyradicals noted above. Di-*tert*-butyl peroxide exhibits an enthalpy of activation for O−O bond cleavage of 36 kcal/mol while the ΔH for the *tert*-butyl trimeth-

Table 2. Proton and Electron Affinities and O−H Bond Dissociation Energies for Alcohol Derivatives

	ΔE (kcal/mol) MP2(full)/ 6-31G*	ΔH_0 (kcal/mol) G2MP2	$\Delta H_{298.15}$ (kcal/mol) G2MP2	$\Delta G_{298.15}$ (kcal/mol) G2MP2
	Proton Affinity			
CH_3O^-	−403.99	−381.54	−381.26	−381.87
H_3SiO^-	−368.29	−356.09	−355.61	−356.59
$(CH_3)_3CO^-$	−396.38	−373.83	−373.62	−374.01
$(CH_3)_3SiO^-$	−371.36	−360.09	−359.63	−360.65
	Electron Affinity			
CH_3O radical	−10.29	−37.11	−37.11	−37.36
H_3SiO radical	−58.60	−77.56	−77.78	−76.95
$(CH_3)_3CO$ radical	−19.51	−46.83	−46.92	−46.29
$(CH_3)_3SiO$ radical	−54.90	−72.90	−73.11	−71.99
	O−H Bond Dissociation Energy			
$CH_3O{-}H$	100.65	104.89	106.10	98.79
$H_3SiO{-}H$	113.26	119.89	121.12	113.10
$(CH_3)_3CO{-}H$	102.25	106.91	108.27	99.86
$(CH_3)_3SiO{-}H$	112.63	119.24	120.47	112.19

ylsilyl peroxide is increased to 41 kcal/mol. However, the thermal decomposition of bis(trimethylsilyl) peroxide, BTSP, ($\Delta H^{\ddagger} = 32$ kcal/mol) is much more facile than either of the above. These data are not consistent with a simple heterolytic O−O bond cleavage but rather suggest the intervention of a 1,2-alkyl migration in concert with O−O bond breaking (eq 2).[10]



(Eq. 2)

We initiated a model study of the thermal decomposition of silyl peroxides by comparing the relative energy of first-order homolytic O−O bond cleavage in trimethylsilyl hydroperoxide (**2**) to that of a 1,2-methyl migration (Figure 2).

The transition state, **TS-3**, for concerted 1,2-methyl migration exhibited a modest Si−C bond elongation (13%) as it migrated to the backside of the O−O bond. The $O_1{-}O_2{-}Si{-}C_5$ dihedral angle of 180° and the extent of O−O bond elongation (26%) excludes a silyl oxygen radical on the reaction pathway for rearrangement. The classical barrier ($\Delta E^{\ddagger} = 47.9$ kcal/mol) for the rearrangement of **2** at the MP2/6-31G* level is 10.0 kcal/mol lower than that for simple homolytic cleavage (57.86 kcal/mol at the MP2/6-31G* level of theory). The predicted activation energy for methyl migration (47.9 kcal/mol, MP4//MP2/6-31G*) is considerably higher than the reported enthalpy (32 kcal/mol)[11] for the thermal decomposition of BTSP **1** but the agreement is improved if consideration is given to the systematically higher MP2 ΔE values for O−O bond cleavage than the G2(MP2) ΔH^{298} values in Table 1. The driving force for this thermally induced rearrangement is the high exothermicity of the reaction ($\Delta E = -41.0$ kcal/mol at the MP4//MP2/6-31G* level). These data corroborate the earlier suggestion made by Curci[10] that simple homolysis of silyl peroxides in solution can be overwhelmed by low energy multiple bond cleavage processes resulting in artificially low apparent enthalpies of O−O bond dissociation. We recently reported a high level ab initio study (G2) for the thermal decomposition of diacyl peroxides where the O−O bond breaking was complicated by the other lower energy processes and was not a simple first-order reaction.[4a] Thus, if the assumption is made that the observed reaction is a first-order process then such lower energy rearrangements involving O−O bond cleavage can lead to a lower assessment of the O−O BDE. This study prompted us to suggest that the average O−O BDE should be increased from a generally accepted value of 34 kcal/mol to about 45 kcal/mol.[4] We also corroborate the general observation[10] that O−O BDE for peroxide XO−OY could be derived from the mean BDE of XO−OX and YO−OY to within ~1 kcal/mol.[4] For the larger peroxides we successfully used the expression 2ROOH = ROOR + HOOH to estimate the BDE of symmetrical peroxides. As evidenced in Table 1 this concept also holds for the series of peroxides considered in the present study.

(c) The Effect of Silicon Bridging in Oxygen Atom Transfer. The effectiveness of a naked alkoxide anion as a leaving group in S_N2-type displacements is notoriously poor. Since the cleavage of the O−O bond in oxygen transfer from an alkyl hydroperoxide is typically heterolytic in nature, stabilization of the developing oxyanion in the transition state (TS) plays a major role in determining the rate of oxidation. Prior ab initio calculations have established that the transfer of oxygen from an alkyl hydroperoxide requires a specific type of acid catalysis.[12a] Although kinetic evidence supports the participation of ROH or ROOH in the rate-determining step,[13] our calculations suggest that some form of protolysis must accompany the O−O bond cleavage in order to have a reasonable rate of oxidation. A 1,2-hydrogen shift to an adjacent heteroatom bearing a lone-pair of electrons is a formally forbidden four-electron process that is associated with a high activation barrier.[12b] The barrier height for the oxidation of ammonia with methyl hydroperoxide (CH_3OOH) in the absence of acid catalysis is 46.5 kcal/mol.[12a] The oxidation of dimethyl sulfide with the dimer of hydrogen peroxide also has a prohibitively high classical barrier ($\Delta E^{\ddagger} = 40.8$ kcal/mol) in the absence of protonation of the leaving group.[12a] The barriers for

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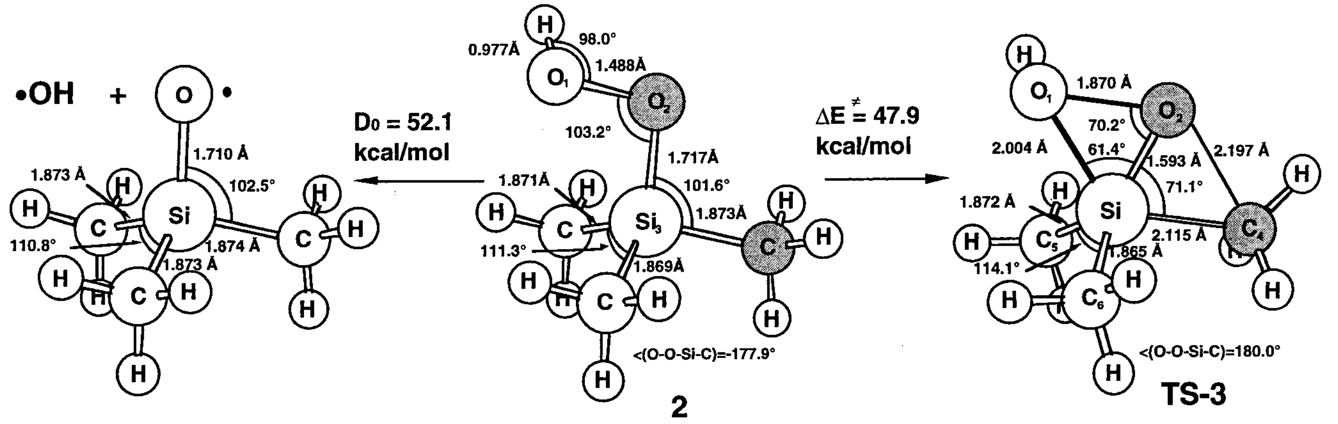

Figure 2. O−O bond dissociation and the transition structure (**TS-3**) for the 1,2-methyl rearrangement in trimethylsilyl hydroperoxide (**2**). Geometries were calculated at the MP2/6-31G*. The O−O D0 is at the G2(MP2) level, and the rearrangement activation energy is at the MP4//MP2/6-31G* level.

oxygen atom transfer in alkyl hydroperoxides can be reduced substantially by transfer of a proton to the departing alkoxide anion in the TS.

Oxygen transfer from peroxy acids, on the other hand, involves an intramolecular 1,4-proton shift that affords a neutral carboxylic acid as a leaving group.[12c] This is indeed a leaving group phenomenon since the proton shift from the OH group of the peroxyacid to the carbonyl oxygen takes place after the barrier is crossed. The rate of oxygen transfer from peroxyacids also does not correlate with the O−O bond dissociation energy (BDE).[4] For example, peroxyformic acid and peroxynitrous acids exhibit the same barrier heights for two-electron oxidations but have widely different O−O BDE (48.4 vs 22.0 kcal/mol at the G2 level).[4a] As noted above peroxyacetic and trifluoroperoxy acetic acids have essentially the same BDE but vastly different reactivities.[5b] These oxidation reactions are two-electron donor processes consistent with heterolytic O−O bond cleavage where the stability of the leaving group plays a dominant role in determining the propensity for oxygen atom donation.

Silicon hydroperoxides exhibit an oxygen donor ability that may be attributed largely to 1,2-bridging of the trimethylsilyl group in the TS for oxygen atom transfer since the hydroxyl group plays no discernible role.[1,10] We now provide quantitative theoretical evidence that the neighboring silicon group effectively stabilizes the negative charge developing on the oxygen leaving group in a concerted transfer of oxygen to nucleophiles. By employing the model bis(trihydridosilyl) peroxide **4** for the oxidation of ammonia to its oxide, we established the 1,2-bridging role of the silyl group in the transition state. This abbreviated model peroxide allows us to separate the effect of the silicon atom in the absence of its methyl substitutents. The origin of the stabilizing effect associated with β-silyl groups has been proposed to be due to three possible factors. (a) induction due to the electropositive silicon, (b) hyperconjugation of the silyl group especially with carbocations, or (c) the ability of the silicon to form a pentavalent siliconium bridge.[14] The classical activation barrier for oxygen atom transfer from **4** to NH_3 is only 13.1 kcal/mol at the MP4/6-31G*//MP2/6-31G* level of theory (Table 3). The H_3Si group is bonded to the distal oxygen atom of **4** with a bond distance of 1.97 Å (Figure 3).

Table 3. Activation Energies for the Oxidation of Selected Nucleophiles by Peroxides

			ΔE≠ (kcal/mol)	
peroxide	nucleophile		MP2/ 6-31G*	MP4//MP2/ 6-31G*
$H_3SiO{-}OSiH_3$	NH_3	**TS-6**	17.69	13.10
$H_3SiO{-}OSiH_3$	CH_4	**TS-7**	50.44	46.97
$H_3SiO{-}OH$	NH_3	**TS-10**	37.17	34.40
$H_3SiO{-}OH$	NH_3	**TS-9**	23.37	19.21
$(CH_3)_3SiO{-}OH$	NH_3	**TS-14**	32.41	
$(CH_3)_3SiO{-}OH$	NMe_3	**TS-15**	23.49	
$CH_3O{-}OH^b$	NH_3			46.52[a]
$CH_3O{-}OCH_3$	NH_3	**TS-13**	58.17	52.22[a]
$H(C{=}O)O{-}OH^c$	NH_3		21.47	18.35[b]
$H(C{=}O)O{-}OH^c$	NMe_3		4.25	0.94
dimethyl dioxirane[d]	NH_3		28.60	23.60
dimethyl dioxirane[d]	NMe_3		10.70	6.30

[a] Includes ZPE values calculated at the MP2/6-31G* level. [b] Values from ref 12a. [c] Values from ref 12c. [d] Values from ref 12e.

This bridging silicon atom is bonded to the adjacent oxygen by a 2p−3p O−Si bonding interaction with no evidence of silicon d-orbital participation. The proximal Si−O bond is only slightly elongated in **TS-6** (0.02 Å), and the overall reaction is slightly endothermic (2.9 kcal/mol). By contrast, the barrier for the oxidation of methane (**TS-7**) is 47.0 kcal/mol despite the exothermicity of −52.1 kcal/mol (Figure 3). This relatively high barrier tends to exclude an oxenoid TS for the oxygen insertion process.[15] An isomeric silyl ether oxide, structure **5**, for this model oxidizing agent is also precluded by the **4**−**5** isomerization energy of 42.1 kcal/mol. In contrast to the corresponding carbon oxygen-ylide analogue ($(CH_3)_2O{-}O$), the silyl ether oxide **5** does not exist as an energy minimum, and the reversion of **5** to **4** occurs without a barrier on the MP2/6-31G* hypersurface.

We next examined the effect of the bridging silyl group relative to a bridging hydrogen atom in oxygen atom transfer. The oxidation of ammonia with the model trihydridosilyl hydroperoxide **8** (Figure 4) can proceed by two distinct pathways.

With the 1,2-silyl bridge acting to reduce the charge separation attending O−O bond cleavage in **TS-9**, the

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(14) For a recent discussion of the β-effect of silicon, see: Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.

(15) Bach, R. D.; Su, M.-D.; Schlegel, H. B. *J. Am. Chem. Soc.* **1994**, *116*, 5379.

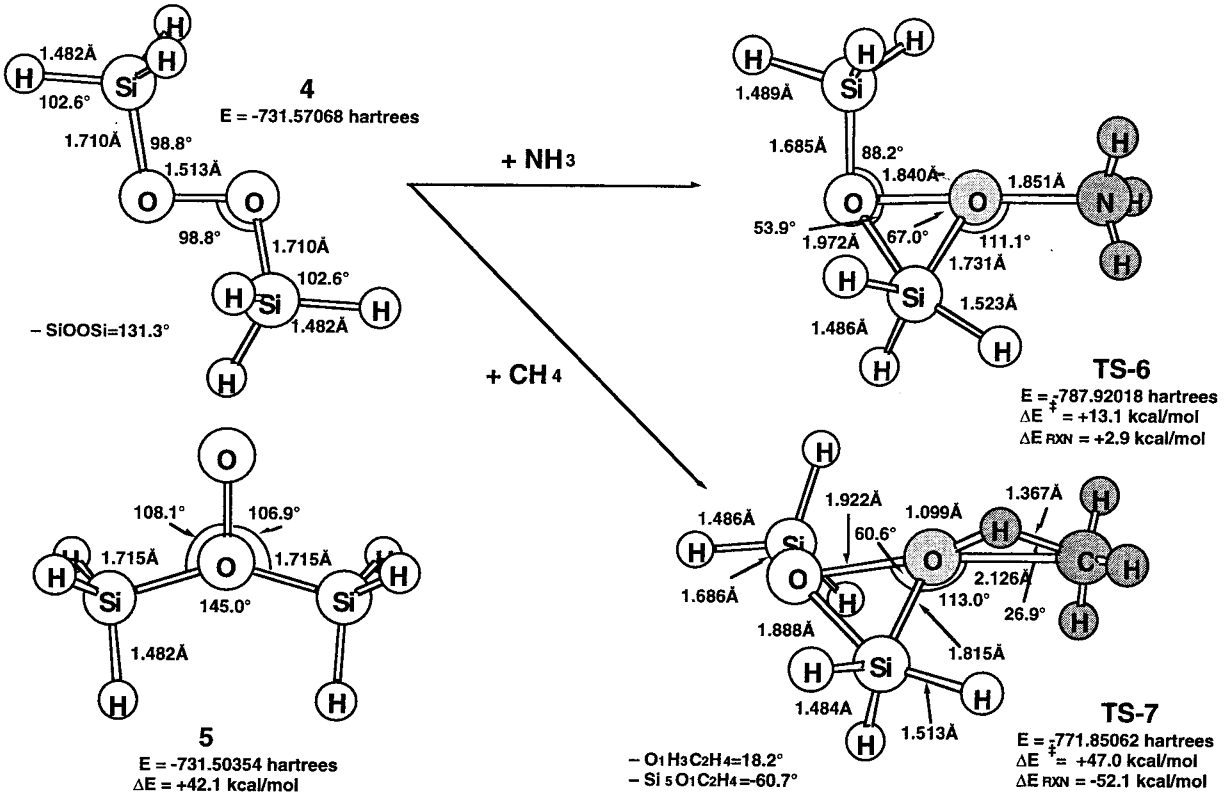

Figure 3. The transition structures (**TS-6** and **TS-7**) for the oxidation of ammonia and methane with the disilyl peroxide (**4**) and its disilyl ether oxide isomer (**5**). Geometries were calculated at the MP2/6-31G*. Energes are at the MP4//MP2/6-31G* level. The ΔE of **5** is relative to **4**. The ΔE_{RXN} is the difference between total energy of reactants and products. The total energies of the reactants, ammonia and methane are −56.37126 and −40.35479 au. The total energies of the products, ammonia oxide, methanol, and disilyl ether are −131.30267, −115.37385, and −656.63461 au

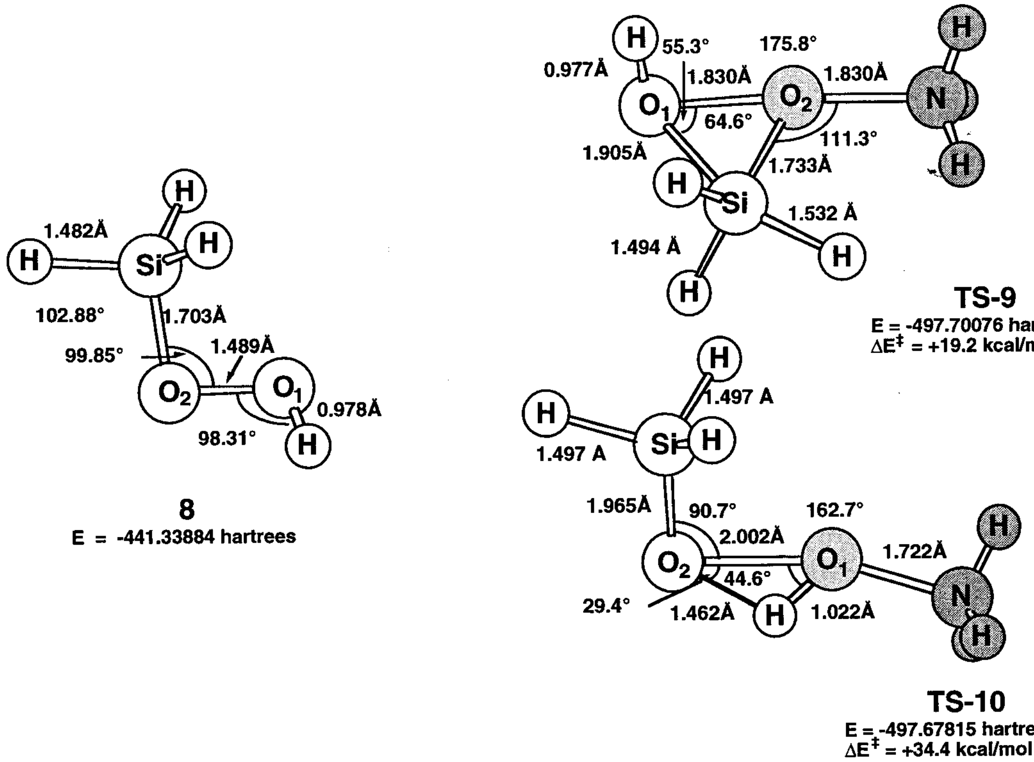

Figure 4. The transition structures (**TS-9** and **TS-10**) for the oxidation of ammonia with silyl hydroperoxide (**5**) optimized at the MP2/6-31G*. Energes are at the MP4//MP2/6-31G* level.

barrier is 19.2 kcal/mol. However, when the hydrogen is bridging as in **TS-10**, the barrier increases to 34.4 kcal/mol providing an internal quantitative estimate of the energetic effect of a 1,2-silyl bridge. The effect of the

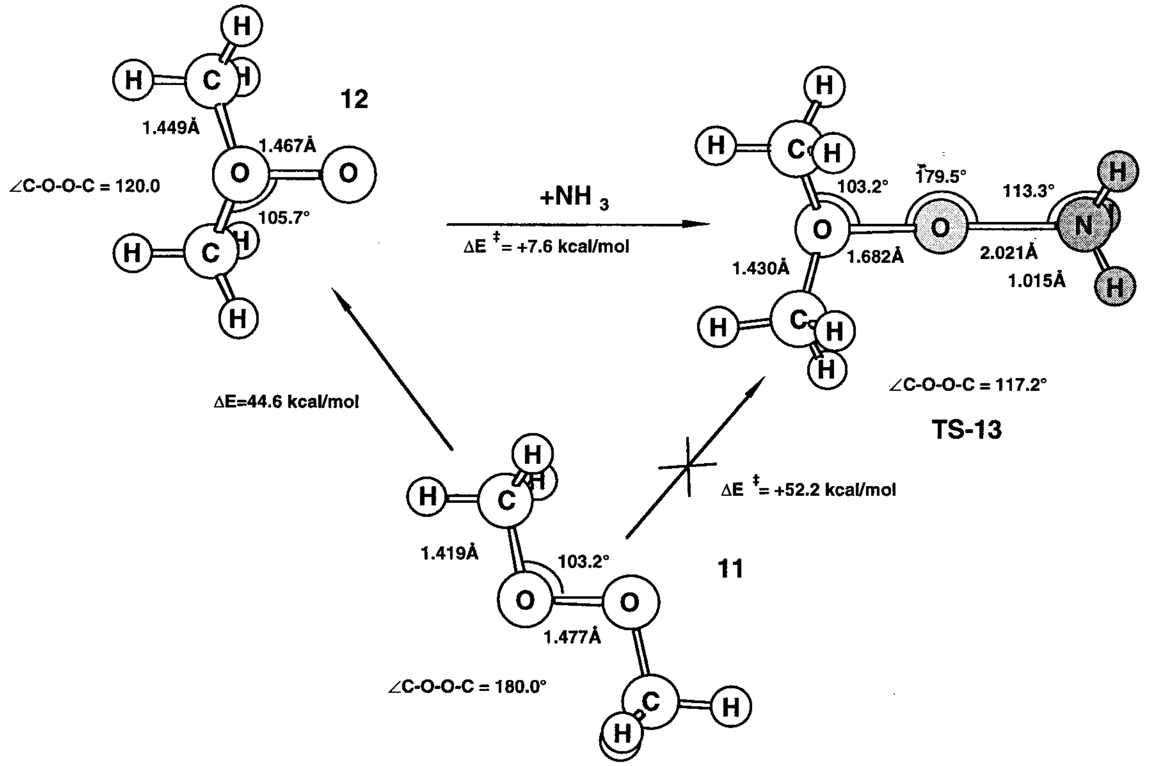

Figure 5. Dimethyl peroxide (**11**) and its dimethyl ether oxide isomer (**12**), and the transition structure for the oxidation of ammonia by dimethyl ether oxide (**TS-13**). The ΔE of **12** is relative to **11**. Geometries were calculated at the MP2/6-31G*. Energies are at the MP4//MP2/6-31G* level.

second silyl group on the barrier for oxygen transfer can be estimated by comparing the energetics of oxygen transfer from disilyl peroxide **4** (**TS-6)** and hydroperoxide **8** (**TS-9)**, the first barrier height being 6.1 kcal/mol lower in energy. A comparison with related oxidizing agents at the MP4//MP2 level is given in Table 3.

In an effort to provide a direct comparison between the efficacy of a bridging silicon relative to a bridging carbon, we attempted to locate a transition state for the oxidation of ammonia with a bridging methyl group. The dimethyl ether oxide form of dimethyl ether **12** does exist as a minimum that is 44.6 kcal/mol higher in energy than **11** (Figure 5).

However, we could not locate a first-order saddle point for oxygen atom transfer from **11** with a bridging methyl group like that in **TS-9** emphasizing the relevance of the pentavalent siliconium bridge in lowering the barrier for O−O bond cleavage. The barrier for oxygen transfer measured from the high energy intermediate is only 7.6 kcal/mol, but the overall barrier from ground state **11** is 52.2 kcal/mol representing nearly a 40 kcal/mol increase in barrier relative to disilyl peroxide **4**.

(d) The Effect of Alkyl (Methyl) Substitution on the Activation Barrier. Prior experience[12d,e] has taught us that alkyl groups on the nucleophile affect both the position of the TS along the reaction coordinate and the magnitude of the barrier. This can be particularly true for a bridging TS where both steric and electronic effects can potentially influence the magnitude of the barrier. To illustrate this point, the classical barriers for the oxidation of ammonia (**TS-14**) versus trimethylamine (**TS-15**) with trimethylsilyl hydroperoxide (**2**) are 32.4 and 23.5 kcal/mol, respectively (Figure 6).

The Mulliken group charge on the trimethylsilyl (TMS) group in the ground-state reagent **2** (group charge = 0.51) and **TS-14** (group charge = 0.24) supports the idea that this neighboring group has effectively reduced the negative charge on the developing anionic leaving group. In the TS the group charge on the departing HO^- group is more negative by 0.3 electrons, and it becomes bonded to the TMS group after the barrier is crossed. The proximal oxygen becomes more positive by 0.2 electrons in **TS-15.** As noted above in **TS-9** the Si−O bond to the proximal oxygen is only slightly elongated (0.03 Å) while the developing Si−O bond of the migrating TMS group in **TS-15** is 1.978 Å. The S_N2-like TS is confirmed by the O−O−NUC angle of 168.9°. The percent O−O bond elongation (25%) and the degree of N−O bond formation (34%) suggest that this is a late TS consistent with the relatively high predicted barrier height (23.5 kcal/mol). The overall reaction energy ($\Delta E = 2.4$ kcal/mol) for this slightly endothermic process is consistent with the relatively high activation barrier. The methyl groups in the TMS functionality raise the activation energy by 9.0 kcal/mol (MP2/6-31G*, Table 3) relative to the hydrido analogue (**TS-9**), an effect contrary to what is observed with increasing substitution on the nucleophile. This increase in activation is most likely the steric influence of the three methyl groups.

On comparison of the barriers for the oxidation of trimethylamine with peroxyformic acid, peroxynitrous acid, and dimethyl dioxirane (DMDO) at the same level of theory ($\Delta E^{\ddagger} = 0.94$, 1.6, and 6.3 kcal/mol, respectively),[16] it becomes obvious that trimethylsilyl hydroperoxide (**2**) is only of modest reactivity despite the intervention of the bridging TMS group (Table 4).

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[16] Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C.; Marquez, M.; Estevez, C. M.; Baboul, A. G.; Schlegel, H. B. *J. Phys. Chem.*, A **1997**, *101*, 6092.

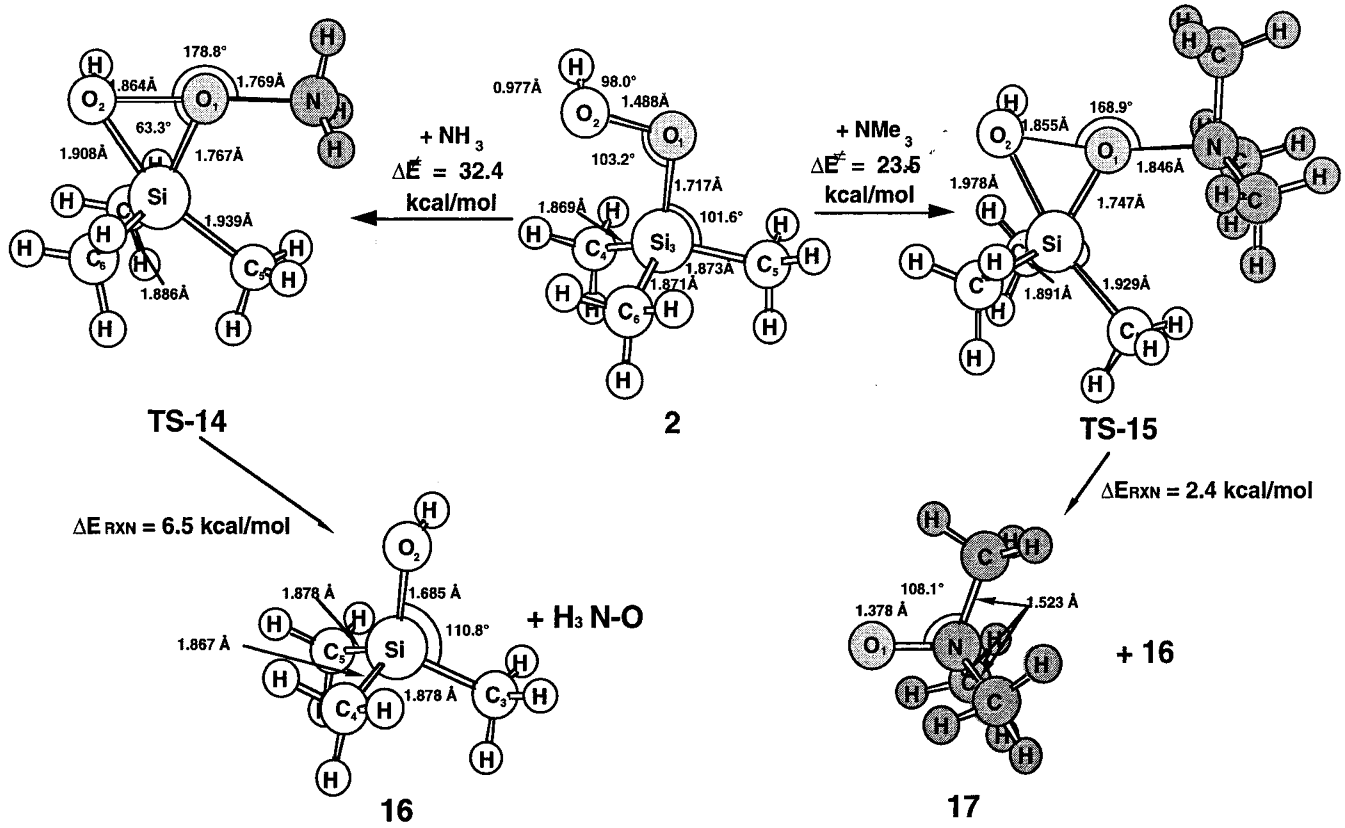


Figure 6. The transition structures for the oxidation of ammonia (**TS-14**) and trimethylamine (**TS15**) with trimethylsilyl hydroperoxide (**2**) optimized at the MP2/6-31G*. The activation barriers are with respect to isolated reactants.

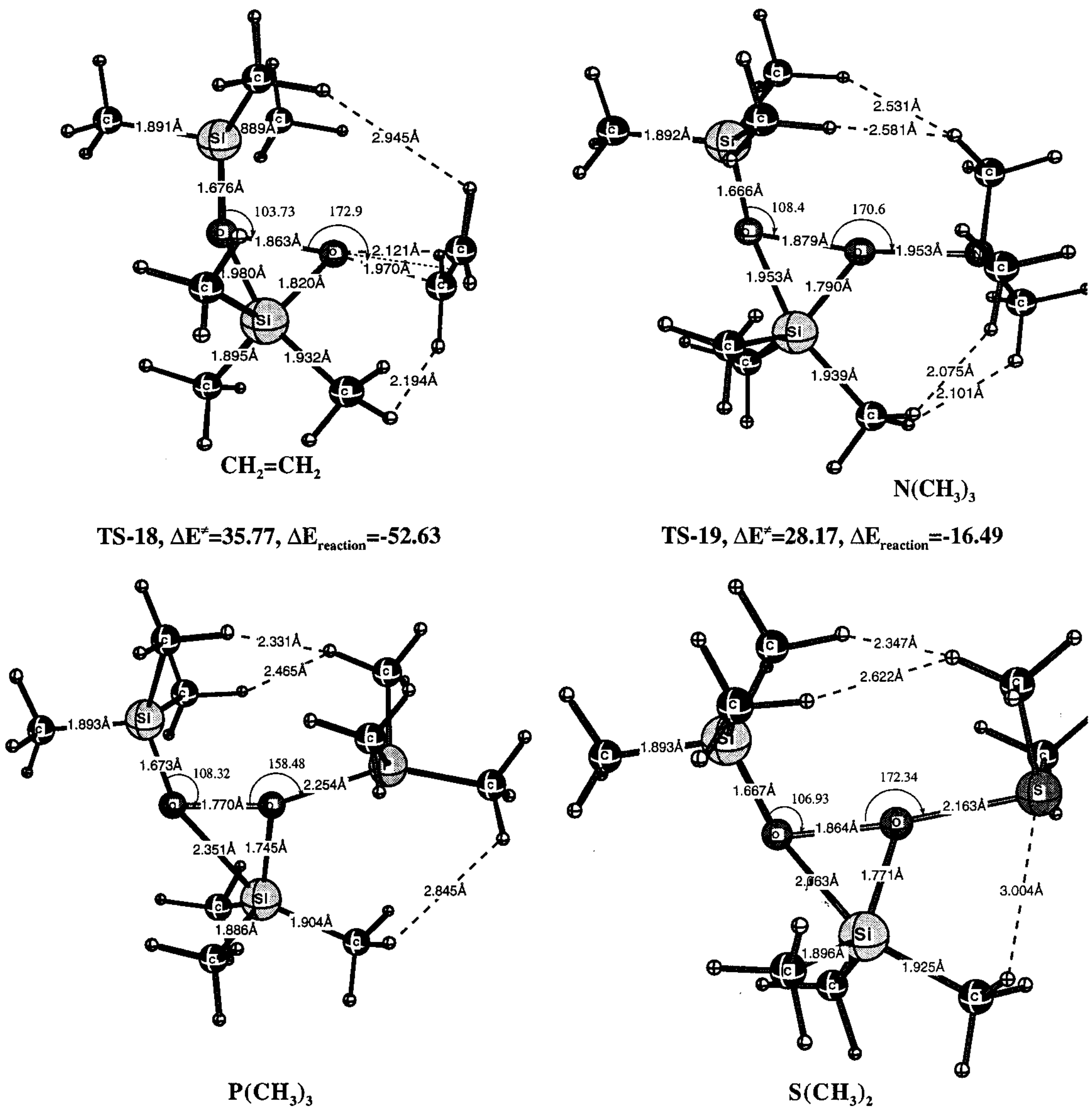
Table 4. DFT (B3LYP) Classical Activation Energies ($\Delta E^{\ddagger}$, kcal/mol) for the Oxidation of Selected Nucleophiles by Peroxides

peroxide	nucleophile	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d,p)
$(CH_3)_3SiOOH$	NH_3	27.05	
$(CH_3)_3SiOOH$	$N(CH_3)_3$	24.94	
$(CH_3)_3SiOOSi(CH_3)_3$	NH_3	25.90	
$(CH_3)_3SiOOSi(CH_3)_3$	$N(CH_3)_3$	25.02	28.17[a]
$(CH_3)_3SiOOSi(CH_3)_3$	$S(CH_3)_2$	22.73	21.53[a]
$(CH_3)_3SiOOSi(CH_3)_3$	$P(CH_3)_3$	15.85	17.44[a]
$(CH_3)_3SiOOSi(CH_3)_3$	ethene	31.95	35.77[a]
$(CH_3)_3SiOOSi(CH_3)_3$	*E*-2-butene	31.65	33.31
$(CH_3)_2CF_3SiOOSi\ CF_3\ (CH_3)_2$	*E*-2-butene	23.52	25.77
$(CH_3)_2CF_3SiOOSi\ CF_3\ (CH_3)_2$	ethene	25.35	
F_3SiOOH	*E*-2-butene	6.85	
$F_3SiOOSiF_3$	*E*-2-butene	2.17	

[a] Barriers are based upon B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d) calculations

(e) Oxidation with Bis(trimethylsilyl) Peroxide (1). The above exercise with the H_3SiOO group has served to distinguish the role of the silicon atom from that of its methyl substitutents in oxygen transfer from $(CH_3)_3SiOO$. We now examine the combined effect of methyl substitutents in bis(trimethylsilyl) peroxide (BTSP) and on the nucleophile itself in an effort to separate out both steric and electronic effects. These data are summarized in Table 4. Even though BTSP(**1**) has a higher O−O G2 BDE ($\Delta\Delta H_{298} = 9.6$ kcal/mol, Table 1), this TMS peroxide is a more efficient oxygen donor than its corresponding carbon analogues as a consequence of 1,2 silicon bridging and the greater stability of the developing TMS oxyanion relative to an alkoxide anion (see above). However, it is also obvious that the activation barriers for oxidation of ammonia and trimethylamine with **1** do not differ significantly (Table 4), and that the barriers for oxygen transfer from bis(trimethylsilyl)peroxide (**1**) and trimethylsilyl hydroperoxide (**2**) to trimethylamine (25.0 and 24.9 kcal/mol) are essentially identical at the B3LYP/6-31G* level of theory. Although $N(CH_3)_3$ is more nucleophilic than NH_3, it also has a greater steric requirement that serves to temper its reactivity. In general, the oxygen donor ability of **1** is intermediate between a peracid and H_2O_2. It would appear that earlier suggestions by Curci[1] that the $(CH_3)_3Si$ group may function as an “organic proton” in these reactions has merit. The barrier heights for the oxidation of dimethyl sulfide (22.7 kcal/mol) and trimethylphosphine (15.9 kcal/mol) are also considerably higher than those calculated for oxidation with either peroxyformic acid or dimethyl dioxirane.

The relative activation barriers are consistent with experiment[1,10] where the oxidation of sulfur in thioxane by **1** occurs over 30 times faster than a tertiary amine (Et_3N) and in $CHCl_3$ is over 700 times faster than the nitrogen in an arylamine (*N*,*N*-dimethyl-*p*-anisidine). In general, silyl peroxides are from 50 to 100 times more effective than analogous alkyl peroxides in oxygen atom transfer to sulfur in $CHCl_3$ solution.[1] Rate data also suggest that the oxidation of thioxane by $(CH_3)_3COOH$ and $(CH_3)_3COOC(CH_3)_3$ is $\approx 10^2$ and 5×10^3 slower than that observed for **1**. However, it is also evident that this bis silyl peroxide will not suffice to oxidize weakly nucleophilic alkenes with any appreciable rate since this barrier for the epoxidation of ethylene (32.0 kcal/mol; B3LYP/6-31G(d)) is substantially higher than that for oxidation of ethylene with peroxyformic acid (14.1 kcal/



TS-18, $\Delta E^{\neq}$=35.77, $\Delta E_{reaction}$=-52.63 **TS-19, $\Delta E^{\neq}$=28.17, $\Delta E_{reaction}$=-16.49**

TS-20, $\Delta E^{\neq}$=17.44, $\Delta E_{reaction}$=-86.41 **TS-21, $\Delta E^{\neq}$=21.53, $\Delta E_{reaction}$=-36.52**

Figure 7. The transition structures for oxidation of the series of nucleophiles with the bis(trimethylsilyl) peroxide (**1**) optimized at the B3LYP/6-31G* level of theory. Energies are at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level.

mol; B3LYP/6-31G(d);18.8 kcal/mol at the QCISD(T)//QCISD/6-31G(d)) level).

For the sake of comparison, we examined the same series of nucleophiles used previously[12d,e] with HCO_3H and DMDO(C_2H_4, $(CH_3)_3N$, $(CH_3)_3P$, and $S(CH_3)_2$). Examination of the transition structures for this series of nucleophiles in Figure 7 (**TS-18**, **TS-19**, **TS-20**, and **TS-21**) suggests that steric inhibition of the approach of the electrophilic oxygen to the nucleophile is problematic, but there is ample evidence of silicon bridging in the TSs.

It would appear that a combination of electronic effects relating to the relatively high BDE for the O−O bonds in **1** and **2**, as well as a relatively late transition state, are responsible for their subdued reactivity relative to a peroxy acid as the oxygen donor. The Si−O distances for the bridging silicon atoms range from 1.95 to 2.40 Å. The O−O bond distance in ground-state bis peroxide **1** is 1.496 Å. Upon the basis of an O−O distance of 1.88 Å, the oxidation of $(CH_3)_3N$ has the latest transition state (**TS-19**, $\Delta E^{\ddagger} = 25.02$ kcal/mol) while the earliest TS for the oxidation of $(CH_3)_3P$ has the shortest O−O distance (1.77 Å, $\Delta E^{\ddagger} = 15.85$ kcal/mol). As noted above (Table 3), these classical barriers are substantially higher than the corresponding reactions where the oxygen donor is peroxyformic acid, peroxynitrous acid, or DMDO. The transition structures resemble a backside S_N2 attack by the nucleophile (NUC) on the O−O bond of the 1,2-silicon bridged peroxide with O−O−NUC angles ranging from 158.5 (**TS-20**) to 173° (**TS-18**).

(f) The Effect of Electron-Withdrawing Groups on the Barrier Heights. It is well established that electron-withdrawing substitutents such as the CF_3 group can increase the rate of oxidation with peroxyacids and dioxiranes. For example, the barrier height for the epoxidation of *E*-2-butene is reduced from 13.5 kcal/mol with peroxyacetic acid to just 6.4 kcal/mol with trifluoroperoxyacetic acid (B3LYP/6-31+G(d,p)).[17] This corre-

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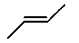
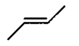
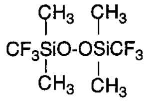
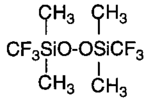
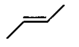
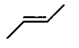
(17) Bach, R. D. in Adam, W.; Degen, H.-G.; Pastor, A.; Saha-Möller, C. R.; Schambony, S. B.; Zhao, C.-G. Preparative Use of Peroxidic Oxidants for Oxygen-Transfer Reactions. In *DFG Research Report on Peroxide Chemistry: Mechanistic and Preparative Aspects of Oxygen Transfer*; Adam, W., Saha-Möller, C. R., Eds.; Wiley-VCH: Weinheim, 2000.

Table 5. Inductive Effect in the Epoxidation of *E*-2-Butene. Activation Barriers ($\Delta E^{\ddagger}$) Are Based upon B3LYP/6-31G(d) Total Energies of the Isolated Reactants and the Corresponding Transition Structures

reaction	$\Delta E^{\ddagger}$, (kcal/mol)	$\Delta E_{reaction}$, (kcal/mol)
 + $(CH_3)_3SiO\text{-}OSi(CH_3)_3$	31.65 (33.31)[a]	-55.73
$CH_2{=}CH_2$ + $(CH_3)_3SiO\text{-}OSi(CH_3)_3$	31.95 (35.77)[b]	-52.63
 +  $CF_3\overset{CH_3}{\underset{CH_3}{Si}}O\text{-}O\overset{CH_3}{\underset{CH_3}{Si}}CF_3$	23.52	-60.11
$CH_2{=}CH_2$ +  $CF_3\overset{CH_3}{\underset{CH_3}{Si}}O\text{-}O\overset{CH_3}{\underset{CH_3}{Si}}CF_3$	25.34	-57.01
 + $F_3SiO\text{-}OH$	6.85	-55.35
 + $SiF_3O\text{-}OSiF_3$	2.17	-65.53

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[a] Numbers calculated by use of B3LYP//B3LYP/6-31+G(d,p) total energies. [b] B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) barriers.

sponds to an estimated increase in the rate of formation of the epoxide of greater than 10^5. If these silyl peroxides are to become useful synthetic reagents, then it appears necessary to activate the oxygen transfer with either electron-withdrawing groups or Lewis acid catalysis or both. For example, the barrier heights for the epoxidation of ethylene and *E*-2-butene with BTSP(**1**) are 32.0 and 31.7 kcal/mol (Table 5) with no apparent effect of the alkyl groups on the double bond.

To test the effectiveness of the CF_3 group, we replaced one methyl group on each TMS group of **1** affording bis silyl peroxide **22** ($(CH3)_2CF_3SiOOSiCF_3(CH3)_2$) and the activation barrier (**TS-23** ,Figure 8) for the epoxidation of *E*-2-butene decreased by 8.2 kcal/mol (23.5 kcal/mol, Table 4) but is still too high for practical laboratory use in the absence of catalysis. When the fluorine substituents are directly attached to the silicon atom as in **24** (F_3SiOOH) and **26** ($F_3SiOOSiCF_3$), the inductive effects are much greater, and the barriers are reduced to 6.9 and 2.2 kcal/mol. These data clearly provide evidence that the oxygen donor propensity of a silyl peroxide responds markedly to the substitution of an electronegative substituent directly on the silicon atom.

Conclusions

Quantitative theoretical evidence suggests that the neighboring silicon group in silyl peroxides effectively stabilizes the developing negative charge on oxygen in a concerted transfer of an oxygen atom to nucleophiles. The

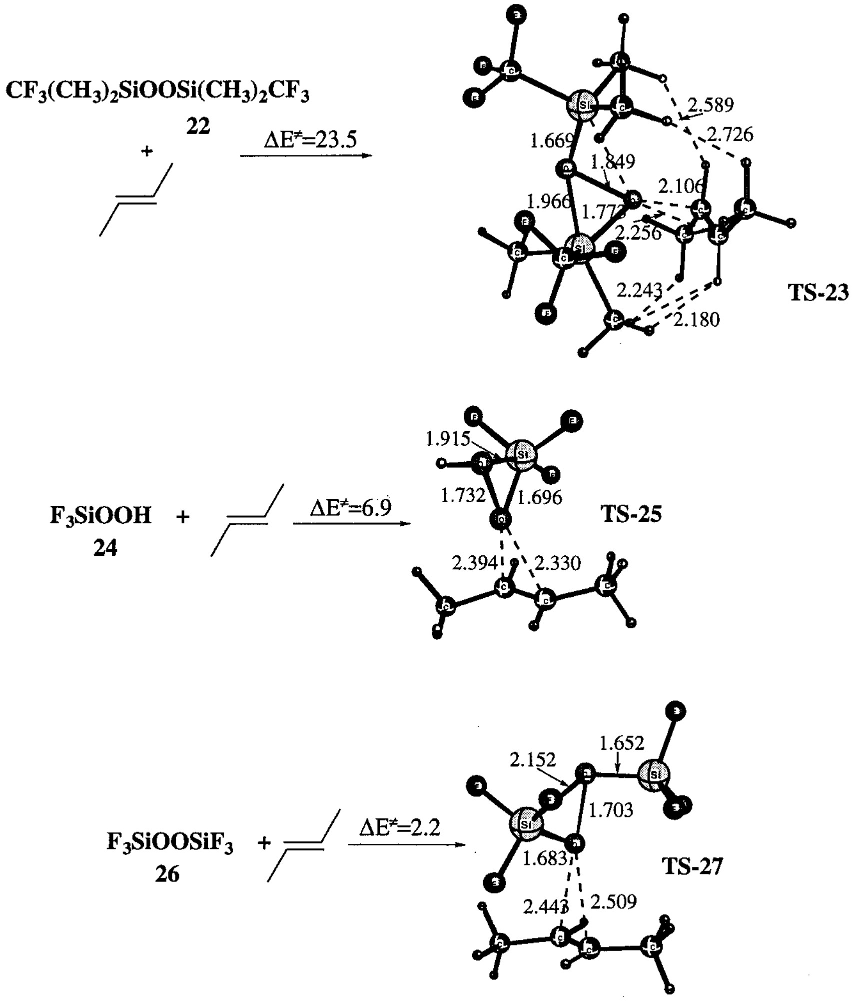

Figure 8. The electron-withdrawing effect of fluoride substitution on the activation barrier ($\Delta E^{\ddagger}$) for the epoxidation of *E*-2-butene. Transition structures are optimized at the B3LYP/6-31G(d) level.

bond dissociation energy of a dialkyl peroxide is 11−12 kcal/mol less than that of the corresponding silyl peroxide. The order of reactivity is in the opposite direction with the silyl peroxide being much more reactive as an oxygen atom donor.

The $(CH_3)_3CO\cdot$ radical is estimated to be from 4.8 to 12.2 kcal/mol more stable than the $(CH_3)_3SiO\cdot$ radical while the order of stability of the corresponding oxyanions is reversed with the more polarizable silyloxy anion being 14.0−26.2 kcal/mol more stable.

The oxygen atom donor propensity of bis(trimethylsilyl) peroxide (**1**) can be markedly enhanced by the presence of electronegative elements such as CF_3−Si or F−Si being directly substituted on the silicon atom.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9901661). We are also thankful to the National Centers for Supercomputing Applications (Urbana, Illinois) and the University of Kentucky (Lexington, Kentucky) for generous amounts of computer time. C.M.E. also thanks the Xunta de Galicia (Spain) for a grant that made his stay at the University of Delaware possible.

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