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Organosilicon peroxides: radicals and rearrangements

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1. Introduction

The alkyl hydroperoxides, **1**, and dialkyl peroxides, **2**, have been known since the beginning of the last century, and they show a wide range of homolytic and heterolytic reactivities which are interesting, and important both mechanistically and experimentally.[1–4]

About 50 years ago, with the burgeoning of organometallic chemistry, the question began to be asked whether there might not be analogous organometallic peroxides, which might show similar interesting and useful properties.

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An obvious family to look for was the silyl hydroperoxides, disilyl peroxides, and silyl alkyl peroxides, **3–5**, and these were the first organometallic peroxides to be isolated.

$ROOH$	$ROOR$	R_3SiOOH	$R_3SiOOSiR_3$	R_3SiOOR'
1	**2**	**3**	**4**	**5**

The silyl peroxides have been reviewed previously.

Brandes and Blaschette's article (1974, in German)[5] and Aleksandrov's (1982)[6] are still useful in that they cover thoroughly the extensive early Russian work, and include comprehensive listings of the silyl hydroperoxides, disilyl peroxides, silyl alkyl peroxides, and silyl heterometal peroxides, which were known at those dates.

More recent reviews by Tamao[7] and Ando,[8] emphasise the use of the silyl peroxides as reagents in organic synthesis. The present review will briefly cover these aspects, but will focus more on the physical organic chemistry, and the comparison with the familiar organic peroxides, which has stimulated much of the work on the organosilicon peroxides, and doubtless will do so in the future. Ricci's review in 1996 in Advances in Silicon Chemistry,[9] covered some of the same ground, but it is not readily available, and the present article brings the subject up to date.

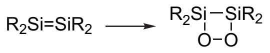
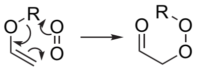
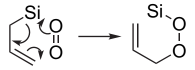
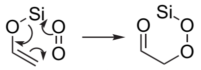
The chemistry of the organic peroxides is dominated by the weakness of the O–O bond. In the organosilicon peroxides, a second important factor is the strength of the Si–O bond, and the combination of these two factors leads to a series of novel and interesting intramolecular rearrangements,[9] where the terms homolytic and heterolytic, nucleophilic and electrophilic, cease to be appropriate, although the reactions may show some of these characteristics. The section headings which include these terms should not be taken too literally.

A few explosions have been reported when silyl peroxides were being prepared or handled. The pure silyl peroxides, including bis(trimethylsilyl) peroxide, which is commercially available, are thermally stable up to about 150 °C, but they are less stable in the presence of impurities, and can readily be hydrolysed to absolute hydrogen peroxide. Our early attempts to prepare bis(trimethylsilyl) peroxide were discouraged when the product from the reaction of concentrated hydrogen peroxide and trimethylchlorosilane exploded when it was being distilled,[10] and there is a similar report of an explosion of the residue from such a distillation.[11] Explosions have also been reported when solutions of the disilyl peroxide came in contact with metal syringe needles.[12] The 1:2 complex, which 1,4-diazabicyclo[2.2.2]octane (DABCO) forms with H_2O_2, has also been reported to explode in the presence of trace metals.[13] A safety screen should always be used when organic and organometallic peroxides are being handled.

2. Preparation

The preparations of peroxides, whether organic or heteroatomic, rarely involve the creation of a new O–O bond:

Table 1. Comparison between the methods of preparing carbon peroxides and silicon peroxides

Reagent	Carbon peroxide	Silicon peroxide
HOOH	$HOO^{-}\curvearrowright R\text{-}X \longrightarrow ROOH$ The most general route to alkyl hydroperoxides and dialkyl peroxides	$HOO^{-}\curvearrowright Si\text{-}X \longrightarrow SiOOH$ The most general route to silyl hydroperoxides and disilyl peroxides
ROOH	$ROO^{-}\curvearrowright R'\text{-}X \longrightarrow R'OOR$ The most general route to dialkyl peroxides $ROOH + C{=}C + HgX_2 \longrightarrow ROOCCHgX$ In common use	$ROO^{-}\curvearrowright Si\text{-}X \longrightarrow SiOOR$ The most general route to alkyl silyl peroxides $SiOOH + C{=}C + HgX_2 \longrightarrow SiOOCCHgX$ Established, but seldom used
$^3O_2$	$RH \longrightarrow [ROO\bullet] \longrightarrow ROOH$ Important for compounds with weak C–H bonds  Restricted to special olefins  Established, but not used preparatively	$SiH \longrightarrow [SiOO\bullet] \longrightarrow SiOOH$ Established mechanistically, but not used preparatively  General for disilenes  Known only in an Ar matrix at 40 K
$^1O_2$	 Unknown for allyl hydrocarbons: hydrogen transfer occurs in preference to carbon transfer  Unknown for enol ethers	 Unknown as yet, but expected under favourable conditions  Well established for silyl enolates
$O_2^{-\bullet}$	$RX \longrightarrow [ROO\bullet] \longrightarrow ROOH \text{ or } ROOR$ Known, but little used preparatively	$SiX \longrightarrow [SiOO\bullet] \longrightarrow SiOOH \text{ or } SiOOSi$ As yet, only siloxanes have been isolated
O_3	$RH \longrightarrow [ROOO\bullet] \longrightarrow ROOOH$ Well established	$SiH \longrightarrow [?] \longrightarrow SiOOOH$ Used as a route to HOOOH

usually that bond is already intact in the reagent, that is, it is hydrogen peroxide or an alkyl hydroperoxide, triplet or singlet oxygen, the superoxide radical anion, or ozone. We were not able to repeat the claim in a patent that disilyl peroxides could be prepared by treating the sodium silanolates with chlorine or bromine, which would involve the formation of a peroxide bond.[14]

A summary of the comparison between the ways of making the more common carbon peroxides and silicon peroxides, classified according to the reagent, is given in Table 1, where the symbol Si refers to any Si(IV) group.

2.1. Silyl hydroperoxides, R_3SiOOH

2.1.1. From HOOH. Hydrogen peroxide is more acidic than water (pK_a 11.6 and 14.0, respectively), but HOO^- is a stronger nucleophile that HO^-. This is commonly ascribed to the orbital interaction of electron pairs on the two peroxidic oxygen atoms, which is referred to as the α-effect (see Section 3).[15] Further, electronegative substituents, which are bonded to silicon are much more readily displaced by nucleophiles than in the corresponding organic compounds, and the most common route to the silyl hydroperoxides and disilyl peroxides is by the nucleophilic substitution of a functionally substituted silane with hydrogen peroxide under basic conditions. Trimethylsilyl hydroperoxide, which was prepared from the chlorosilane and hydroperoxide in the presence of pyridine, appeared at first to be unstable,[16] but this was probably due to the presence of impurities, and the pure, stable, hydroperoxide can be obtained from the reaction of 98% hydrogen peroxide with a silylamine, which is prepared in situ from the chloride and ammonia, e.g., Eq. 1.[17] Hydroperoxides prepared in this way are stable at room temperature for several weeks.

$$Ph_3SiCl \xrightarrow[\text{ii. 98\% } H_2O_2,\ 0\ ^\circ C]{\text{i. } NH_3} [Ph_3SiNH_2] \longrightarrow Ph_3SiOOH\ 56\% \tag{1}$$

It is rather surprising that there appear to be no reports of attempts to avoid the rather hazardous 98% hydrogen peroxide by using instead one of its safer amine complexes such as DABCO·$2H_2O_2$ or urea·H_2O_2 (hyperol), which have been used for preparing the disilyl peroxides (see Section 2.2).

The number of silyl hydroperoxides, which have been isolated is still small enough for a complete list to be given (Table 2).

2.1.2. From $^3O_2$. The autoxidation of hydrocarbons to give alkyl hydroperoxides is an extremely important process, which is involved in many reactions in industry and in the environment. It has been studied extensively, and is well established to be a radical chain process, propagated by the $R^•$ and $ROO^•$ radicals. Much less has been done on the autoxidation of the Si–H bond. Silane itself, SiH_4, is pyrophoric, but the flammability of the chlorosilanes, $Cl_{4-n}SiH_n$, decreases with increasing chlorination, and pure Cl_3SiH is not flammable in air, any flammability being ascribed to the presence of Cl_2SiH_2. When autoxidation does occur, any hydroperoxide formed is usually reduced by the silane, and the observed product is the silanol.

Table 2. Silyl hydroperoxides

R_3SiOOH	Bp (°C/mmHg) or mp (°C)	Preparative method[a]	Ref.
Me_3SiOOH	30–32/11	A, B	16,17
$(PhCH_2)_3SiOOH$	60–61	B	17
$(C_6H_{13})_3SiOOH$	Oil	B	17
$^tBuMe_2SiOOH$	—	C	18
$MePh_2SiOOH$	40–41	B	17
$Ph_2(4\text{-}MeC_6H_4)SiOOH$	75	B	17
Ph_3SiOOH	110–112	B	17

[a] A: 100% H_2O_2, pyridine, R_3SiCl. B: 98% H_2O_2, NH_3, R_3SiCl. C: $^3O_2$, R_3SnH.

Organosilyl hydrides are more reactive than hydrocarbons towards oxygen, but, with some exceptions, can be handled in air. Autoxidation can be induced with a radical initiator, and the mechanism of the reaction has recently been investigated and shown to be the same as that for hydrocarbon autoxidation.[18] The autoxidation of *tert*-butyldimethylsilane, initiated by azodiisobutyronitrile, gave the hydroperoxide in 99–100% yield (Eq. 2), and the kinetics of the reaction (Eq. 7) were those required by the radical chain process, which is shown in Eqs. 3–6, where R_i is the rate of initiation.

$$^tBuMe_2SiH + O_2 \xrightarrow{\text{AIBN}} {}^tBuMe_2SiOOH \tag{2}$$

$$\text{Initiation} \quad \text{Initiator} \xrightarrow{R_i} R_3Si\bullet \tag{3}$$

$$\text{Propagation} \begin{cases} R_3Si\bullet + O_2 \longrightarrow R_3SiOO\bullet & (4) \\ R_3SiOO\bullet + R_3SiH \xrightarrow{k_p} R_3SiOOH + R_3Si\bullet & (5) \end{cases}$$

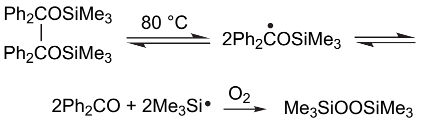
$$\text{Termination} \quad 2R_3SiOO\bullet \xrightarrow{2k_t} \text{products} \tag{6}$$

$$\frac{-d[O_2]}{dt} = k_p[R_3SiH]\left(\frac{R_i}{2k_t}\right)^{1/2} \tag{7}$$

As the termination rate constant, k_t, is not known, the value of the propagation rate constant, k_p, cannot yet be derived.

Presumably, the spontaneous inflammability of silanes, SiH_nCl_{4-n} (n=2–4), implies a more rapid value of k_p for the rate-limiting abstraction of hydrogen by silylperoxyl radicals.

Bis(trimethylsilyl) peroxide has also been obtained from the reaction of the disilyl ether of benzpinacol with oxygen.[19] The most likely mechanism would appear to be via the silyl radical, which is formed by dissociation (Eq. 8).



$$\begin{matrix} Ph_2COSiMe_3 \\ | \\ Ph_2COSiMe_3 \end{matrix} \underset{}{\overset{80\ ^\circ C}{\rightleftharpoons}} 2Ph_2\dot{C}OSiMe_3 \rightleftharpoons 2Ph_2CO + 2Me_3Si\bullet \xrightarrow{O_2} Me_3SiOOSiMe_3 \tag{8}$$

Polyhydrosilanes H(–RSiH–)$_n$H are similarly sensitive to air. The reaction of the model compound $(Me_3Si)_2MeSiH$ was shown to follow a radical chain mechanism, to give the compound $(Me_3SiO)_2MeSiH$ via the radical $(Me_3Si)_2MeSiOO^•$, which rearranges by migrations of silicon to oxygen.[20]

The silylperoxyl radicals $R_3SiOO^{\bullet}$ (R_3=Et_3, Bu_3, $^{t}Bu_3$, Ph_3, or $MePh_2$) have been identified by ESR spectroscopy.[21] Photolysis of di-*tert*-butyl peroxide in solutions of the hydrosilane gives the *tert*-butoxyl radical, which abstracts hydrogen from the silane to give the silyl radical, which in turn reacts with oxygen to give the silylperoxyl radical (Eqs. 9–11). It is surprising that Me_3SiH showed only the spectrum of the $Me_3Si^{\bullet}$ radical.

$$^{t}\mathrm{BuOO}^{t}\mathrm{Bu} \xrightarrow{h\nu} 2\,^{t}\mathrm{BuO}\bullet \qquad (9)$$

$$^{t}\mathrm{BuO}\bullet + \mathrm{Me_3SiH} \longrightarrow {}^{t}\mathrm{BuOH} + \mathrm{Me_3Si}\bullet \qquad (10)$$

$$\mathrm{Me_3Si}\bullet + \mathrm{O_2} \longrightarrow \mathrm{Me_3SiOO}\bullet \qquad (11)$$

$$2\mathrm{Me_3SiOO}\bullet \rightleftharpoons \mathrm{Me_3SiOOOOSiMe_3} \qquad (12)$$

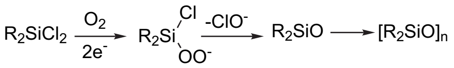
The silylperoxyl radicals are very persistent below about 233 K, and showed *g* values 2.027–2.029. The isotopically labelled radicals $^{t}Bu_3Si^{17}OO^{\bullet}$ and $^{t}Bu_3SiO^{17}O^{\bullet}$ showed ^{17}O hyperfine coupling with $a^{17}O$ 14.6 and 25.4 G, respectively, confirming that the two oxygen atoms are nonequivalent, and that the radical is linear and not cyclic (as the stannylperoxyl radical is).[21] A line at *g* 2.083, which was observed during the γ-radiolysis of solid $^{t}Bu_3SiH$ at 77 K, was assigned to g_z for the $^{t}Bu_3SiOO^{\bullet}$ radical, and it was suggested that the high *g*-value was the result of an expanded SiOO angle, through $O2p(\pi)$–$Si3d(\pi)$ bonding,[22] but no such expansion is apparent in the structures of the disilyl peroxides compared with the dialkyl peroxides.

The silylperoxyl radicals are in equilibrium with the corresponding disilyl tetraoxides $R_3SiOOOOSiR_3$ (Eq. 12), with ΔH^{o} -11 ± 2 kcal mol^{-1}, $\Delta S^{o}<-30$ cal mol^{-1} deg^{-1}. Above about 233 K, the silylperoxyl radicals decayed; the products were not identified, but they are probably $R_3SiOOSiR_3$ and O_2, by analogy with the behaviour of the *tert*-alkylperoxyl radicals.[21]

2.1.3. From $O_2^{-\bullet}$. Superoxides such as $K^{+}O_2^{-\bullet}$, react nucleophilically with alkyl halides to give alkylperoxyl radicals, $ROO^{\bullet}$, which then react by electron transfer with further superoxide to give the peroxide anions ROO^{-}, or self-react to give ROOR and O_2.[23] The reactions are usually carried out in an organic solvent in the presence of a crown ether, but they find little application in synthesis compared with $O_2^{=}$ or HOO^{-}, except in biologically important investigations.

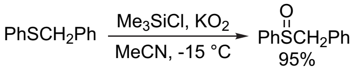
There have been few reports of the reaction of superoxide with silanes, and none as yet which describe the formation of silyl peroxides.

KO_2 reacts with trimethylchlorosilane to give hexamethyldisiloxane and oxygen.[24] Cathodic reduction of oxygen in the presence of a dialkyldichloro- or dialkyldialkoxy-silane under anhydrous conditions in DMSO, MeCN, or an ionic liquid, gives oligosiloxanes that are suggested to be formed via the silanones (Eq. 13), but it is not clear whether the nucleophile is $O_2^{-\bullet}$ or $O_2^{=}$, and what is the precise mechanism by which the silanone is formed.[25,26]


(13)

$$\mathrm{R_2SiCl_2} \xrightarrow[2e^-]{O_2} \mathrm{R_2Si}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{OO^-}\end{smallmatrix} \xrightarrow{-\mathrm{ClO^-}} \mathrm{R_2SiO} \longrightarrow [\mathrm{R_2SiO}]_n \qquad (13)$$

Sulfides are oxidised in excellent yield to sulfones by KO_2 in the presence of Me_3SiCl. The reaction is inhibited by DABCO, which is a radical scavenger, and it seems likely that the oxidising species is the $Me_3SiOO^{\bullet}$ radical (Eq. 14).[27]


(14)

$$\mathrm{PhSCH_2Ph} \xrightarrow[\mathrm{MeCN,\ -15\ °C}]{\mathrm{Me_3SiCl,\ KO_2}} \underset{95\%}{\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{CH_2Ph}} \qquad (14)$$

2.2. Disilyl peroxides, $R_3SiOOSiR_3$

2.2.1. From HOOH. The disilyl peroxides are more stable than the silyl hydroperoxides, and can be prepared from the reaction of hydrogen peroxide with a chlorosilane in the presence of a base (e.g., Eq. 15),[16] or by an extension of the reaction shown in Eq. 1, with an appropriate ratio of reagents (Eq. 16).[17]

$$\mathrm{Me_3SiCl} \xrightarrow[\mathrm{anhyd.\ H_2O_2,\ 0\ °C}]{\mathrm{H_2O_2,\ C_5H_5N}} \mathrm{Me_3SiOOSiMe_3} \qquad (15)$$

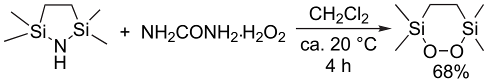
$$\mathrm{Ph_3SiCl} \xrightarrow[\substack{\mathrm{ii.\ 98\%\ H_2O_2,\ 0\ °C}\\ \mathrm{98\ s}}]{\mathrm{i.\ NH_3}} [\mathrm{Ph_3SiNH_2}] \longrightarrow \underset{56\%}{\mathrm{Ph_3SiOOSiPh_3}} \qquad (16)$$

To avoid the use of concentrated hydrogen peroxide, $DABCO\cdot2H_2O_2$ can be used (e.g., Eq. 17),[28] and details are given in *Organic Syntheses* by which $Me_3SiOOSiMe_3$ can be obtained on a 40 g scale by this reaction, with a yield of 71%.[29] $Me_3Si^{18}O^{18}OSiMe_3$ has been prepared using $DABCO/H^{18}O^{18}OH$.[30]

$$4\mathrm{Me_2PrSiCl} + \mathrm{N(CH_2CH_2CH_2)_3N.2H_2O_2} \xrightarrow[\mathrm{CH_2Cl_2,\ rt,\ 2\ h}]{\mathrm{N(CH_2CH_2CH_2)_3N}} \underset{96\%}{4\mathrm{Me_2PrSiOOSiPrMe_2}} \qquad (17)$$

The hexamethylenetetramine complex can similarly be used,[31] and details have been given for preparing bis(trimethylsilyl) peroxide on a 75 g scale in 86% yield, by use of the urea/H_2O_2 complex and bis(trimethylsilylurea) (Eq. 18).[13] A 1,2-dioxa-3,6-disilacyclohexane has been prepared by an analogous process (Eq. 19).[32]

$$\underset{0.5\ \mathrm{mol}}{\mathrm{Me_3SiNHCONHSiMe_3}} + \underset{0.5\ \mathrm{mol}}{\mathrm{NH_2CONH_2{\cdot}H_2O_2}} \xrightarrow[\substack{\mathrm{reflux}\\ \mathrm{12\ h}}]{\mathrm{CH_2Cl_2}} \underset{86\%}{\mathrm{Me_3SiOOSiMe_3}} \qquad (18)$$


(19)

The alternative of using the urea/H_2O_2 complex and R_3SnCl does not appear to have been reported.

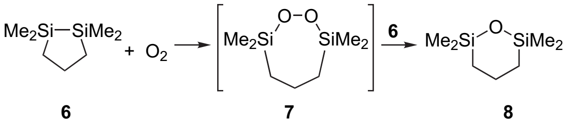
Mixed disilyl peroxides, $R_3SiOOSiR'_3$, can be prepared from the reaction between R_3SiOOH and R'_3SiCl in the presence of base (e.g., Eq. 20);[33] germyl silyl peroxides,

$Ph_3GeOOSiR'_3$ are formed from the equivalent reaction of Ph_3GeOOH and R'_3SiCl, and antimonyl silyl peroxides, $Ph_4SbOOSiPh_3$ and $Ph_3Sb(OOSiPh_3)_2$ from Ph_4SbX or Ph_3SbX_2 and Ph_3SiOOH.[34]

$$Me_3SiCl + Ph_3SiOOH \xrightarrow{NH_3} Me_3SiOOSiPh_3 \quad 71\% \tag{20}$$

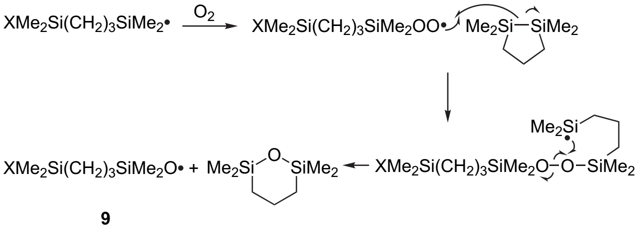
In 1974, Brandes and Blaschette could list 20 disilyl peroxides in their review, and in 1982 there are 35 in Aleksandrov's review. Some typical members are given in Table 3. Bis(trimethylsilyl) peroxide is commercially available, and has a growing popularity as a reagent in organic synthesis (see Section 4).

2.2.2. From $^3O_2$. Simple hexaalkyldisilanes are stable to air, but if the SiSi bond is strained (e.g., **6**) or carries more than two fluorine atoms, exothermic autoxidation occurs, but the products that can be isolated are the disiloxanes, e.g., **8**. Disilyl peroxides were shown to be reduced by disilanes to disiloxanes, and it was assumed that the initial product was the cyclic disilyl peroxide **7** (Eq. 21).[37]



(21)

This may be an oversimplification. The autoxidation is inhibited by tri-*tert*-butylphenol, and is a chain reaction, propagated presumably by the silyl and silylperoxyl radical, in which case the reaction must be inter- rather than intramolecular (Eq. 22), and the peroxide would be a linear or cyclic oligomer or polymer. Alternatively, intramolecular attack of the silyl radical on the peroxide bond could give the cyclic disiloxane, in which case the siloxyl radical **9** would be the propagating species.



(22)

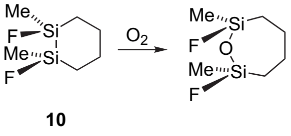
Table 3. Disilyl peroxides

$R_3SiOOSiR_3$	Bp (°C/mmHg) or mp (°C)	Preparative method[a]	Ref.
$Me_3SiOOSiMe_3$[b]	38/30	A	16
$Et_3SiOOSiEt_3$	62/0.02	B	28
$Pr_3SiOOSiPr_3$	95/0.01	B	28
$Me_2(EtO)SiOOSi(OEt)Me_2$	82–84/20	B	28
$(PhCH_2)_3SiOOSi(CH_2Ph)_3$	110–111	C	17
$PhMe_2SiOOSiMe_2Ph$	32.5–33.5	A	6
$Ph_3SiOOSiPh_3$	140–141	C	17
$Me_3SiOOSiPh_3$	66.5–67	D	35
$Et_3SiOOGePh_3$	40–41	E	35
$Ph_3SiOOGePh_3$	155	E	36

[a] A: 100% H_2O_2, pyridine, R_3SiCl. B: DABCO·$2H_2O_2$, DABCO, R_3SiCl. C: 98% H_2O_2, NH_3, R_3SiCl. D: Ph_3SiOOH, Me_3SiCl, base. E: Ph_3GeOOH, R_3SiCl, base.

[b] NMR: δ ^{1}H 0.16, δ ^{13}C −1.27, δ ^{29}Si 27.35 ppm. IR: ν OO 944 cm^{-1}.

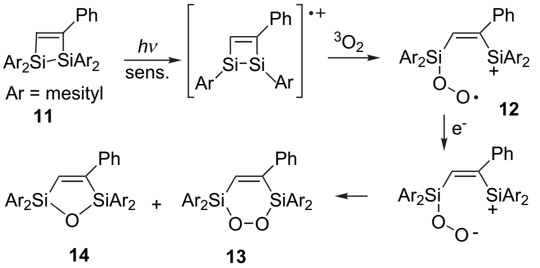
The corresponding tetramethyldisilacyclohexane is unreactive towards oxygen, but *cis*- and *trans*-dimethyldifluorodisilacyclohexanes (e.g., **10**) react with oxygen to give the disiloxanes with retention of stereochemistry (Eq. 23); this does not disprove a radical mechanism, as silyl radicals are pyramidal and can retain configuration, unlike alkyl radicals, which are normally planar, and cannot. Both the tetramethyl- and the dimethyldifluoro-disilacyclohexanes react with bis(trimethylsilyl) peroxide to give the disiloxanes in good yield, but the latter compounds are much the more reactive, and again are oxidised stereospecifically.[38]



(23)

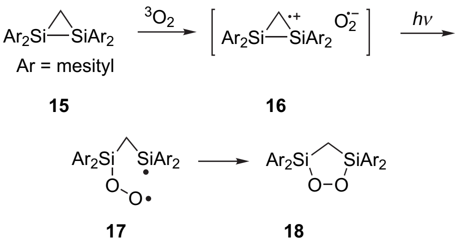
The reactivity of the fluorodisilanes would result from the increased reactivity of the silicon centre towards the electrophilic peroxyl or oxyl radical, and the increased stability of the fluorosilyl radical.

In the absence of a photosensitiser, the disilete **11** is stable towards triplet or singlet oxygen, but if it is irradiated in the presence of 9,10-dicyanoanthracene it gives a mixture of the dioxadisilin **13** and the oxadisilene **14**. The same products are formed with oxygen in the presence of $(BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ as an electron-transfer agent. It appears that electron transfer occurs to give the radical cation of **11**. This reacts with triplet oxygen to give the solvated distonic peroxyl radical cation **12**, which is reduced to the peroxide anion, and ring closes (Eq. 24).[39]



(24)

1,1,2,2-Tetramesityldisilirane **15**, in solution, forms a charge-transfer complex **16** with oxygen. If this is irradiated into the charge-transfer band at 300 nm, the dioxadisilolane **18** is formed via the intermediate triplet diradical (or singlet zwitterion) **17**, which can be observed (δ O–O 1078 cm^{-1}) in an oxygen matrix at 16 K (Eq. 25).[40] On silica gel, the 1,2-dioxalane **18** rearranges to the oxetane **19** (Eq. 26) (see Section 4.1).



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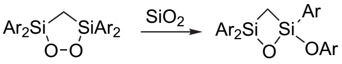
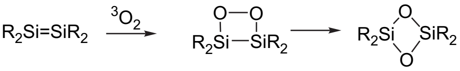


18 19 (26)

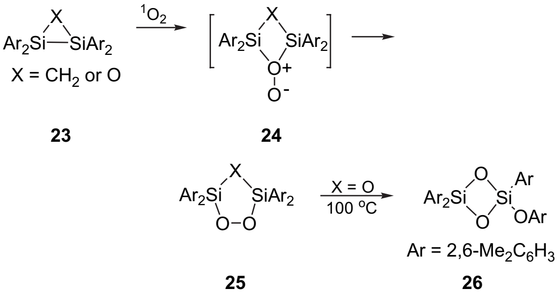
Triplet oxygen reacts at C=C double bonds to give 1,2-dioxetanes only when the olefins have low-lying triplet states. Disilenes (**20**), on the other hand, are very reactive to oxygen, and, at low temperatures, give the corresponding 1,2-dioxadisiletanes (**21**) as the major products (R_2=Mes_2 or ^{t}Bu, Mes). cis and trans Diastereomerically substituted disilenes, RR′Si=SiRR′, react with retention of symmetry. Above about 250 K, these 1,2-dioxadisiletanes rearrange intramolecularly in solution, or in the solid state, to give 1,3-dioxadisiletanes (**22**; Eq. 27), whereas the carbon analogues, the 1,2-dioxetanes, decompose to give ketones with photoluminescence.[41,42]



20 21 22 (27)

1,2-Dioxasiletanes are similarly believed to be intermediates in both the thermal and photochemical reaction of silenes, R_2Si=CR'_2, with oxygen, but even at 10 K they were too labile to be observed spectroscopically.[43]

2.2.3. From $^1O_2$. Singlet oxygen can insert into strained Si–Si σ bonds in disiliranes and oxadisiliranes (**23**) (Eq. 28) to give the corresponding di- or tri-oxa-disilolanes, respectively (**25**) (cf. Eq. 25).[44]



(28)

Irradiation of the disilirane under oxygen in the presence of tetraphenylporphine gives the disilolane (**25**) and disiletane (**26**), in varying yields depending on the nature of X and of the aryl group. The same products are obtained with other sources of singlet oxygen, and the structure of one trioxadisilolane (**25**, X=O, Ar=2,6-$Me_2C_6H_3$) has been confirmed by X-ray diffraction;[45] at 100 °C, it rearranges to the aryloxydioxadisiletane **26** (see Section 4.1).[44]

The insertion of O_2 into the Si–Si bond of *cis* and *trans* diastereomeric tetraaryldioxadisilolanes proceeds with retention of configuration, and the most likely intermediate appears to be the peroxonium ion **24**.[46,45]

2.3. Silyl alkyl peroxides, $R_nSi(OOR')_{4-n}$

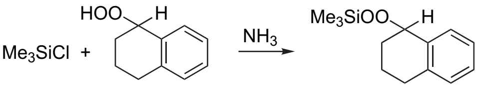
2.3.1. From ROOH. The silyl alkyl peroxides (alkylperoxysilanes) can routinely be prepared by the reaction of an alkyl hydroperoxide with a chlorosilane in the presence of a base such as ammonia, pyridine, triethylamine, or imidazole (e.g., Eq. 29), and a large number are known. The complexes that hydroperoxides form with tertiary amines such as DABCO (e.g., ^{t}BuOOH·N(CH_2CH_2)$_3$N·HOO^{t}Bu) can also be used.[47]

Table 4. Alkylperoxysilanes

R_3SiOOR'	Bp (°C/mmHg) or mp (°C)	Preparative method[a]	Ref.
$Me_3SiOOCMe_3$[b]	78/95	A	10
$Me_3SiOOCMe_2Ph$	43/0.05	A	10
$Me_3SiOOC_{10}H_{11}$	53/0.1	B	10
$Et_2Si(OOCMe_3)_2$	40/1	A	10
$Me_2(OOSiCMe_2Ph)_2$	Liquid	C	47
$[Si(OO^tBu)_2O]_8$	—	B	52
$MeSi(OOCMe_3)_3$	50/0.1	B	10
$Si(OOCMe_3)_4$	53	B,C	10,47
$HMeSi(OO^tPe)_2$	64–65/3	A	53
$HSi(OO^tBu)_3$	120 dec	C	47
$(MeO)_3SiOOCMe_3$	49/6	B	10
$Cl_3SiOOCMe_3$	36/10	A	54
$[MeSi(OO^tBu)O]_4$	—	B	52

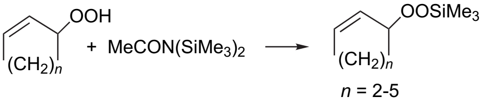
[a] A: Chlorosilane, hydroperoxide, pyridine. B: Chlorosilane, hydroperoxide, ammonia. C: Chlorosilane, hydroperoxide, DABCO.
[b] NMR: δ ^{1}H 0.16 (CMe), 0.12 ppm (SiMe). IR: ν OO 910 cm^{-1}.

Some examples of silyl alkyl peroxides are given in Table 4. Like all secondary alkyl peroxides, the tetrahydronaphthyl silyl peroxide which is shown in Eq. 29 undergoes a base-catalysed elimination, giving the silanol and α-tetralone.[10]



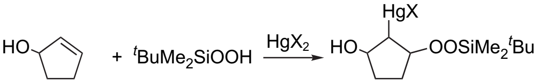
(29)

Silylation with bis(trimethylsilyl acetamide) has been used for protecting a hydroperoxide during a bromination reaction (Eq. 30).[48]



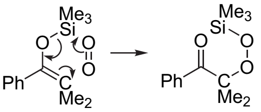
(30)

Corey prepared cyclopentanyl- and cyclohexanyl-peroxysilanes by silylperoxymercuration of the cycloalkenols (e.g., Eq. 31), but the method has not caught on.[49]



(31)

2.3.2. From $^1O_2$. When enols react with singlet oxygen, they do so by transfer of hydrogen from the OH group; this is an extension of the ene reaction, which more commonly involves the transfer of the hydrogen of an allylic CH group. It was found accidentally that silyl enolates could react with singlet oxygen by silicon transfer to give a β-ketoalkyl silyl peroxide,[50] and provides an example of the common behaviour of hydrogen and metals or pseudometals (Eqs. 32 and 33).



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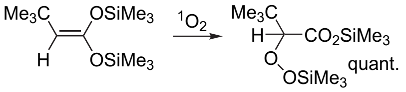


(33)

Yields are very good when there is no alkyl substituent on the double bond, which can take part in competitive hydrogen transfer.

There is an intriguing early Russian report of a reaction which is formally analogous to the silyl enolate ene reaction, and which does not appear to have been followed up, of the reaction of an *N*-silylenamine with oxygen by transfer of the silyl group (Eq. 34, R=Me or Et).[6,51]

$$O_2 + Me_2C{=}CHNRSiMe_3 \xrightarrow[60\text{-}70\ °C]{\text{dioxane}} Me_3SiOOCMe_2CH{=}NR \quad R = Me,\ 71\%;\ Et,\ 84\% \qquad (34)$$

However, the reagent appears to have been triplet rather than singlet oxygen, in which case a radical chain reaction involving the silyl and silylperoxyl radicals may be involved (Eqs. 35 and 36). Such a mechanism is not yet known for the silyl enolates; enols themselves may undergo autoxidation, but it seems more likely then that the chain carriers then are $C{=}C\text{–}O^{\bullet}$ and $^{\bullet}OOC\text{–}C{=}O$ rather than $HOO^{\bullet}$ and $H^{\bullet}$.

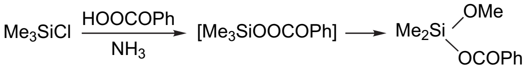
$$Me_3SiOO^{\bullet} + Me_2C{=}CHNRSiMe_3 \longrightarrow Me_3SiOOCMe_2\text{-}CH{=}NR + Me_3Si^{\bullet} \qquad (35)$$

$$Me_3Si^{\bullet} + O_2 \longrightarrow Me_3SiOO^{\bullet} \qquad (36)$$

2.4. Silyl acyl peroxides $R_nSi(OOCOR')_{4-n}$

Alkyl peroxyesters, $R_3COOCOR'$, can be isolated from the reaction of an alkyl hydroperoxide with an acyl chloride or anhydride, but they rearrange more or less readily, depending on the nature of R and R′, to give $R_2C(OR)OCOR'$.

No silyl acyl peroxides (silyl peroxyesters) have yet been isolated. Rearrangement now takes place more readily, and the reaction of a peroxyacid and a chlorosilane at room temperature under basic conditions gives only the corresponding alkoxy acyloxy silane (Eq. 37) (see Section 4.2).[10]



(37)

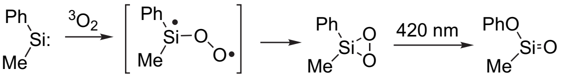
Trimethylsilyl *tert*-butyl peroxide reacts with succinic or phthalic anhydride in the presence of pyridine, with cleavage of the Si–O bond, to give the corresponding *tert*-butyl peroxyesters, e.g., Eq. 38. Bis(trimethylsilyl) peroxide, in the absence of pyridine gives the non-peroxidic product from the rearrangement of the silyl peroxyester.[55]

There appear to be no reports of attempts to prepare the peroxyesters at low temperature, nor to prepare them from the reaction of a silyl hydroperoxide with an acyl halide or anhydride. It would be surprising if they are not stable at low temperature as the peroxysulfate, $MeOS(O)_2OOSiMe_3$, derived from a much stronger acid, is stable in solution at −30 °C (Section 4.3).

Many examples of this type of rearrangement are now known, and its various ramifications provide the basis of a number of important synthetic methods, which have been developed particularly by Fleming and by Tamao. The mechanism of these reactions is considered in Section 4.2.

2.5. Dioxasiliranes, *cyclo*-R_2SiOO

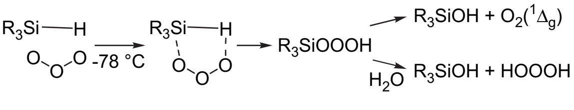
Singlet carbenes react with triplet oxygen to give carbonyl oxides, which, on irradiation, give dioxiranes.[56] Silylenes, R_2Si:, react with oxygen in an argon matrix at 40 K to give dioxasiliranes, presumably via the initial triplet dialkylsilylperoxyl diradicals. The dioxasiliranes have been identified by the IR spectra, which were reproduced by DFT calculations, of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ species. On irradiation with UV light, rearrangement occurs to give an alkoxysilanone,[57] e.g., Eq. 39.



(39)

2.6. Trialkylsilyl hydrotrioxides, $R_3SiOOOH$

Ozonation of trialkylsilanes in solution at −78 °C gives the corresponding silyl hydrotrioxides in 70–90% yield, which have been characterised by ^1H, ^{13}C, ^{17}O and ^{29}Si NMR spectroscopy. DFT Calculations suggest that the reaction involves the direct pericyclic insertion of ozone into the Si–H bond. At higher temperature, the hydrotrioxides decompose by first order kinetics to give the corresponding silanols in high yield, and singlet oxygen; in the presence of water, up to 40% of hydrogen trioxide, HOOOH, is also formed.[58,59] Triethylsilyl hydroperoxide provides a good source of $^1\Delta_g$ oxygen (Eq. 40).[60]



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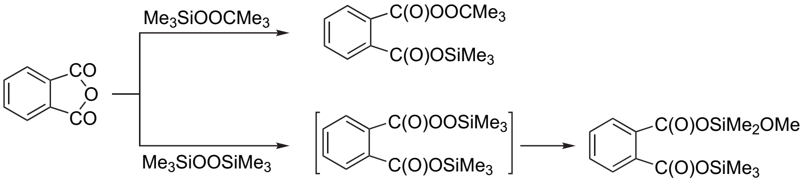


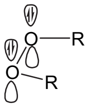
(38)

3. Structure and bonding

Organic peroxides are regarded as having one electron pair on oxygen in a 2p orbital, and the other in an orbital with largely 2s character.[61,62] The structures are then determined by the interplay of a number of effects.

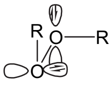
1. The molecules adopt a conformation about the O–O bond, which minimises the exchange repulsion between these lone pairs. This is one aspect of the α-effect.
2. There may be steric repulsion between the terminal groups R, as well as repulsive interaction between the OR σ-bonding electrons.

On these two grounds, a cis conformation (**27**) will be least stable, maximising both p–p and steric repulsion. A *gauche* conformation (**28**) will minimise p–p repulsion, and a trans (**29**) conformation will again maximise *p–p* repulsion, but with minimal steric repulsion. The barrier to rotation between the two enantiomeric *gauche* forms and the trans form is never more than a few kilocalories per mole, and, in the crystal, these intramolecular effects may be overridden by intermolecular forces, and particularly, if the OOH group is present, by hydrogen bonding.



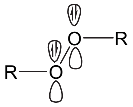
cis

27



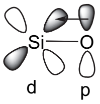
gauche

28



trans

29



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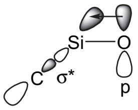

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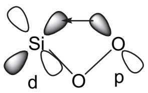
In the silyl peroxides:

3. Overlap of the doubly occupied 2p orbital on the α-oxygen, with a vacant 3d orbital on silicon (**30**), or (when the conformation permits) with a σ* orbital of a Si–C bond (**31**), will reduce the electron density in the oxygen p orbital, and reduce the extent of the p–p destabilising overlap. This would be expected to open up the dihedral angle, and shorten and strengthen the O–O bond.
4. Overlap of the doubly occupied 2p orbital on the β-oxygen, with a vacant 3d orbital on silicon (**32**), or (again, if the conformation is appropriate) with a σ* orbital of a Si–C bond (**33**), will confer some attractive interaction.[63] The Si–βO separation is well within the van der Waals distance, and this weak bonding in the silyl peroxides has been represented as shown in **34** and **35**.[64]
5. Si–O And Si–C bonds are longer than C–O and C–C bonds; this will increase the distance between the groups R and reduce their steric repulsion.



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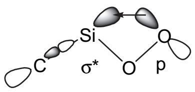

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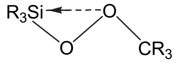

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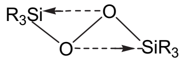

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It is difficult to disentangle these effects. Data on the structures of hydrogen peroxide, di(*tert*-butyl) peroxide, and the acyclic disilyl peroxides are collected in Table 5.

In hydrogen peroxide the steric repulsion is negligible, and, in the gas phase, the molecule has a *gauche* conformation with an HOOH torsional angle τ of 120°; the *trans* and *cis* forms are calculated to be about 4.5 kJ mol^{-1} (1.1 kcal mol^{-1}), and about 30.4 kJ mol^{-1} (7.4 kcal mol^{-1}) less stable, respectively, than the *gauche* form. In the solid, τ is 90.2° due to hydrogen bonding.

In $Me_3COOCMe_3$, τ is increased to 166° in the gas phase because of steric repulsion between the *tert*-butyl groups. The O–O bond length is greater than that in hydrogen peroxide, which could result from increased p–p repulsion, or from steric repulsion between the bulky alkyl groups, and the structure is the same in the crystal.[68]

Bis(trimethylsilyl) peroxide in the gas phase has a torsional angle of 144°, smaller than that in di-*tert*-butyl peroxide, but the O–O bond length is the same within experimental error.[68]

The calculated (MP2/6-31G*) optimised geometry (rO–O 1.511 Å, τ 144.3°, δ 101.8°) is in good agreement with the experimental data.[73] At the MINDO/3 level, the values which were obtained were r 1.393 Å, τ 179.9°, δ 111.3°.[74]

In the crystal, τ is 180°, and the O–O bond is slightly longer, and the compounds $Ph_3SiOOSiPh_3$,

Table 5. Structures of peroxides ROOR

R	Method[a]	rO–O/Å	rR–αO/Å	R–βO/Å	δ OOR/°	τ ROOR/°	Ref.
H (gas)	MW	1.475	0.950		94.8	120	65
H (solid)	X-ray	1.49			97	94	66
H (solid)	ND	1.453			103	90	67
Me_3C (gas)	ED	1.480[b]	1.460		104	166	68
Me_3C (solid)	X-ray	1.478	1.439		107	164	69
Me_3Si (gas)	ED	1.481	1.681	2.538	107	144	68
Me_3Si (solid)	X-ray	1.497	1.677	2.508	104	180	70
$Me_2(4\text{-}ClC_6H_4)Si$ (solid)	X-ray	1.498	1.691	2.541	105	180	71
Ph_3Si (solid)	X-ray	1.487	1.669	2.491	104	180	72
$Me_2(PhCH_2)Si$ (solid)	X-ray	1.501	1.687	2.523	104	180	71

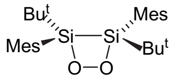
[a] MW=microwave. ED=electron diffraction. ND=neutron diffraction.

[b] Assumed.

$Me_2(4\text{-}ClC_6H_4)SiOOSi(4\text{-}ClC_6H_4)Me_2$ and $Me_2(PhCH_2)SiOOSi(CH_2Ph)Me_2$ have the same centrosymmetrical structure.[71] The silyl germyl peroxide $Ph_3SiOOGePh_3$ has r 1.481 Å, δ 107°, τ 143°.

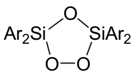
In all these disilyl peroxides the separation between silicon and the β-oxygen atom (2.49–2.54 Å) is less than the sum of the van der Waal's radii (2.1+1.52=3.62 Å), implying a weak intramolecular interaction.

In the cyclic peroxides **36**,[41,45] **37**,[75] **38**[76] and **39**,[46] the structures are dominated by the constraints of the ring.



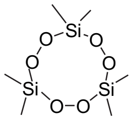
rO–O 1.482 Å
rSiαO 1.732
θSiOO° 103.3
rSiβO 2.532 Å
τ 8.9°

36



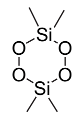
rO–O 1.451Å
θSiOO° 106.0°
Ar = 2,6-$Me_2C_6H_3$

37



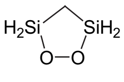
rO–O 1.492 Å
rSiαO 1.676
θSiOO° 104.9°
τ 135.6°

38



rO–O 1.492 Å
rSiαO 1.681
θSiOO° 104.9°
τ 143°

39



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Calcd. (HF/6-31G*)
rO-O 1.43 Å
θSiOO 106.0°

The structure of no silyl hydroperoxide appears to have been determined, and of only one alkylperoxysilane: an X-ray study of $(^tBuOO)_3SiOSi(OO^tBu)_3$ reports r_{av}O–O 1.477 Å, τ 139°.[76] However, the structure of Me_3SiOOH has been calculated at the MP2/6-31G* level of theory, and shows rO–O 1.488 Å, rSi–αO 1.717 Å, rSi–βO 2.516 Å, δ OOR 103.2°, δ OOH 98.0°.[73]

Dialkyl peroxides undergo clean O–O homolysis above about 120 °C, by first order kinetics, to give two alkoxyl radicals, and the activation energy of the reaction (e.g., $Me_3COOCMe_3$, 38 kcal mol^{-1}) can be equated to the bond dissociation energy.[77,78] The disilyl and silyl alkyl peroxides similarly decompose by first order kinetics, but the activation energies cannot safely be equated with the O–O bond dissociation energy because simple O–O homolysis is accompanied or replaced by intramolecular rearrangement with a lower activation energy (which is discussed below).[79] By combustion calorimetry, $Me_3SiOOCMe_3$ gave an O–O bond dissociation energy of 47 kcal mol^{-180} and computed values[73] are HOOH 50.5, $^tBuOO^tBu$ 45.2, ^tBuOOH 48.3, $Me_3SiOOSiMe_3$ 54.8 and Me_3SiOOH 53.1 kcal mol^{-1}.

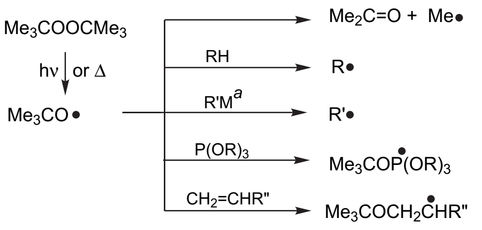
4. Reactions

4.1. O–O homolysis and rearrangement

The peroxide bond in organic peroxides is weak and shows an absorption band rising into the ultraviolet. Irradiation into this band brings about $n\rightarrow\sigma^*$ excitation, and the O–O bond cleaves to give two oxygen-centred radicals. Thermolysis of the organic peroxides similarly gives alkoxyl radicals, though some compounds (e.g., peroxyesters) undergo a more facile, largely heterolytic, rearrangement.

If organic peroxides are photolysed at low temperature, clean homolysis of the peroxide bond occurs, and the radicals which are formed can be monitored by ESR spectroscopy.

The principal reactions of *tert*-butoxyl radicals are shown in Scheme 1.



[a] R'M = RLi, R_2Zn, RMgX, R_nBX_{3-n}, R_nSnCl_{4-n}, etc

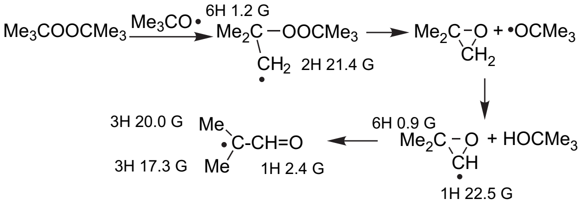
Scheme 1. Reactions of *tert*-butoxyl radicals.

The alkoxyl radicals cannot be observed directly in fluid solution by ESR spectroscopy because the orbital degeneracy of the electrons on oxygen broadens the signal beyond detectability, but above about 100 °C the *tert*-butoxyl radicals undergo β-scission to give acetone and show the spectrum of methyl radicals; if the peroxide is photolysed in the presence of a trace of HCl or of a Lewis acid such as $SnCl_4$, the ESR spectrum of the methyl radical can be detected at low temperature (Eq. 41).

$$Me_3COOCMe_3 \xrightarrow[\text{or }\Delta]{h\nu} 2Me_3CO\bullet \longrightarrow Me_2C{=}O + Me\bullet \qquad (41)$$

The other most characteristic reactions of the alkoxyl radicals are bimolecular homolytic substitution (S_H2) at hydrogen or a metal, and addition to an alkene, which, with suitable substituent groups at the double bond, can lead to polymerisation. Addition to phosphorus(III) compounds generates phosphoranyl radicals, which show a large ^{31}P ESR coupling constant.

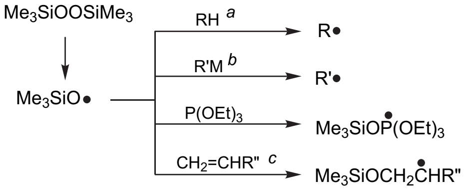
If di-*tert*-butyl peroxide is photolysed neat, or in an inert solvent, the *tert*-butoxyl radicals abstract (S_H2) hydrogen from a methyl group in the peroxide as shown in Eq. 42. Ring closure then occurs to give the oxirane, and hydrogen abstraction from this gives the oxiranyl radical. These carbon-centred radicals can be identified by the hyperfine coupling constants (a) and g values in the ESR spectra, and values of a are given on the formulae in Eq. 42.



(42)

On irradiation with UV light, the trimethylsilyl peroxides, $Me_3SiOOSiMe_3$ and $Me_3SiOOCMe_3$, like $Me_3COOCMe_3$, undergo straightforward homolysis to give the siloxyl, or siloxyl and alkoxyl radicals, respectively.[81] Dissociation into radicals occurs in the singlet $n \rightarrow \sigma^*$ excited state, and with a dilute solution in hexane (0.001–0.02 M), the quantum yield is close to unity. Higher concentrations give higher quantum yields, because of induced decomposition as described below.[82] The yields of products from $Me_3SiOOSiMe_3$ do not appear to have been determined, but from the decomposition of $Me_3SiOOCMe_3$, 0.005 M in hexane, the yields per mole of peroxide are Me_3COH 0.87, $Me_2C{=}O$ 0.09, MeH 0.10, Me_3SiOH 0.93 and $(Me_3Si)_2O$ 0.01. Clearly, the main reaction here of the siloxyl (and *tert*-butoxyl) radicals is to extract hydrogen from the solvent.

The characteristic reactions of the trimethylsiloxyl radicals are shown in Scheme 2. The siloxyl radicals, like the alkoxyl radicals, cannot be observed directly in fluid solution by ESR. Like the $Me_3CO^•$ radical, the $Me_3SiO^•$ radical brings about bimolecular homolytic substitution (S_H2) at hydrogen or a metal, and addition at a phosphorus(III) centre to give a phosphoranyl radical, and the reaction products can be monitored by ESR spectroscopy.



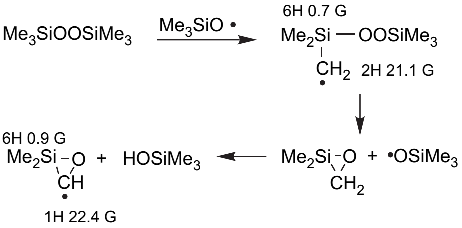
[a] RH = c-C_5H_{10}, Me_2EtCH, PhMe, $EtOCH_2Me$, THF, Bu^tOOH
[b] R'M = Bu_3B, Bu_3SnCl
[c] R" = H, Me, EtO, $CH_2{=}CH$

Scheme 2. Reactions of trimethylsiloxyl radicals.

The principal differences between the $Me_3CO^•$ and $Me_3SiO^•$ radicals are, first, that there appears to be no evidence for β-scission of the siloxyl radical to give a methyl radical and dimethylsilanone, $Me_2Si{=}O$. Approximate bond energies are Me–C 85, $\pi C{=}O$ 80, Me–Si 88, $\pi Si{=}O$ 38–63 kcal mol^{-1}; thus, whereas the β-scission of the $Me_3CO^•$ radical is almost thermally neutral, that of the $Me_3SiO^•$ radical would be endothermic by at least 25 kcal mol^{-1}.

The second principal difference is that siloxyl radicals add to alkenes more readily than do alkoxyl radicals (Scheme 2, reaction *c*).[81,83]

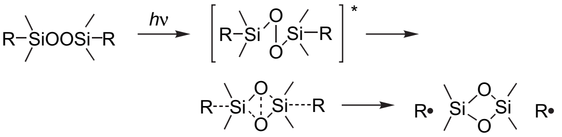
In the absence of a reactive solvent, the reactions that occur (Eq. 43) are equivalent to those that are observed with di-*tert*-butyl peroxide (Eq. 42), and the equivalent ESR hyperfine coupling constants of the radicals which are formed are given in Eq. 43.



(43)

The behaviour is different when higher alkyl groups are involved: substantial differences in the properties of methylmetal compounds and their higher homologues are often observed. Whereas the higher homologues of the carbon peroxides continue along the same lines as $Me_3COOCMe_3$, the higher silyl peroxides show fission of the C–Si bond. Thus, photolysis of $Et_3SiOOSiEt_3$ or $Pr_3SiOOSiPr_3$ in an inert solvent (cyclopropane or CF_2Cl_2) between −120 and −50 °C, showed principally the ESR spectrum of the ethyl or propyl radical, respectively. These alkyl radicals, $R^•$, would not be expected to result from the unimolecular β-scission of the corresponding trialkylsiloxyl radicals, and this is confirmed by the fact that photolysis of the silyl alkyl peroxides, $R_3SiOOCMe_3$, does give siloxyl radicals, but not the radicals $R^•$. Again, photolysis of $Et_3SiOOSiEt_3$, in a mixture of cyclopentane and cyclopropane, shows spectra of the ethyl and cyclopentyl radicals in a ratio that is independent of the concentration of cyclopentane, showing that the bimolecular (S_H2) reaction at hydrogen is not in competition with unimolecular fission of the siloxyl radical.

Free siloxyl radicals therefore do not appear to be involved in the cleavage of the R–Si bond, and the most likely mechanism for the reaction appears to be a cyclic concerted process such as that shown in Eq. 44. It turns out that multicentre reactions of this type often take place in the silyl peroxides to the exclusion of simple homolysis, as described below.[9]



(44)

The degree to which the O–O bond is cleaved, and the new Si–O bonds are formed, in the transition state is open to question, but should be susceptible to computation. The extreme case would be complete cleavage of the peroxide bond, followed by interaction of the two siloxyl radicals within the solvent cage. The even more extreme case of diffusion of the siloxyl radicals into the solvent, followed by an S_H2 reaction of a siloxyl radical at a silicon centre in the parent peroxide, with displacement of an alkyl radical, seems unlikely. Homolytic alkoxydealkylation reactions are known for some organometallic compounds (e.g., the trialkyltin chlorides), but with the organosilanes, the S_H2 reaction normally occurs at a hydrogen centre of the alkyl group, and photolysis of $Et_3SiOOCMe_3$, which does give both $Et_3SiO^•$ and $Me_3CO^•$ radicals, shows the spectrum of $(MeCH^•)Et_2SiOOCMe_3$, and no ethyl radical. Further, if S_H2 reactions at H in C_5H_{10} and at Si to give $Et^•$ were in competition, the ratio of $Et^•/C_5H_{11}$ would be dependant on $[C_5H_{10}]$, which is not observed.

The decomposition of Ph_3SiOOH in chloroform is greatly accelerated by UV light, when straightforward homolysis into $Ph_3SiO^•$ and $^•OH$ radicals probably occurs.[84]

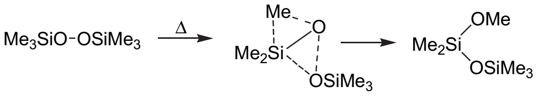
The disilyl peroxides decompose thermally by first order kinetics, and are more stable than the alkyl peroxides (Table 6). The extensive Russian work in this field is tabulated in, and is best accessed through, Aleksandrov's review.[6]

Table 6. Kinetics of the thermal decomposition of peroxides in the gas phase

Peroxide	$Me_3COOCMe_3$	$Me_3SiOOCMe_3$	$Me_3SiOOSiMe_3$
$E^{\#}$/kcal mol^{-1}	38.0	32.7	32.3
Log A	15.9	11.3	12.5
k/s^{-1} at 150 °C	1.8×10^{-4}	2.5×10^{-6}	6.3×10^{-5}
$t_{1/2}$/h at 150 °C	1.1	77	3.1

There is a marked difference between the thermolysis of the dialkyl and disilyl peroxides. Whereas the former show clean homolysis of the O–O bond and the formation of two alkoxyl radicals (Eq. 45), the disilyl peroxides rearrange, both in the gas phase and in solution, to give only the alkoxydisiloxanes (Eq. 46).[85]

$$Me_3CO{-}OCMe_3 \xrightarrow{\Delta} 2Me_3CO\bullet \qquad (45)$$



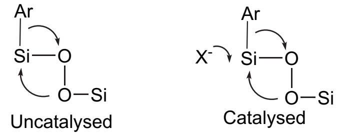
(46)

It might be suggested that the reaction involves a caged pair of trialkylsilyloxyl radicals, in which one rearranges to a dialkyl(alkoxy)silyl radical, followed by radical recombination, but the activation energy is less than that of the bond dissociation energy, the same reaction occurs in the gas phase where there can be no solvent effect,[86] and it would be difficult to account for the fact that no product ($MeOMe_2SiOSiMe_2OMe$) is obtained in which both siloxyl radicals have rearranged.[87] Again, therefore, a four-centre cyclic mechanism as shown in Eq. 46 best fits the evidence.

For the arylsilyl peroxides (p-MeC_6H_4)$Ph_2SiOOSiPh_2$(C_6H_4Me-p) and (p-$MeOC_6H_4$)$Ph_2SiOOSiPh_2$(C_6H_4OMe-p), the relative migratory aptitudes are p-anisyl 6.0, p-tolyl 1.1 and phenyl, 1.0,[36] and the rates increase with the electron donating power of substituents in the aryl rings, Br<H<Me<MeO.

The reactions are faster in polar solvents such as anisole, dibutyl ether, or cyclohexanone, which can associate with the silicon, and under these conditions, $Me_3SiOOSiMe_3$ shows some O–O homolysis.[88] The reason why disilyl peroxides, which normally do not decompose homolytically, can be used for initiating free radical polymerisation[16,6] is that they, and the silyl alkyl peroxides, form 1:1 acceptor–donor complexes with alkenes, and other electron donors, which lowers the activation energy for homolysis and tips the competition between homolysis and rearrangement in favour of the generation of radicals.[89]

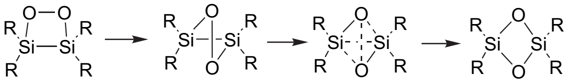
The decomposition of the peroxides (p-XC_6H_4)$Me_2SiOOSiMe_2$(C_6H_4X-p) is catalysed by KCN, KF, or CsF in isopropyl alcohol, and the migratory aptitude of the aryl groups is now reversed, with substituent groups in the sequence MeO<Me<H<Cl, and the uncatalysed reaction follows a log k–σ^+ correlation, whereas the catalysed reaction follows a log k–σ correlation. It appears that there is a change in mechanism, and it is suggested that the catalysed rearrangement involves nucleophilic attack of the anion at silicon (Scheme 3); at that site, the reaction then has the local characteristics of an S_N2 rather than an S_N1 reaction, and is retarded by electron-repelling substituents.[90]



Scheme 3. Rearrangement catalysed by nucleophilic attack on silicon.

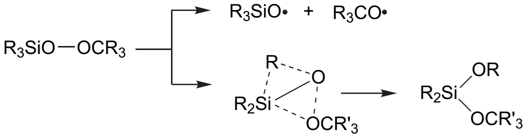
Remarkably, in the absence of a catalyst, the silyl germyl peroxide $Ph_3SiOOGePh_3$ rearranges to give $Ph_2(PhO)SiOGeR_3$, whereas, in the presence of a catalyst, the direction of rearrangement is reversed, and the product is $Ph_3SiOGe(OPh)Ph_2$, i.e., from a reaction with local characteristics of an S_N1 reaction at silicon, to an S_N2 reaction at germanium.[91]

The rearrangement of the disiladioxetanes, which is shown in Eq. 27 similarly occurs by an intramolecular rearrangement (Eq. 47); when R_2 is *tert*-butyl and mesityl, the activation energy is 21.7(1.0) kcal mol^{-1}.[41]



(47)

The silyl alkyl peroxides, $R_3SiOOCR_3$, usually show, in competition, both the homolysis which characterises the dialkyl peroxides, R_3COOCR_3, and the rearrangements which characterise the disilyl peroxides, $R_3SiOOSiR_3$ (Eq. 48).



(48)

Both reactions show first order kinetics, the balance depending on the structure of the peroxides and on the reaction conditions. The migratory aptitude of the groups R in peroxides $RMe_2SiOOCMe_3$ falls in the sequence Me<Bu<Et<Pr, Ph<PhCH$_2$<thienyl, and for thermolysis in anisole at 180 °C, the ratio of k_{homo}/k_{rearr} is given in Table 7. Both the homolysis and rearrangement reactions are accelerated at high pressure, but with little effect on their ratio, and this has been taken to suggest that both the reactions occur through the same transition state.[92]

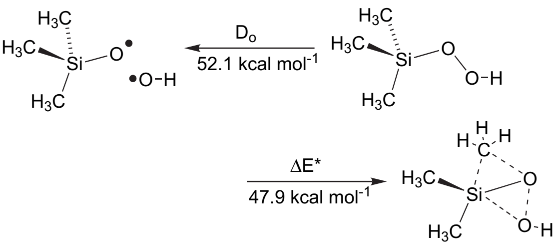
There has been only one report of an experimental study of the kinetics of the thermal decomposition of silyl hydroperoxides.[84] The thermolysis of triphenylsilyl hydroperoxide in a number of aromatic solvents is first order kinetically, with an energy of activation of 22–27 kcal mol^{-1} and an A-factor of 10^{10}–10^{11}, but the reaction is complex,

Table 7. Balance between homolysis and rearrangement for the peroxides $RMe_2SiOOCMe_3$

R	Et	Pr	Bu	$PhCH_2$	Ph	Thienyl
k_{homo}/k_{rearr}	3.1	1.5	4.1	0.16	0.49	0.11

giving a mixture of triphenylsilanol, diphenylsilanediol and phenol. The reaction is unaffected by acid, but is accelerated by base, when it is kinetically zeroth order and has an activation energy of 11.8 kcal mol^{-1}. Methyldiphenylsilyl and tribenzylsilyl hydroperoxides decompose in chlorobenzene at similar rates, with activation energies of 26.7±0.4 kcal mol^{-1}. It is not clear what reactions are being followed; disproportionation into hydrogen peroxide and the disilyl peroxide may be a complicating factor.

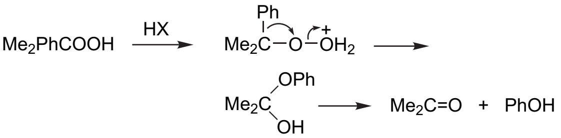
The O–O homolysis and Si-to-O 1,2-rearrangement for trimethylsilyl hydroperoxide have been investigated at the MP4/MP2/6-31G* level of theory,[73] which shows that the rearrangement has a lower activation energy than that for cleavage of the O–O bond (Eq. 49).[73] In the transition state, the O–O bond is elongated by 26%, excluding a siloxyl radical on the pathway to rearrangement. The overall reaction to give $Me_2Si(OMe)OH$ is calculated to be exothermic by 41 kcal mol^{-1}.



(49)

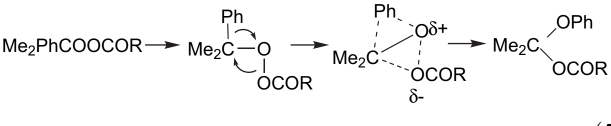
4.2. O–O heterolysis and rearrangement

If the O–O bond in an organic peroxide is made sufficiently polar, a nucleophilic 1(C)–2(O) rearrangement occurs, which is clearly heterolytic in character. This provides the basis of the commercial preparation of phenol from cumene hydroperoxide (Eq. 50).



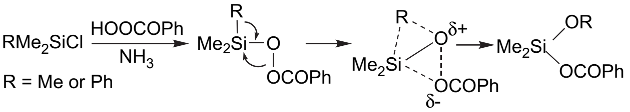
(50)

A similar reaction occurs with peroxyesters. The reaction is kinetically first order, and the rate increases with the strength of the esterifying acid (e.g., peroxybenzoate<*p*-nitroperoxybenzoate<trichloroperoxyacetate). An ^{18}O-labelled carbonyl group retains its integrity during the reaction, implying that the reaction involves a polar bicyclic transition state or at least an intimate ion pair (Eq. 51).



(51)

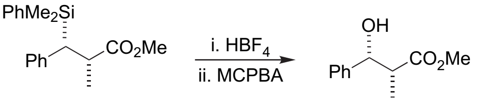
The first example of the nucleophilic rearrangement from silicon to oxygen, with the cleavage of the O–O bond was observed in an attempt to prepare acylperoxysilanes, when the alkoxy acyloxy silane was obtained (Eq. 52).[10]



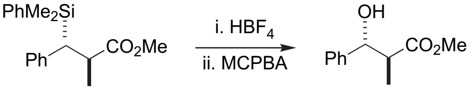
(52)

Many examples of this type of rearrangement are now known, and its various ramifications provide the basis of a number of important synthetic methods, which have been developed particularly by Fleming and by Tamao. These have been well reviewed elsewhere.[7,9,93,94]

These procedures often use the phenyldimethylsilyl substituent as a masked hydroxyl group, $PhMe_2SiR$ being converted into HOR. The tetraorganosilane is inert to peroxide reagents, and the phenyl group is first removed with an electrophile to give XMe_2SiR, then the silicon–carbon bond is cleaved by a reaction of the type shown in Eqs. 53 and 54. The electrophile is commonly an acid, particularly HCl, HBF_4, or trifluoroacetic acid, but Br_2 and HCl have also been used. The rearrangement takes place with complete retention of configuration at the carbon centre.

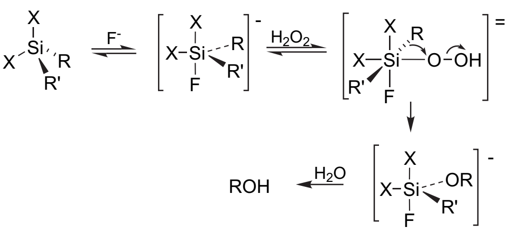


(53)



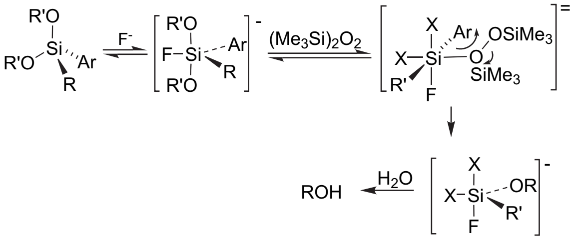
(54)

The Tamao–Kumada procedure converts functionally substituted silanes into alcohols by oxidative rearrangement with hydrogen peroxide or a peroxyacid. The ease of cleavage follows the order aryl>alkyl>methyl, and in the phenylfluorosilanes, $PhSiMe_{3-n}F_n$, the reactivity follows the order where $n=2\ll1>3$. These fluorosilanes, however, need the presence of a further fluorine anion for oxidation to occur. $PhSiMeF_2$ reacts with Bu_4NF in solution to give the five-coordinate $PhSiMeF_3^-$ ion, which is oxidised by hydrogen peroxide to give phenol in a reaction, which is first order in $[PhSiMeF_3]$ and [HOOH] (Eq. 55). The relative reactivities of substituted phenyl groups follow a Hammett ρ–σ_p relationship.



(55)

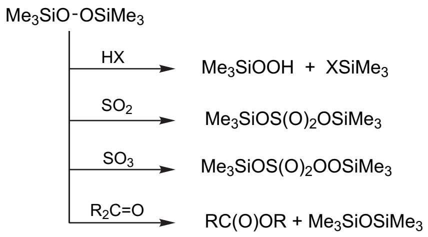
If the silane carries a CN-substituted aryl group, which is sensitive to hydrogen peroxide, the oxidation can be carried out instead with $Me_3SiOOSiMe_3$ under anhydrous conditions, and for this reaction a modified mechanism has been suggested, which involves a 1,3- rather than a 1,2-nucleophilic shift of the aryl group to oxygen (Eq. 56).



(56)

4.3. Reactions with electrophiles

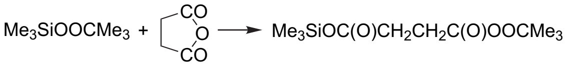
Bis(trimethylsilyl) peroxide reacts with electrophiles by (initial) cleavage of the Si–O bond as shown in Scheme 4.



Scheme 4. Reaction of bis(trimethylsilyl) peroxide with electrophiles.

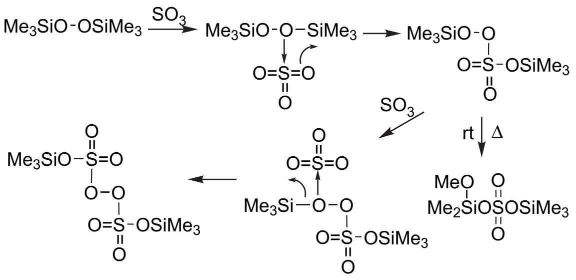
The silyl peroxides have sometimes been washed with water when a preparation was being worked up, but the α-silylperoxy silyl ester in Eq. 33 was hydrolysed with methanol at 5–10 °C, to give the α-hydroperoxy ester.[95] The SiO bond is cleaved by mineral acids to give the silanol and hydrogen peroxide or an alkyl hydroperoxide. Silyl hydroperoxides, on warming, disproportionate to disilyl peroxides, the hydroperoxide acting as its own protic acid,[16] and they readily react with stronger acids. *tert*-Butyl hydroperoxide, on the other hand, does not diproportionate into di-*tert*-butyl peroxide and hydrogen peroxide, and is inert to water and dilute mineral acids.

Silyl peroxides react with acyl halides and anhydrides by cleavage of the Si–O bond. Silyl alkyl peroxides give the alkylperoxy esters (e.g., Eq. 57), but surprisingly little use has been made of these reactions. Trimethylsilyl *tert*-butyl peroxide and phthalic anhydride give the silyl *tert*-butyl monoperoxyphthalate, and bis(trimethylsilyl) peroxide gives the disilyl monoperoxyphthalate, which immediately rearranges (Eq. 38).[55]



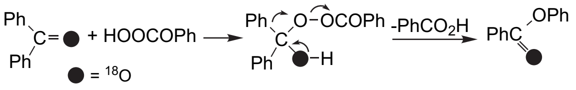
$$Me_3SiOOCMe_3 + (CH_2CO)_2O \longrightarrow Me_3SiOC(O)CH_2CH_2C(O)OOCMe_3 \quad (57)$$

Sulfur dioxide does not react with di-*tert*-butyl peroxide, but the disilyl peroxide reacts with liquid SO_2 at −20 °C to give the disilyl sulfate in 98% yield.[96] Di-*tert*-butyl peroxide is decomposed by SO_3, but the disilyl peroxide at −30 °C gives first the disilyl peroxysulfate, $Me_3SiOS(O)_2OOSiMe_3$ (disilyl caroate); further reaction of the silylperoxysulfate with SO_3 at low temperature then gives the disilyl peroxydisulfate $Me_3SiOS(O)_2OOS(O)_2OSiMe_3$.[96] The caroate decomposes thermally in the same way as the silyl peroxycarboxylates by intramolecular rearrangement to give trimethylsilyl methoxydimethylsilyl sulfate, $Me_3SiOS(O)_2OSiMe_2OMe$ (Eq. 58).[97,30]



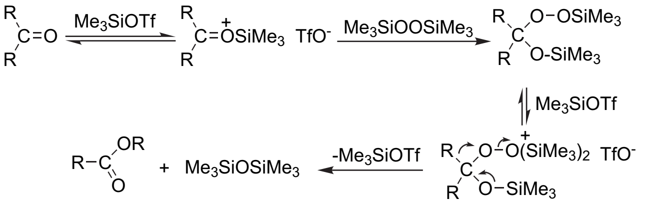
(58)

The Baeyer–Villiger oxidation of ketones to esters is usually carried out with a peroxycarboxylic acid such as trifluoroperoxyacetic acid or *m*-chloroperoxybenzoic acid, though hydrogen peroxide under acid conditions, and peroxysulfuric acid (Caro's acid, $HOS(O)_2OOH$) has also been used. Labelling of benzophenone with ^{18}O shows that the carbonyl group retains its integrity in forming the ester, and the relative migratory aptitude of the groups depends on the nature of the peroxyacid. Migration therefore must begin before the peroxide bond is fully cleaved, and the reaction is concluded to follow what is known as the Criegee mechanism (Eq. 59).[98]



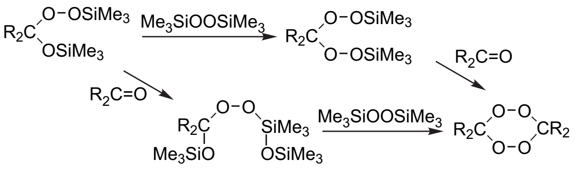
(59)

Baeyer–Villiger type oxidations can also be achieved with $Me_3SiOOSiMe_3$ and with $Me_3SiOS(O)_2OOSiMe_3$. The reaction with the disilyl peroxide is carried out in the presence of ca. 10 mol % of trimethylsilyl trifluoromethanesulfonate (Eq. 60)[99] or a stoichiometric amount of $SnCl_4$ or $BF_3 \cdot OEt_2$;[100] $Me_3SiOOSiMe_3$ has the advantages that it is more nucleophilic than H_2O_2 in adding to the double bond, and is soluble in organic solvents, and, unlike the peroxycarboxylic acids, it does not epoxidise a carbon–carbon double bond. No studies appear to have been carried out on the other types of multiply-bonded acceptor molecules (isocyanates, isothiocyanates, carbodiimides, carbon disulfide, nitriles, acetylene dicarboxylic esters, etc.) that are often susceptible to addition by M–O bonds.



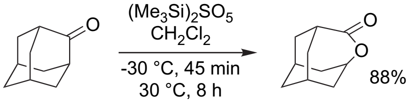
(60)

Under appropriate conditions, the reaction may take the alternative route of further addition and substitution, rather than rearrangement, to give 1,2,4,5-tetraoxanes (Eq. 61).[101]



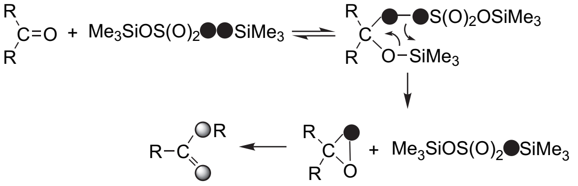
(61)

Bis(trimethylsilyl) peroxysulfate has the advantages over Caro's acid, $HOS(O)_2OOH$, that it is soluble in non-polar solvents, and its reduction product, bis(trimethylsilyl) sulfate, is not a strong acid. It readily oxidises ketones to esters in excellent yield in a few hours at room temperature (e.g., Eq. 62).[102]



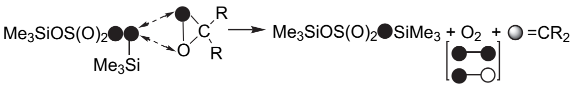
(62)

Experiments with ^{18}O-labelled $Me_3SiOS(O)_2{}^{18}O^{18}OSiMe_3$, however, show that the mechanism is different from that of the reaction with a peroxycarboxylic acid. In the ester, which is formed, both the carbonyl and alkoxyl oxygen atoms carry the ^{18}O at half the intensity of the original label. This is illustrated in Eq. 63, where the grey oxygen atoms indicate half the degree of labelling of the black oxygen atoms.[30] It is concluded that an ^{18}O and an ^{16}O atom become chemically equivalent in an intermediate dioxirane. This is therefore one of the few examples of an O–O bond being formed by attack of oxygen upon oxygen (the reaction of $KHSO_5$ with a ketone to give a dioxirane may be a second, similar, example).



(63)

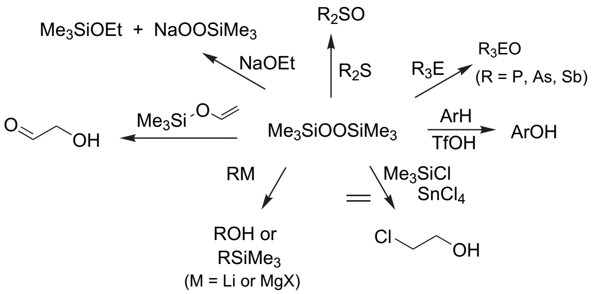
The uncatalysed decomposition of the disilyl peroxysulfate to give dioxygen occurs slowly at low temperature, but much more rapidly in the presence of a ketone. The ^{18}O labelling showed that, in the uncatalysed reaction, both the oxygen atoms in the O_2 are derived from the peroxide group, but in the ketone-catalysed decomposition, one out of four of the oxygen atoms is unlabelled. This can be rationalised on the basis of a reaction between the dilabelled peroxysulfate and the half-labelled dioxirane (Eq. 64), though the mechanism of this interesting reaction is not clear.[30]



(64)

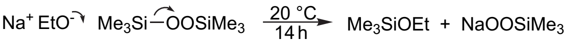
4.4. Reactions with nucleophiles

By protecting hydrogen peroxide with two silyl groups, nucleophilic attack can usually be directed from hydrogen to oxygen, when the disilyl peroxide acts as a sython for Me_3SiO^+ or HO^+, though some nucleophiles will react at silicon. The principal reactions are outlined in Scheme 5.



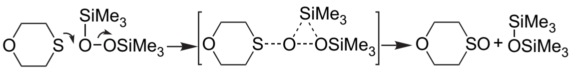
Scheme 5. Reaction of bis(trimethylsilyl) peroxide with nucleophiles.

The simplest example of nucleophilic attack on silicon is the reaction of sodium ethoxide with $Me_3SiOOSiMe_3$, which gave the previously unknown sodium trimethylsilyl peroxide (Eq. 65).[96]



(65)

Sulfides are oxidised to sulfoxides by nucleophilic attack of sulfur on oxygen.[96] The reaction of thioxane with $Me_3SiOOSiMe_3$ (Eq. 66) or $Me_3SiOOCMe_3$ is first order in each reagent and, for the reaction in $CHCl_3$ at 25 °C, the rate constants are $Me_3COOCMe_3$ 0.005×10^{-4}, Me_3COOH 0.3×10^{-4}, $Me_3SiOOCMe_3$ 14.7×10^{-4} and $Me_3SiOOSiMe_3$ 24.0×10^{-4} $l\ mol^{-1}\ s^{-1}$. The Me_3SiO^- anion should be a better leaving group than the Me_3CO^- anion, but if one allows for a factor of 2 for the monosilyl peroxide, the rates for the monosilyl and disilyl peroxides are essentially equal, suggesting that a more important factor may be bridging by the silyl group in the transition state.[103] Sulfoxides can then be oxidised further to the sulfones.



(66)

Under the same conditions, *p*-methoxydimethylaniline as a nitrogen nucleophile is oxidised 1000 times more slowly than the sulfide.

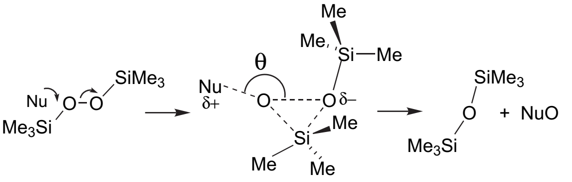
Phosphites are oxidised to phosphates (Eq. 67),[96] and triphenyl-phosphine, -arsine, and -stibine to the corresponding oxides, with the relative reactivities P>As>Sb, but triphenylbismuthine is recovered unchanged under the same conditions.

$$(EtO)_3P + Me_3SiOOSiMe_3 \xrightarrow[15\ h,\ 20\ °C]{pet.\ ether} \underset{100\%}{(EtO)_3PO} + Me_3SiOSiMe_3 \qquad (67)$$

Calculation of the geometries (MP2/6-31G*) and energies (MP4//MP2/6-31G*) of the oxidation of ammonia by $H_3SiOOSiH_3$ shows that the transition state involves bridging by H_3Si to the β-oxygen atom, with $\Delta E^{\#}$

+13.1 kcal mol^{-1}, and ΔE_{RXN} +2.9 kcal mol^{-1}. The activation energy for the reaction of ammonia with the hydroperoxide, H_3SiOOH, is 15 kcal mol^{-1} less for attack at oxygen α to silicon, with Si bridging to β-O, than at the oxygen β to silicon, with hydrogen bridging to α-O.[73]

The reactions of $Me_3SiOOSiMe_3$ with the nucleophiles $CH_2{=}CH_2$, NMe_3, PMe_3 and SMe_2 (B3LYP/6-31G* geometries and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G energies) all show bridged transition states; the approximate structure is shown in Eq. 68 and the activation energies are given in Table 8. The entering nucleophile, oxygen reaction centre and departing oxygen form an angle θ in the range 158.5–173°, resembling the geometry of an S_N2 substitution.[73] By bridging, the silyl group stabilises the negative charge that is developing on the oxygen atom that is being displaced; though the O–O bond in $Me_3SiOOSiMe_3$ is 11–12 kcal mol^{-1} stronger than it is in $Me_3COOCMe_3$, the order of reactivity is reversed.

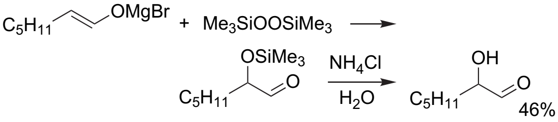


(68)

Table 8. Calculated activation energies for nucleophilic substitution at oxygen in $Me_3SiOOSiMe_3$

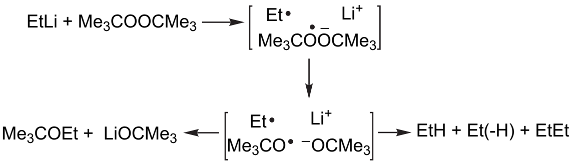
Nu	$CH_2{=}CH_2$	Me_3N	Me_3P	Me_2S
$E^{\#}$/kcal mol^{-1}	35.7	28.17	17.44	21.53

Organolithium compounds and Grignard reagents, RM, bring about the cleavage of the O–O bond. The alkoxysilane, $ROSiMe_3$, is usually formed, but is often accompanied by $RSiMe_3$ and sometimes by RMe (Table 9).[96,104,105] Alkyl- and aryl-metallic compounds give good yields, after hydrolysis, of the corresponding hydroxyl compounds and the reactions provide a useful method for regiospecific introduction of a hydroxyl group. Alkynyllithium compounds and alkynylmagnesium bromides, on the other hand, give only the alkynyltrimethylsilanes. Enolates give the β-ketoalcohols (Eq. 69).



(69)

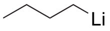
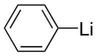
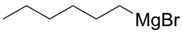
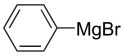
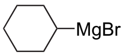
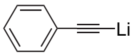
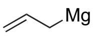
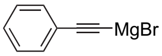
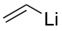
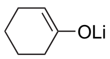
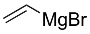
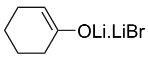
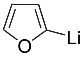
These reactions are often discussed in terms of attack by the carbon nucleophile at the alternative oxygen and silicon sites, and this may be the best picture for the formation of silanes $RSiMe_3$, but there is good evidence, including CIDNP, that the reaction of organolithium compounds and Grignard reagents with di-*tert*-butyl peroxide, which gives the alkyl *tert*-butyl ether and lithium *tert*-butoxide, together with some alkane and alkene, proceeds by an electron-transfer mechanism as shown in Eq. 70.[106]



(70)

Similarly, the reactions of butyllithium with $Me_3SiOOSiMe_3$, $Me_3SiOOCMe_3$ and $Me_2Si(OOCMe_3)_2$[107–109] are, at least in part, radical processes. The chemical balance of the first reaction in heptane, and the second in benzene, is given in Eqs. 71 and 72.

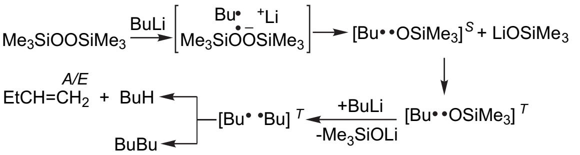
Table 9. Products of the reaction of organolithium compounds and Grignard reagents with $Me_3SiOOSiMe_3$

RM	$ROSiMe_3$ (%)	$RSiMe_3$ (%)	RM (%)	$ROSiMe_3$ (%)	$RSiMe_3$ (%)
	98	2		93	7
	100	0		100	0
	100	0		0	100
	100	0		0	100
	20	80		100	0
	0	100		100	0
	90	10			

$$\begin{aligned}&BuLi + 0.75Me_3SiOOSMe_3 \longrightarrow\\ &\quad Me_3SiOLi + 0.4Me_3SiOBu + 0.2BuBu + 0.005C_4H_8 + 0.05C_4H_{10}\end{aligned} \tag{71}$$

$$\begin{aligned}&1.4BuLi + Me_3SiOOCMe_3 \longrightarrow 0.8Me_3COLi + 0.6Me_3SiOLi +\\ &\quad 0.2Me_3COPh + 0.4Me_3SiOBu + 0.3BuBu + 0.1C_4H_8 + 0.1C_4H_{10}\end{aligned} \tag{72}$$

Electron transfer into the π* orbital gives the radical anion, which dissociates into a siloxyl radical and anion. The siloxyl radical, in a singlet pair with the butyl radical, then reacts by a rapid S_H2 reaction with butyllithium to give a second butyl radical within the solvent cage. A CIDNP effect in the ^1H NMR spectrum of the protons of the butane and the butene then arises from the reaction between two butyl radicals with uncorrelated spins (Eq. 73).

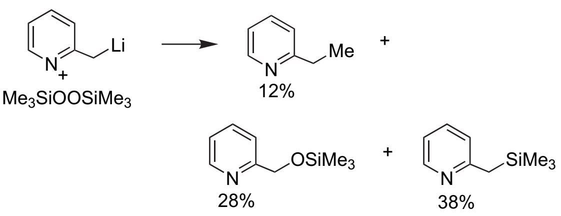


(73)

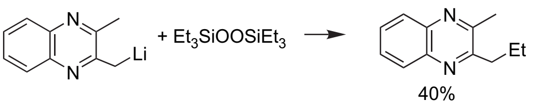
The reactivity towards butyllithium decreases in the order $Me_3SiOOSiMe_3 > Me_3SiOOCMe_3 > Me_3COOCMe_3$, and this is ascribed to the $(p_O–d_{Si})\pi$ interaction between oxygen and silicon, which lowers the electron density on the peroxide group, and facilitates the formation of a peroxide radical anion.

This electron-transfer mechanism could explain why alkenyl- and alkynyl-metal compounds react to give mainly $RSiMe_3$: the ionisation energy increases in the sequence sp^3 alkyl<sp^2 alkenyl<sp alkynyl (though the values for the gas phase are not directly useful because, in solution, the lithium and magnesium compounds are molecular oligomers). The radical ion route becomes less accessible, and nucleophilic substitution at the Me_3Si group is easier.

A very interesting and unexpected aspect of these reactions is that metalloalkyl derivatives of various heterocyclic aromatics, where the metal is Li, MgBr, or ZnBr, become alkylated with an alkyl group from the silyl peroxide. Two examples are given in Eqs. 74 and 75.[110,111]

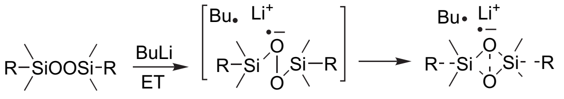


(74)

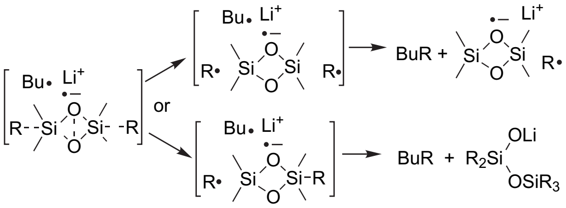


(75)

Nucleophilic attack at the alkyl group of the peroxide, with displacement of silanone and silanolate ion, which has been considered, seems unlikely. In the light of the electron-transfer (ET) mechanism, one possibility would be that the radical anion behaves in the same way that we have suggested for the photoexcited peroxide (Eq. 44), and that the alkane is formed from the reaction, within the solvent cage, of butyl and alkyl radicals, as shown in Eqs. 76 and 77. Interaction between the heteroatom and the silicon may also be involved, and the reaction deserves further investigation.

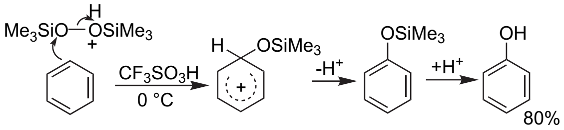


(76)



(77)

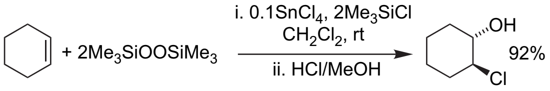
In the presence of triflic acid, aromatic hydrocarbons can be electrophilically hydroxylated (Eq. 78). With *o*-xylene, some *ipso* attack with shift of the methyl group is also observed. Hydroxylation can also be brought about by hydrogen peroxide under acid conditions by a similar mechanism, but the silyl peroxide is safer and more effective.[112]



(78)

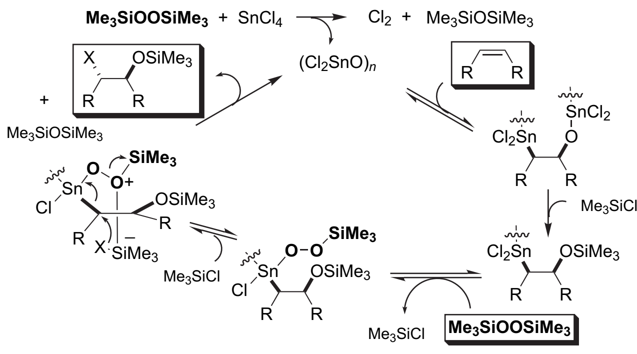
4.5. Reactions via peroxides of other metals

Medial alkenes can be converted into chlorohydrins by treatment with bis(trimethylsilyl) peroxide in the presence of $SnCl_4$ and Me_3SiCl.[113]



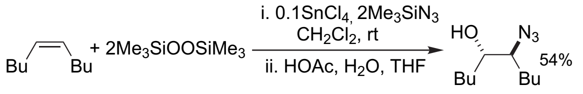
(79)

Evidence was adduced that the active catalyst is $(Cl_2SnO)_n$, which can be prepared independently, and it is suggested that the alkene inserts into an Sn–O bond to establish the postulated catalytic cycle which is shown in Scheme 6 (X=Cl). The insertion of polar multiple bonds into the Sn–O bond is well known, but this would be the first example of the insertion of a simple alkene.[114] The peroxide, as picked out in bold in Scheme 6, is involved in the formation of the catalyst, and in forming an intermediate stannyl silyl peroxide, thereby inducing the conjugate S_N2 introduction of the chloride group.

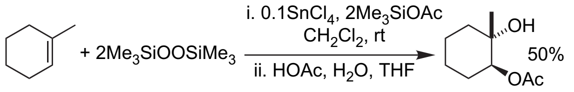


Scheme 6. Siloxyhalogenation of alkenes.

A similar reaction occurs with trimethylsilyl azide (Scheme 6, X=N_3), and with trimethylsilyl acetate (Scheme 6, X=OAc), to give the corresponding azidohydrins or acetoxyhydrins (Eqs. 80 and 81).[115]

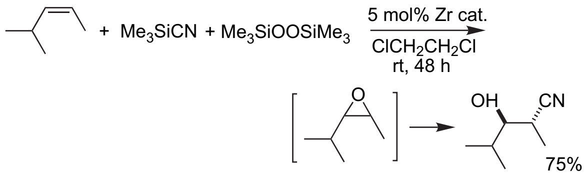


(80)

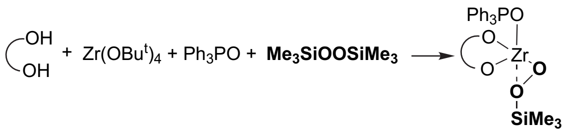


(81)

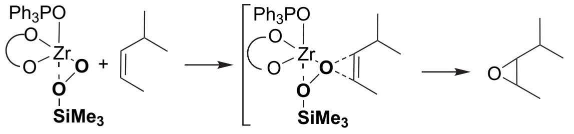
Cyanohydrins can be prepared by treating alkenes with $Me_3SiOOSiMe_3$ and Me_3SiCN in the presence of a zirconium catalyst (Eq. 82). The most effective catalyst is a mixture of zirconium tetrabutoxide and a diol in the presence of triphenylphosphine oxide, when the peroxide is involved in forming a zirconium silyl peroxide (Eq. 83), which oxidises the alkene to the intermediate epoxide (Eq. 84).[116]



(82)

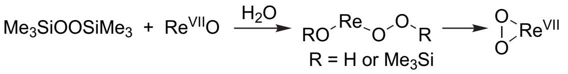


(83)

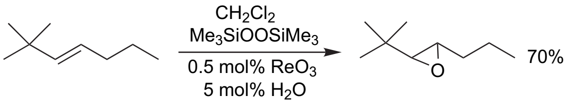


(84)

Bis(trimethylsilyl) peroxide in the presence of a catalytic amount of a proton source, in conjunction with an inorganic rhenium catalyst such as ReO_3 or Re_2O_7, forms a cyclic rhenium(VII) peroxide, which oxidises a wide variety of alkenes to epoxides in good yield (e.g., Eqs. 85 and 86).[117]

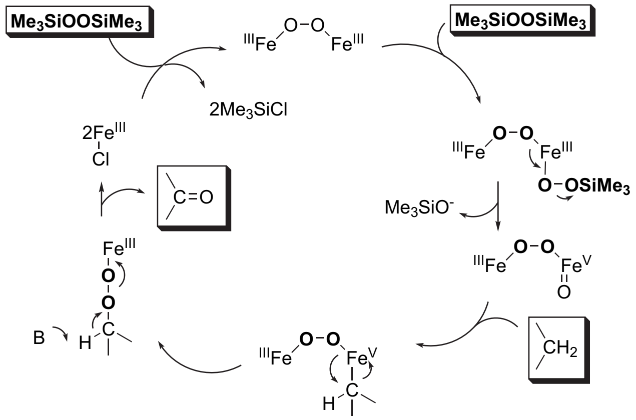


(85)

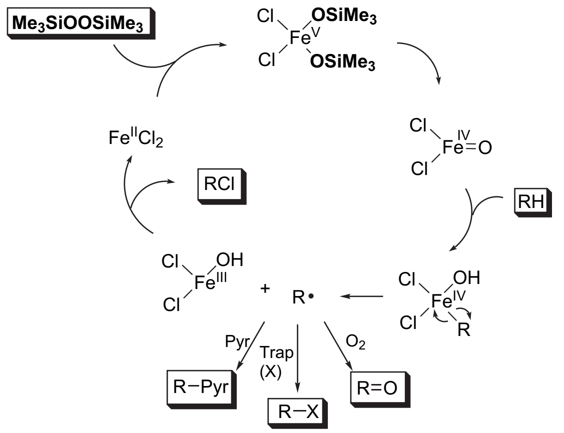


(86)

Extensive work has been carried out on the functionalisation of hydrocarbons, particularly by Barton's group (the Gif reactions), using oxygen, peroxides, or superoxides and iron catalysts, and the silyl peroxides have been included. The reactions are mechanistically complicated, and permit a variety of interpretations.[118,119] Barton's picture of the reactions which involve $Me_3SiOOSiMe_3$ is that those which operate through the Fe(III)–Fe(V) manifold are non-radical processes which involve Fe(III)/Fe(III), Fe(III)/Si, Fe(III)/Fe(V) and Fe(III)/C peroxides as outlined in Scheme 7,[120] whereas those which operate through the Fe(II)–Fe(IV) manifold follow a radical mechanism (Scheme 8).



Scheme 7. Functionalisation of alkenes through the Fe(III)–Fe(V) manifold.



Scheme 8. Functionalisation of alkenes through the Fe(II)–Fe(IV) manifold.

5. Conclusions

The preparations of the silyl peroxides follow the mechanistic models, which are familiar from the chemistry of the organic peroxides, but their reactions are substantially different. The weakness of the peroxide bond is now combined with the strength of the Si–O bond, resulting in a variety of mechanisms, which have little precedent, in which, in a cyclic process, the silicon becomes bonded to the β-oxygen of the peroxide group.[9] Frequently, a silicon peroxide can react by two different mechanisms, resulting in different products, and the balance of the two reactions depends sensitively on the structure and the environment.

The main established and postulated mechanisms are summarised in Table 10.

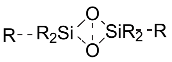
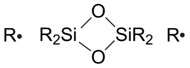
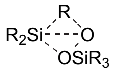
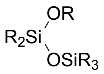
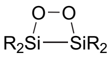
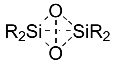
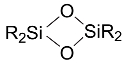
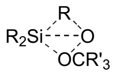
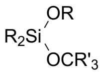
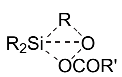
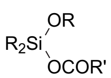
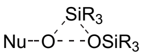
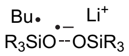
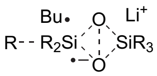
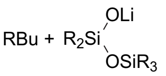
Straightforward homolysis of the peroxide bond in disilyl peroxides to give two siloxyl radicals has been identified only for the photolysis of $Me_3SiOOSiMe_3$; the photolysis of even $Et_3SiOOSiEt_3$ is complicated by some cleavage of the Et–Si bond to give ethyl radicals.

The thermolysis of disilyl peroxides in the gas phase or in inert solution appears to follow wholly a cyclic process, though in the presence of an alkene, homolysis can occur to give radicals which can initiate polymerisation. The silyl alkyl peroxides show behaviour intermediate between that of the disilyl and the dialkyl peroxides, thermolysing by both homolysis and rearrangement.

The silyl acyl peroxides, like the alkyl acyl peroxides (peroxyesters), undergo a Criegee-type rearrangement with a high degree of polar character.

Computational studies suggest that the attack of nucleophiles on the peroxide bond occurs with the formation of a bond between silicon and the departing β-oxygen atom, and the cleavage of the peroxide bond by organolithium and organomagnesium reagents is best regarded as an electron-transfer process resulting in the formation of caged radicals from the peroxide radical anion.

Table 10. Mechanisms, established and postulated, for reactions involving cleavage of the O–O bond

Peroxide	Conditions	Transition state	Products
$R_3SiOOSiR_3$ (R=Me)	*hν*	$R_3Si{-}{-}SiR_3$	$R_3SiO\bullet \quad \bullet OSiR_3$
$R_3SiOOSiR_3$ (R=Et, Pr)	*hν*		
$R_3SiOOSiR_3$	Δ		
	Δ		
$R_3SiOOCR'_3$	Δ		
$R_3SiOOCOR'$	Δ		
$R_3SiOOSiR_3$	Nu:		$NuO + R_3SiOSiR_3$
$R_3SiOOSiR_3$	BuLi		$R_3SiOBu + LiOSiR_3$
$R_3SiOOSiR_3$	BuLi		

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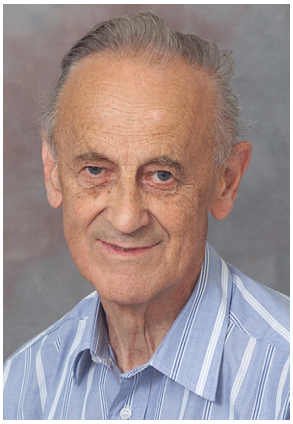
References and notes

1. Davies, A. G. *Organic Peroxides*; Butterworths: London, 1961.
2. *Organic Peroxides*; Ando, W., Ed.; Wiley: Chichester, UK, 1992.
3. *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: Chichester, UK, 1983.
4. *The Chemistry of Peroxides*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 1992; Vol. 2, Parts 1 and 2.
5. Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1974**, *78*, 1–48.
6. Aleksandrov, Y. A. *J. Organomet. Chem.* **1982**, *238*, 1–78.
7. Tamao, K. *Science of Synthesis*; Moloney, M. G., Ed.; Thieme: Stuttgart, 2002.
8. Ando, W. *Chemistry of Peroxides*; Rappoport, Z., Ed.; John Wiley and Sons: 2006; pp 775–830.
9. Ricci, A.; Seconi, G.; Curci, R.; Larson, G. L. *Adv. Silicon. Chem.* **1996**, *3*, 63–104.
10. Buncel, E.; Davies, A. G. *J. Chem. Soc.* **1958**, 1550–1556.
11. Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785–2812.
12. Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan, H. B. *J. Org. Chem.* **1997**, *62*, 6733–6745.
13. Jackson, W. P. *Synlett* **1990**, 536.
14. Berry, K. L.; E. I. du Pont de Nemours and Co. U.S. Patent 2,692,887, 1954.
15. Ren, Y.; Yamataka, H. *Org. Lett.* **2006**, 119–121 and papers quoted therein.
16. Hahn, W.; Metzinger, L. *Makromol. Chem.* **1956**, *21*, 113–120.
17. Dannley, R. L.; Jalics, G. *J. Org. Chem.* **1965**, *30*, 2417–2419.
18. Lutsik-Maksim, D. S.; Timokhin, V. I.; Zaborovskii, A. B.; Pristanskii, R. E.; Turovskii, A. A.; Chatgiliaoglu, C. *Russ. J. Gen. Chem.* **2004**, *74*, 1508–1512.
19. Hillgaertner, H.; Neumann, W. P.; Schulten, W.; Zarkadis, A. K. *J. Organomet. Chem.* **1980**, *201*, 197–211.
20. Chatgilialoglu, C.; Guerrini, A. L. M.; Pedulli, G. F.; Carrozza, P.; Da Roit, G.; Borzatta, V.; Lucchini, V. *Organometallics* **1998**, *17*, 2169–2176.
21. Howard, J. A.; Tait, J. C.; Tong, S. B. *Can. J. Chem.* **1979**, *57*, 2761–2766.
22. Rhodes, C. J. *J. Organomet. Chem.* **1993**, *443*, 19–23.
23. Nagano, T.; Takizawa, H.; Hirobe, M. *Organic Peroxides*; Ando, W., Ed.; Wiley: Chichester, UK, 1992.
24. Schmidt, M.; Bipp, H. *Z. Anorg. Allg. Chem.* **1960**, *303*, 190–200.
25. Fattakhova, D. S.; Jouikov, V. V.; Voronkov, M. G. *J. Organomet. Chem.* **2000**, *613*, 170–176.
26. Martiz, B.; Keyrouz, R.; Gmouh, S.; Vaultier, M.; Jouikov, V. *Chem. Commun.* **2004**, 674–675.
27. Chen, Y.-J.; Huang, Y.-P. *Tetrahedron Lett.* **2000**, *41*, 5233–5236.

28. Cookson, P. G.; Davies, A. G.; Fazal, N. *J. Organomet. Chem.* **1975**, *99*, C31–C32.
29. Dembech, P.; Ricci, A.; Seconi, G.; Taddei, M. *Org. Synth.* **1997**, *74*, 84–90.
30. Camporeale, M.; Fiorani, T.; Troisi, L.; Adam, W.; Curci, R.; Edwards, J. O. *J. Org. Chem.* **1990**, *55*, 93–98.
31. Babin, P.; Bennetau, B.; Dunogues, J. *Synth. Commun.* **1992**, *22*, 2849–2852.
32. Adam, W.; Albert, R. *Tetrahedron Lett.* **1992**, *33*, 8015–8016.
33. Tarabarina, A. P.; Yablokov, V. A.; Yablokova, N. V. *Zh. Obshch. Khim.* **1970**, *40*, 1094–1095.
34. Razuvaev, G. A.; Zinov'eva, T. I.; Brilkina, T. G. *Dokl. Akad. Nauk SSSR* **1969**, *188*, 830–832.
35. Yablokov, V. A.; Khorshev, S. A.; Tarabarina, A. P.; Sunin, A. N. *Zh. Obshch. Khim.* **1973**, *43*, 607–611.
36. Dannley, R. L.; Shubber, A. K. *J. Org. Chem.* **1971**, *36*, 3784–3787.
37. Tamao, K.; Kumada, M.; Takahashi, T. *J. Organomet. Chem.* **1975**, *94*, 367–376.
38. Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1971**, *31*, 17–34.
39. Akasaka, T.; Sato, K.; Kako, M.; Ando, W. *Tetrahedron Lett.* **1991**, *32*, 6605–6608.
40. Akasaka, T.; Kako, M.; Nagase, S.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1990**, *112*, 7804–7806.
41. McKillop, K. L.; Gillette, G. R.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1992**, *114*, 5203–5208.
42. Millevolte, A. J.; Powell, D. R.; Johnson, S. G.; West, R. *Organometallics* **1992**, *11*, 1091–1095.
43. Trommer, M.; Sander, W.; Patyk, A. *J. Am. Chem. Soc.* **1993**, *115*, 11775–11783.
44. Ando, W.; Kako, M.; Akasaka, T.; Nagase, S.; Kawai, T.; Nagai, Y.; Sato, T. *Tetrahedron Lett.* **1989**, *30*, 6705–6708.
45. Ando, W.; Kako, M.; Akasaka, T.; Kabe, Y. *Tetrahedron Lett.* **1990**, *31*, 4177–4180.
46. Ando, W.; Kako, M.; Akasaka, T.; Nagase, S. *Organometallics* **1993**, *12*, 1514–1522.
47. Fan, Y. L.; Shaw, R. G. *J. Org. Chem.* **1973**, *38*, 2410–2412.
48. Bloodworth, A. J.; Eggelte, H. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1375–1382.
49. Corey, E. J.; Schmidt, G.; Shimoji, K. *Tetrahedron Lett.* **1983**, *24*, 3169–3170.
50. Rubottom, G. M.; Lopez Nieves, M. I. *Tetrahedron Lett.* **1972**, 2432–2435.
51. Belavin, I. Y.; Yu, I.; Lutsenko, I. F. *Khim. Elementoorg. Soedin.* **1976**, 74–76.
52. Tomadze, A. V. Y.; Yablokov, V. A.; Yablokova, N. V.; Aleksandrov, Y. A. *Zh. Obshch. Khim.* **1977**, *47*, 2549–2552.
53. Ol'dekop, Y. A.; Livshits, F. Z.; Beresnevich, L. B. *Vestsi Akademii Navuk BSSR, Seryya Khimichnykh Navuk* **1975**, 113–115.
54. Brandes, D.; Blaschette, A. *Monatsh. Chem.* **1975**, *106*, 1299–1306.
55. Razuvaev, G. A.; Basova, G. V.; Dodonov, V. A.; D'yachkovskaya, O. S.; An, A. K. *Izv. Akad. Nauk, Ser. Khim.* **1978**, 180–184.
56. Sander, W. W. *J. Org. Chem.* **1989**, *54*, 333–339.
57. Sander, W.; Bettinger, H. F.; Bornemann, H.; Trommer, M.; Zielinski, M. *Silicon Chemistry*; Jutzi, P., Schubert, U., Eds.; Wiley-VCH: Weinheim, 2003; pp 58–70.
58. Tarunin, B. I.; Tarunina, V. N.; Kurskii, Y. A. *Zh. Obshch. Khim.* **1988**, *58*, 1060–1062.
59. Cerkovnik, J.; Tuttle, T.; Kraka, E.; Lendero, N.; Plesnicar, B.; Cremer, D. *J. Am. Chem. Soc.* **2006**, *128*, 4090–4100.
60. Corey, E. J.; Mehrotra, M. M.; Khan, A. U. *J. Am. Chem. Soc.* **1986**, *108*, 2472–2473.
61. Exner, O. *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: Cirencester, 1983; pp 85–96.
62. Hartung, J.; Svoboda, I. *The Chemistry of Organic Peroxides*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 2006; pp 93–144.
63. Schraml, J.; Chvalovsky, V.; Magi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1978**, *43*, 3365–3372.
64. Khorshev, S. Y.; Egorochkin, A. N.; Skobeleva, S. E.; Sluchevskaya, N. P.; Ganyushkin, A. V.; Yablokov, V. A. *Zh. Obshch. Khim.* **1978**, *48*, 1353–1357.
65. Oelfke, W. C.; Gordy, W. *J. Chem. Phys.* **1969**, *51*, 5336–5343.
66. Abrahams, S. C.; Collin, R. L.; Lipscomb, W. N. *Acta Crystallogr.* **1951**, *4*, 15–20.
67. Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1965**, *42*, 3054–3059.
68. Käss, D.; Oberhammer, H.; Brandes, D.; Blaschette, A. *J. Mol. Struct.* **1977**, *40*, 65–75.
69. Slovokhotov, Yu. L; Timofeeva, T. V.; Antipin, M. Yu.; Struchkov, Yu. T. *J. Mol. Struct.* **1984**, *112*, 127–140.
70. Königstein, D.; Jansen, M. *Monatsh. Chem.* **1996**, *127*, 1221–1227.
71. Shklover, V. E.; Timofeeva, T. V.; Struchkov, Y. T.; Ganyushkin, A. V.; Yablokov, V. A. *Zh. Strukt. Khim.* **1981**, *22*, 68–75.
72. Shklover, V. E.; Struchkov, Y. T.; Ganyushkin, A. V. *Zh. Strukt. Khim.* **1985**, *26*, 180–182.
73. Estevez, C. M.; Dmitrenko, O.; Winter, J. E.; Bach, R. D. *J. Org. Chem.* **2000**, *65*, 8629–8639.
74. Kokorev, V. N.; Vyshinskii, N. N.; Maslennikov, V. P.; Acronin, I. A.; Zhidomirov, V. P.; Aleksandrov, Y. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *22*, 9–15.
75. Razuvaev, G. A.; Yablokov, V. A.; Ganyushkin, A. V.; Shklover, V. E.; Zinker, I.; Struchkov, Y. T. *Dokl. Akad. Nauk SSSR* **1978**, *242*, 132–135.
76. Shklover, V. E.; Struchkov, Y. T. *J. Organomet. Chem.* **1987**, *322*, 269–298.
77. Benson, S. W.; Shaw, R. *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, NY, 1970; pp 105–139.
78. Benson, S. W.; Cohen, N. *Peroxyl Radicals*; Alfassi, Z., Ed.; Wiley: Chichester, UK, 1997; pp 49–68.
79. Hiatt, R. R. *Can. J. Chem.* **1964**, *42*, 985–989.
80. Rabinovich, I. B.; Kiparisova, E. G.; Aleksandrov, Y. A. *Dokl. Chem.* **1971**, *200*, 842–844.
81. Cookson, P. G.; Davies, A. G.; Fazal, N. A.; Roberts, B. P. *J. Am. Chem. Soc.* **1976**, *98*, 616–618.
82. Petrenko, V. V.; Turovskii, A. A.; Litkovets, A. K. *Zh. Obshch. Khim.* **1981**, *51*, 598–603.
83. Edge, D. J.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 182–190.
84. Dannley, R. L.; Jalics, G. *J. Org. Chem.* **1965**, *30*, 3848–3851.
85. Yablokov, V. A.; Sunin, A. N.; Yablokova, N. V.; Ganyushkin, A. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1973**, *44*, 2405–2408.
86. Yablokov, V. A.; Ganyushkin, A. V.; Yablokova, N. V. *Zh. Obshch. Khim.* **1977**, *47*, 2553–2556.
87. Yablokov, V. A. *Russ. Chem. Rev.* **1980**, *49*, 833–842.
88. Gorbatov, V. V.; Yablokova, N. V.; Kheidorov, V. P.; Aleksandrov, Y. *Zh. Obshch. Khim.* **1980**, *50*, 2482–2486.

89. Aleksandrov, Y. A.; Gorbatov, V. V.; Yablokova, N. V.; Tsvetkov, V. G. *J. Organomet. Chem.* **1978**, *157*, 267–274.
90. Razuvaev, G. A.; Yablokov, V. A.; Ganyushkin, A. V.; Yablokova, N. V.; Kalinina, G. S. *J. Organomet. Chem.* **1979**, *165*, 281–286.
91. Yablokov, V. A.; Kalinina, G. S.; Yablokova, N. V.; Basalgina, T. A.; Vyazankin, N. S.; Razuvaev, G. A. *J. Organomet. Chem.* **1978**, *153*, 25–30.
92. Antonovskii, V. L.; Zhulin, V. M. *Kinet. Catal. (Translation of Kinetika i Kataliz)* **2003**, *44*, 74–81.
93. Fleming, I. *Chemtracts: Org. Chem.* **1996**, *9*, 1–64.
94. Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599–7662.
95. Adam, W.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2894–2895.
96. Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1974**, *73*, 217–227.
97. Bressel, B.; Blaschette, A. *Z. Anorg. Allg. Chem.* **1970**, *377*, 182–195.
98. Renz, M.; Meunier, B. *Eur. J. Org. Chem.* **1999**, 737–750.
99. Suzuki, M.; Takada, H.; Noyori, R. *J. Org. Chem.* **1982**, *47*, 902–904.
100. Matsubara, S.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2029–2032.
101. Jefford, C. W.; Jaber, A.; Boukouvalas, J. *Synthesis* **1988**, 391–393.
102. Adam, W.; Rodriguez, A. *J. Org. Chem.* **1979**, *44*, 4969–4970.
103. Curci, R.; Mello, R.; Troisi, L. *Tetrahedron* **1986**, *42*, 877–883.
104. Taddei, M.; Ricci, A. *Synthesis* **1986**, 633–635.
105. Camici, L.; Dembech, P.; Ricci, A.; Seconi, G.; Taddei, M. *Tetrahedron* **1988**, *44*, 4197–4206.
106. Nugent, W. A.; Bertini, F.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 4945–4954.
107. Kurskii, Y. A.; Baryshnikov, Y. N.; Vesnovskaya, G. I.; Kaloshina, N. N.; Aleksandrov, Y. A. *Dokl. Akad. Nauk SSSR* **1981**, *258*, 936–938.
108. Kurskii, Y. A.; Baryshnikov, Y. N.; Kaloshina, N. N.; Vesnovskaya, G. I. *Zh. Obshch. Khim.* **1981**, *51*, 362–366.
109. Baryshnikov, Y. N.; Kurskii, Y. A.; Kaloshina, N. N.; Vesnovskaya, G. I. *Zh. Obshch. Khim.* **1982**, *52*, 2288–2292.
110. Florio, S.; Troisi, L. *Tetrahedron Lett.* **1989**, *30*, 3721–3724.
111. Epifani, E.; Florio, S.; Troisi, L. *Tetrahedron* **1990**, *46*, 4031–4038.
112. Olah, G. A.; Ernst, T. D. *J. Org. Chem.* **1989**, *54*, 1204–1206.
113. Sakurada, I.; Yamasaki, S.; Goettlich, R.; Iida, T.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 1245–1246.
114. Davies, A. G. *Organotin Chemistry*, 2nd ed.; Wiley-VCH: Weinheim, 2004.
115. Sakurada, I.; Yamasaki, S.; Kanai, M.; Shibasaki, M. *Tetrahedron Lett.* **2000**, *41*, 2415–2418.
116. Yamasaki, S.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 1256–1257.
117. Yudin, A. K.; Chiang, J. P.; Adolfsson, H.; Coperet, C. *J. Org. Chem.* **2001**, *66*, 4713–4718.
118. Perkins, M. J. *Chem. Soc. Rev.* **1996**, 229–236.
119. Barton, D. H. R. *Chem. Soc. Rev.* **1996**, 237–239.
120. Barton, D. H. R.; Chabot, B. M. *Tetrahedron* **1997**, *53*, 487–510.

Biographical sketch



Alwyn Davies did his first degree, and Ph.D. with Sir Christopher Ingold, at University College London. After four years as a lecturer at Battersea Polytechnic, with Joseph Kenyon, he returned to University College. He has held visiting professorships at the National Research Council, Ottawa, and at Indiana, Bordeaux, ANU Canberra, and Deakin Universities, and a Senior Humbolt Fellowship at Freiburg University. He has been awarded the Ingold Lectureship, and the prize for Organic Reaction Mechanism, of the Royal Society of Chemistry, and was made a Fellow of the Royal Society in 1989.

His published work is in the related fields of organic peroxides, main group organometallic chemistry, free radical reactions and ESR spectroscopy, and he has published books on *Organic Peroxides* (1960) and *Organotin Chemistry* (1997 and 2004).