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THE SILICON—OXYGEN DOUBLE-BONDED INTERMEDIATES

A NEW METHOD FOR THE FORMATION OF ORGANOSILANONES

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Summary

The kinetics and mechanism of thermal decomposition of $R^1R^2(H)SiOOR^3$ silylperoxides have been studied. It has been shown that peroxides generated diorganosilanones, $R^1R^2Si{=}O$, with a high yield in the temperature range 130—180° C. A mechanism is suggested for the silanone formation. The interaction of silanones with cyclosiloxanes, triethylsilane, α-methylstyrene has been investigated as well as the cyclisation of silanones.

Introduction

There is now good reason to believe that intermediates containing a double Si=O bond have been detected. The pyrolysis products of cyclosiloxanes [1,2] and silacyclobutanes in the presence of ketones [3,4] at temperature above 500° C, as well as reactions of dimethylsulfoxide with dimethylsilylene [5], 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silyrene and hexamethylsilyrane [6] at room temperature are explained by generation of silanones.

The formation of silanones in these reactions has been confirmed by means of traps such as $(Me_2SiO)_3$ [5,6], $Me_2Si(OMe)_2$ [6], Me_3SiCl [2] and silyrene [6], giving the products from insertion of the silanones into the Si—O, Si—Cl or Si—C single bond. In addition [7,8], molecules of SiO_2 and $Cl_2Si{=}O$ have been stabilised by matrix isolation in argon and their IR spectra studied. These are indicative of silicon multiply bonded to oxygen, and thus finally confirmed the existence of multiple Si=O bonds.

We would like to report a new method of generating diorganosilanones [9,10] allowing production of the substituted silanones and the study of their reactivity at temperatures of 130—180° C.

Results and discussions

It is known [11,12] that the thermal decomposition of $R_3MOOC(H)R^1R^2$ peroxides (M = Si, Ge, Sn; R, R^1, R^2-alkyl, aryl) is accompanied by formation of a considerable amount of ketones. Rearrangement and homolysis are parallel reactions.

$$R_3MOOC(H)R^1R^2 \begin{cases} \rightarrow R_3MOH + R^1R^2C{=}O & (1) \\ \rightarrow (RO)R_2MOC(H)R^1R^2 & (2) \\ \rightarrow R_3MO^\cdot + {}^\cdot OC(H)R^1R^2 & (3) \end{cases}$$

Reaction 1 occurs as a concerted intramolecular transfer of the α-hydrogen from the silicon to the peroxide oxygen. We hoped that silylperoxides containing an α-hydrogen at the silicon atom would be decomposed by migration reaction to produce silicon analogs of ketones. For this purpose the thermal decomposition of eight $R^1R^2Si(H)OOR^3$ silylperoxides was studied in nonane (Table 1). The peroxide decomposition is a first order reaction with a degree of conversion of 70—80%. Rate constants and activation parameters of the peroxide decomposition are listed in Table 2. The main decomposition products of the peroxides are listed in Table 3.

The decomposition of the silylperoxides consists of three parallel reactions A, B and C (Scheme 1). The peroxides VI—VIII, containing phenyl groups at

SCHEME 1

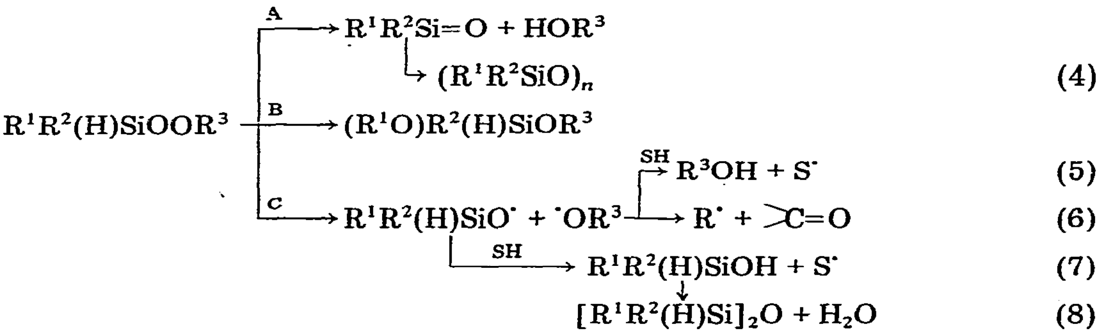


TABLE 1

SOME DATA OF THE SILICON PEROXIDES SYNTHESIZED

No.	Peroxide	n_D^{20}	B.p. (°C/mmHg)	Molec. weight Found	Molec. weight Calc.	% O—O
I	$Me_2(H)SiOOCMe_3$	1.3950	43/65	148	144	95
II	$Me_2(H)SiOOCMe_2Ph$	1.4840	57—58/0.05	197	210	95
III	$MeEt(H)SiOOCMe_3$	The solutions of individual compounds were prepared in nonane without isolation in the pure form by the reaction: $R^1R^2(H)SiCl + HOOR^3 \xrightarrow{Et_3N} R^1R^2(H)SiOOR^3 + Et_3N \cdot HCl$				
IV	$MeEt(H)SiOOCMe_2Ph$					
V	$Et_2(H)SiOOCMe_3$					
VI	$MePh(H)SiOOCMe_3$					
VII	$MePh(H)SiOOCMe_2Ph$					
VIII	$Ph_2(H)SiOOCMe_3$					

TABLE 2

KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF THE PEROXIDES $R^1R^2(H)SiOOR^3$ (C_0 = 0.2 mol l^{-1}) IN NONANE [a]

Peroxide	k X 10^5 (s^{-1})						$E^\#$ (kJ mol^{-1})	log K_0	$\Delta S^\#$ (J mol^{-1} deg^{-1})
	130°C	140°C	150°C	160°C	170°C	180°C			
$Me_2(H)SiOOCMe_3$			9,66	32,4	68,5	109	129	11,9	—29
$Me_2(H)SiOOCMe_2Ph$			5,73	10,9	25,0	37,3	102	8,4	
$MeEt(H)SiOOCMe_3$		11.5	17,5	34,0	61,9		87	7,0	—121
$MeEt(H)SiOOCMe_2Ph$		4,88	9,09	19,0	31,2		96	7,8	
$Et_2(H)SiOOCMe_3$		10,9	16,9	33,7	74,0		108	9,2	—80
$MePh(H)SiOOCMe_3$		7,36	16,7	40,4	76,4		120	11,0	
$MePh(H)SiOOCMe_2Ph$	10,7	17,9	41,0	100			109	10,1	
$Ph_2(H)SiOOCMe_3$	9,53	17,7	38,7	59,9			87	7,2	

[a] k, $E^\#$ and log k_0 are calculated by the least square method, the mean square errors of $E^\#$ and log k_0 did not exceed ±8 J mol^{-1} and ±0.8 respectively. k is independent of changing peroxide concentration at 0,02—0,2 mol l^{-1}.

TABLE 3

MAIN DECOMPOSITION PRODUCTS OF $R^1R^2(H)SiOOR^3$ IN NONANE (IN MOL PER MOL OF PEROXIDE) (C_0 = 0.2 mol l^{-1}, T = 160°C) [a]

Peroxide	R^3OH	ketone	$(R^1R^2SiH)_2O$	$(R^1R^2SiO)_3$	$(R^1R^2SiO)_4$	$(R^1O)R^2(H)SiOR^3$
$Me_2(H)SiOOCMe_3$	0,81	—	—	0,02	0,13	—
$Me_2(H)SiOOCMe_2Ph$	0,60	0,28	0,09	0,01	0,2	—
$MeEt(H)SiOOCMe_3$	0,79	—	—	0,03	0,07	—
$MeEt(H)SiOOCMe_2Ph$	0,47	0,2	0,11	0,04	0,04	—
$Et_2(H)SiOOCMe_3$	0,83	—	—	0,13	0,01	—
$MePh(H)SiOOCMe_3$	0,75	—	—	0,14	0,12	0,14
$MePh(H)SiOOCMe_2Ph$	0,66	0,13	0,09	0,07	traces	0,14
$Ph_2(H)SiOOCMe_3$	0,56	—	—	0,06	0,05	0,21

[a] The yields of cyclosiloxanes are given in gram-equivalent of R^1R^2SiO fragment per mol of peroxide.

silicon, only rearrange to isomeric siloxanes (reaction B). Reaction C is typical for peroxides II, IV and VII.

We used hexamethylcyclotrisiloxane (D_3) and hexamethyldisiloxane as traps to confirm the formation of silanones. The insertion of silanones into the Si—O σ-bond occurs after the decomposition of peroxides (reaction 9 and 10):

$$R^1R^2Si{=}O + (Me_2SiO)_3 \rightarrow R^1R^2\overline{SiO(Me_2SiO})_3 \qquad (9)$$

$$Me_2Si{=}O + (Me_3Si)_2O \rightarrow (Me_3SiO)_2SiMe_2 \qquad (10)$$

The analytical data for the decomposition products of silylperoxides in siloxanes as solvents are listed in Table 4.

We succeeded in finding a more effective trap for silanones; this was triethylsilane. The decomposition of $R^1R^2(H)SiOOR^3$ in pure triethylsilane leads to the formation of $Et_3SiOSi(H)R^1R^2$. The formation of this product is probably a result of the insertion of the silanone into the Si—H bond of triethylsilane:

$$R^1R^2Si{=}O + Et_3SiH \rightarrow Et_3SiOSi(H)R^1R^2 \qquad (11)$$

The yield of the insertion product for peroxide I is equal to 0.98 and for VI 0.85 mol per mol of peroxide. The participation of peroxide VI in a parallel rearrangement reaction decreases the yield of the silanones. To confirm the absence of a direct reaction of peroxide with triethylsilane, both trimethyl(tert.-butylperoxy)silane and triphenyl(tert.-butylperoxy)silane were decomposed in the presence of triethylsilane. It was demonstrated that reaction 12 did not take place.

$$R_3SiO{-}OCMe_3 + Et_3Si{-}H \rightarrow R_3SiOSiEt_3 + HOCMe_3 \qquad (12)$$

Substitution of hydrogen in the $R^1R^2(H)Si$ group of the peroxide by Ph or Me did not change the reactivity of the latter with respect to triethylsilane. The considerable reactivity of triethylsilane as a trap for silanones in comparison with siloxanes may be explained by the difference in energy of the bonds which participate in the reaction with silanones (D(Si—H) = 314 kJ mol^{-1} and D(Si—O) = 444 kJ mol^{-1}). More effective sources of silanones are peroxides I, III and V, which decompose to the silanones quantitatively (reaction A, Scheme 1). There are alternative routes for the decomposition other peroxides. One involves rearrangement of a silyl group (reaction B) and the other includes free radical decomposition (reaction C).

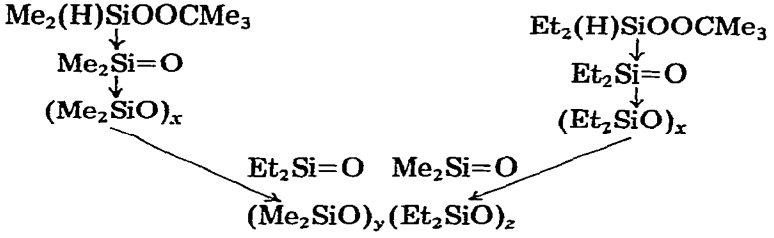
TABLE 4

THE YIELD OF INSERTION OF SILANONES AFTER THE DECOMPOSITION OF $R^1R^2(H)SiOOR^3$ IN $(Me_2SiO)_3$ AND $(Me_3Si)_2O$ (T = 160°C; C_0 = 0.4 mol l^{-1})

Peroxide	The yield of insertion products (mol per mol of peroxide)	
	D_3	$(Me_3Si)_2O$
$Me_2(H)SiOOCMe_3$		0.02
$Et_2(H)SiOOCMe_3$	0.09	
$MePh(H)SiOOCMe_3$	0.06	
$Ph_2(H)SiOOCMe_3$	0.09	

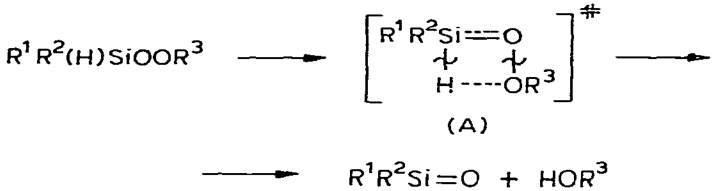
Direct evidence for the existence of the short lived species $Me_2Si{=}O$ and $Et_2Si{=}O$ was obtained by combined thermal decomposition of $Me_2(H)SiOOCMe_3$ and $Et_2(H)SiOOCMe_3$. The formation of mixed cyclosiloxanes, containing one Me_2SiO or Et_2SiO fragment, confirmed the possibility of obtaining Si—O doubly bonded intermediates (Scheme 2).

SCHEME 2



$x = 3, 4; y = 1–3; z = 1–3; y + z = 3, 4$

The first order kinetics, the lack of influence of the concentration of peroxide on the rate constants, and the absence of ketone in the decomposition products of peroxides I, III and V suggest that the generation of silanones is not a radical process. It is known that photolysis of peroxides leads to the radical products. As was expected, UV irradiation ($\lambda = 253.7$ nm, $T = 20°C$, nonane) of silylperoxides also led to the products of radical decomposition. No cyclosiloxanes which might have been derived from silanones were observed. This agrees well with the formation of silanones being an intramolecular reaction.



$$R^1R^2(H)SiOOR^3 \longrightarrow \left[\begin{matrix} R^1R^2Si{=}O \\ H \cdots OR^3 \end{matrix}\right]^{\ne} \longrightarrow R^1R^2Si{=}O + HOR^3 \qquad (13)$$

(A)

Negative values for the entropies for peroxides I, III and V (Table 2) confirm that the reaction proceeds via the cyclic complex A. This complex is not polar and the rate constants are slightly dependent on the electronic effects of the substituents (Table 2) and the polarity of the solvent (Table 5).

The low yields of cyclosiloxanes are related to the competition between cyclization of the silanones and their reaction with solvents. At an increasing concentration of peroxide the yield of cyclosiloxanes becomes significant (Table 6).

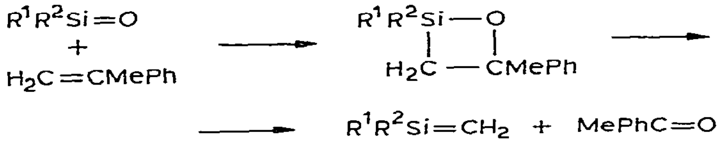
The formation of cyclosiloxanes cannot be explained as a bimolecular reaction of peroxides, since the reaction is a first order one with respect to the peroxide and the rate constants did not depend on initial concentration of peroxide. At the same time, the yield of cyclization products from silanones depended on the initial concentration of peroxide (Table 6) and the nature of solvents (Table 5). We did not succeed in isolating the products of interaction of silanones and solvents. Perhaps silanone is added to the double bond of

TABLE 5

THERMAL DECOMPOSITION OF $Me_2(H)SiOOCMe_3$ (C_0 = 0.2 mol l^{-1}, T = 160°C). INFLUENCE OF SOLVENT UPON RATE CONSTANTS AND YIELD OF CYCLOSILOXANES

Solvent	$k \times 10^5$ (s^{-1})	Yield of cyclosiloxanes (mol per mol of peroxide)	
		$(Me_2SiO)_3$	$(Me_2SiO)_4$
nonane	32.4	0.02	0.13
cyclohexane	35.5	0.06	0.04
benzene	54.0	0.25	0.32
isopropylbenzene	30.6	0.03	0.03
α-methylstyrene	69.9	traces	traces
anisole	49.2	0.15	0.55
chlorobenzene	107	traces	traces

α-methylstyrene if it is a solvent. The silaoxetane formed is not stable [13] and decomposes into acetophenone and unstable silene. The yield of acetophenone is 0.1—0.12 mol per mol of peroxide.



(14)

GLC and iodometrical methods were used to determine the concentration of silylperoxide and peroxide oxygen. When the initial peroxide (concentration was determined by GLC) disappeared, the peroxide oxygen remained in solution (iodometrical method) in the amount of 5—10%. Reaction 15 is assumed to take place.

$$R^1R^2Si{=}O + R^1R^2(H)SiOOR^3 \rightarrow R^1R^2(H)SiO(R^1R^2)SiOOR^3 \qquad (15)$$

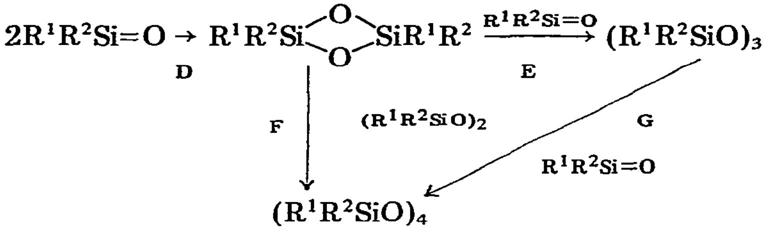
The peroxide formed is more stable than the initial one. It is known that silylperoxides containing the silyloxygroup [14] decompose only at temperature of 200—240°C. It will be noted that reaction 15 is observed for peroxides I and II having small R^1 and R^2 substituents. The silylperoxides thus formed (reaction 15) were not isolated; their structure was confirmed from their NMR spectrum.

TABLE 6

DEPENDENCE OF THE YIELD OF CYCLOSILOXANES ON THE CONCENTRATION OF $MePh(H)SiOOCMe_3$ (in nonane, T = 165°C)

C_0 (mol l^{-1})	Yield of $(MePhSiO)_x$ (gram-equivalent per mol of peroxide)
0.1	0.13
0.2	0.26
0.4	0.49
0.5	0.57

The formation of cyclosiloxanes on thermal decomposition of silylperoxides confirms the generation of silanones. We assume that cyclosiloxane is obtained via a bimolecular reaction of silanones as shown in Scheme 3:



The rates of reactions E and F are almost equal, since the yields of products are comparable. The bimolecular interaction G is negligible as the addition reaction of silanone, even with pure hexamethylcyclotrisiloxane, proceeds with a yield of not more than 10—25%.

Experimental

Preparation of silylperoxides

With vigorous stirring an equimolecular amount of triethylamine and hydroperoxide in pentane was added dropwise to an equimolecular amount of chlorosilane at 0° C, and the mixture was allowed to stand for 10 hours. The solution was filtered and the solvent was distilled off completely under reduced pressure at room temperature. Then silylperoxide was distilled under reduced pressure at ca. 60° C. Peroxides III—VIII were synthesized in nonane, filtered and these solutions were used for kinetic investigations.

Analysis

Peroxides were analysed iodometrically [15]. Products of decompositions were analysed by GLC. GLC analysis was carried out on a Tsvet-104 chromatograph with a heat conductivity detector using a 100 × 0.4 cm column packed with SE-30 (5%) or Reoplex-400 (15%) on Chromatone N-AW HMDS (0.2—0.25 mm). We used a Tesla BS-487 C NMR spectrometer for the NMR investigation.

Kinetic studies

Kinetic measurements were carried out by the literature method [15]. The reaction rate was followed iodometrically by the change in the concentration of peroxide oxygen.

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