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KINETICS OF THE CATALYTIC REARRANGEMENT OF ORGANOSILICON PEROXIDES

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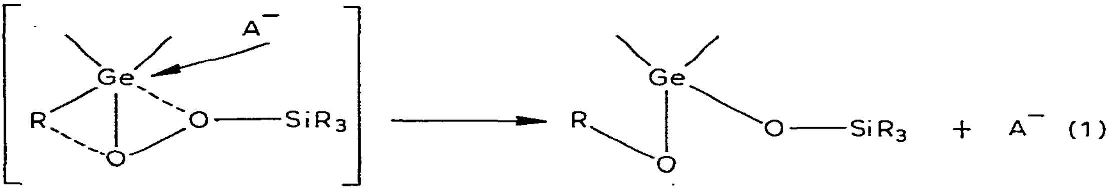
Summary

Kinetics of the rearrangement of bis[(*para*-substituted phenyl)dimethylsilyl] peroxides in the presence of catalytic amounts of potassium cyanide, potassium and caesium fluorides in isopropyl alcohol have been studied. The peroxide rearrangement proceeds to form aryloxysiloxanes and is first order with respect to both the peroxide and the catalyst. On increasing the catalyst concentration, the intramolecular rearrangement competes with solvolysis of the peroxide at the Si—O bond.

Introduction

Earlier it was established [1] that in the presence of catalytic amounts of a nucleophile the mixed germylsilicon peroxide $Ph_3GeOOSiPh_3$ is rearranged intramolecularly. The attack on the sterically available germanium atom by a nucleophile A^- is sufficiently effective and results in the migration of the internal nucleophile R from the germanium to the oxygen atom and also the migration of the silyloxy group $OSiR_3$ from the oxygen to the germanium atom [1].



It is known [2] that properties and reactions of organosilicon compounds are determined to a great extent by the properties of the siloxane bond. Thus, the cleavage of the Si—O bond, catalyzed by nucleophiles, is of great significance in the preparation of siloxane polymers and in the regulation of their properties. In this connection, we wished to investigate the catalytic transformations of compounds containing the silylperoxy group Si—O—O.

Proceeding from the fact of the catalytic rearrangement of the germylsilicon peroxide (eq. 1) we could expect that organosilicon peroxides should be rearranged as well. In order to check this suggestion it was necessary to select a suitable nucleophilic reagent and organosilicon peroxide to avoid the catalytic decomposition of the peroxide. Such a decomposition was observed by Brandes and Blaschette [3] when studying nonradical reactions of bis(trimethylsilyl) peroxide (eq. 2).

$$Me_3SiOOSiMe_3 \xrightarrow{A^-} Me_3SiA + {}^-OOSiMe_3 \qquad (2)$$

Results and discussion

The following peroxides of the structure $XC_6H_4Me_2SiOOSiMe_2C_6H_4X$, where X = *p*-MeO (I), *p*-Me (II), H (III) and *p*-Cl (IV) were used in the present investigation. Potassium cyanide and potassium and caesium fluorides were used as catalysts. The reactions were carried out in isopropyl alcohol solution. In some experiments the catalyst was added in solution together with dibenzo-18-crown-6 ether.

The thermal rearrangement of organosilicon peroxides proceeds at a noticeable rate in the temperature range 80—120°C or higher [4].

$$XC_6H_4Me_2SiOOSiMe_2C_6H_4X \rightarrow (XC_6H_4O)Me_2SiOSiMe_2C_6H_4X \qquad (3)$$

Electron-donating substituents X increase the thermal rearrangement rate. Thus, in anisole at 100°C, the rate constants increase in the order of *p*-substituents: Br < H < Me < MeO. We have established that in isopropyl alcohol solution in the presence of 3.8×10^{-4} mol l^{-1} of potassium cyanide or potassium and caesium fluorides, peroxides I—IV ($C_0 = 5 \times 10^{-2}$ mol l^{-1}) are quantitatively rearranged to form isomeric non-peroxide products $(XC_6H_4O)Me_2SiOSiMe_2C_6H_4X$ in the temperature range 0—60°C. The rearrangement of peroxides I—IV is a first order reaction with 80—95% conversion. The kinetic results are listed in Table 1.

The sequence of the ease of aryl group migration in order of substituent, MeO < Me < H < Cl, is reverse to that observed in the thermal rearrangement. This result is quite unexpected. The rate of a rearrangement is known to increase with increasing electron-donor properties of a group, which is migrating to an electron-deficient reaction centre. This was used to explain the rearrangement of peresters [5] catalyzed by acids, the rearrangement of arylalkyl hydroperoxides [6] and also the thermal rearrangement of organosilicon peroxides [4]. Therefore it was difficult to predict a priori that electron-donating substituents X would decrease the rate of the catalytic rearrangement of organosilicon peroxides. The reason for the change in the order of aryl group migration ability in the catalytic rearrangement has to be a change in the reaction mechanism. In Scheme 1 process 1 corresponds to the thermal rearrangement of the peroxide in the absence of the nucleophile A^- (S_N1). The rate of this process increases if the migrating group, being the internal nucleophile with respect to the electron-deficient peroxide oxygen, has an electron-donating substituent X. A deficit in the electron density at the oxygen atom is due to a $(p-d)_\pi$-contribution to the Si—O bond.

The catalytic rearrangement proceeds according to a S_N2 mechanism (process

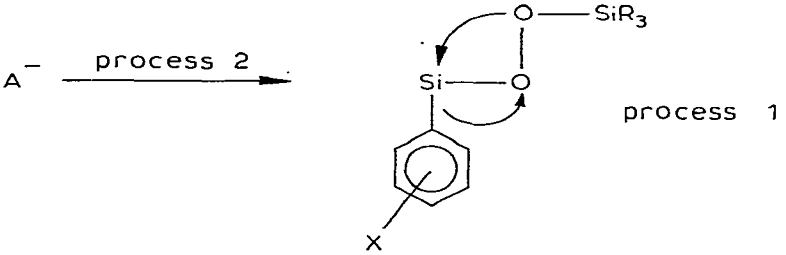
TABLE 1

KINETIC PARAMETERS FOR THE CATALYTIC REARRANGEMENT OF $XC_6H_4Me_2SiOOSiMe_2C_6H_4X$ (C_0 = 5 × 10^{-2} mol l^{-1}) IN ISOPROPYL ALCOHOL[a]
Catalyst KCN (C_0 = 3.8 × 10^{-4} mol l^{-1})

p-X	Temperature (°C)	*K* × 10[b] (l mol^{-1} s^{-1})	*E* (kcal mol^{-1})	log K_0
MeO	30	3.43	20.9 ± 1.1	14.63 ± 0.77
	40	13.0		
	50	30.0		
	60	82.2		
Me	20	1.95	20.0 ± 3.3	14.09 ± 2.4
	30	3.19		
	40	10.8		
	50	45.9		
H	10	1.48	17.6 ± 0.3	12.75 ± 0.2
	20	4.61		
	30	12.0		
	40	29.9		
Cl	0	6.88	14.2 ± 0.7	11.21 ± 0.55
	10	20.2		
	20	39.6		
	30	96.4		

[a] *K*, *E* and log K_0 in the Arrhenius' equation have been calculated by the least-squares method, the mean-square error is also given. [b] *K* has been calculated per unit of catalyst concentration.

2). The attack on the peroxide by the nucleophile A^- is a rate-limiting step in the process. Therefore electron withdrawing substituents accelerate the reaction as they increase the effective positive charge on the silicon atom. This scheme is confirmed by the log *k* — $\sigma(\sigma^+)$ correlation. The rate constants of the thermal rearrangement given in ref. 4 correlate well with σ^+ constants (see Fig. 1, line 1). The dependence on σ^+ indicates a direct polar conjugation between X and the electron-deficient peroxide oxygen in the transition state (process 1). The rate constants of the catalytic rearrangement correlate better with σ constants. The dependence on σ (Fig. 1, line 2) confirms the supposition that the attack on the peroxide by the nucleophile A^- is a rate-limiting step (process 2). In this case the role of X is effected by a change in the effective positive charge on the silicon atom. Since peroxide I is symmetrical the probability of the rearrangement with the participation of either of the silyl fragments is similar. It was necessary to ensure that the correlation dependence is not complicated by the variable substituent located in the phenyl group not participating in the mi-



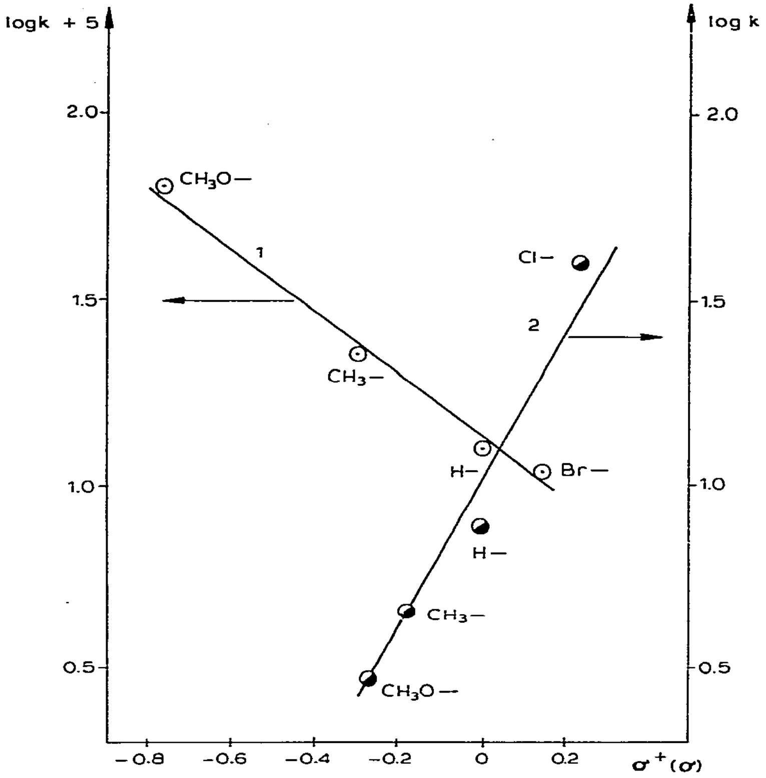


Fig. 1. The correlation in log k — σ^+ coordinates (straight line 1 was based on data in ref. 4 for thermal rearrangement of peroxides I—IV in anisole at 100°C; $\rho = -0.88$, $r = 0.99$, $s = 0.007$) and log k—σ coordinates (straight line 2 based on data in Table 1 at 50°C; $\rho = +2.04$, $r = 0.98$, $s = 0.01$).

gration. In fact, as has been shown in ref. 7 the role of such substituents is not considerable.

The influence of the catalyst on the reaction rate was studied (Table 2). In the presence of potassium and ceasium fluorides the reaction rate is higher than

TABLE 2

KINETIC PARAMETERS FOR THE CATALYTIC REARRANGEMENT OF $PhMe_2SiOOSiMe_2Ph$ ($C_0 = 5 \times 10^{-2}$ mol l^{-1}) IN ISOPROPYL ALCOHOL IN THE PRESENCE OF VARIOUS CATALYSTS ($C_0 = 3.8 \times 10^{-4}$ mol l^{-1})

Catalyst	Temperature (°C)	$K \times 10$ (l mol^{-1} s^{-1})[a]	E (kcal mol^{-1})	log K_0 lo
KF	10	15.2	12.9 ± 1.7	10.12 ± 1.33
	15	20.0		
	20	36.5		
	25	44.7		
CsF	5	15.1	12.3 ± 0.3	9.84 ± 0.25
	10	22.9		
	15	32.3		
	20	47.5		

[a] K has been calculated per unit of catalyst concentration.

TABLE 3

DEPENDENCE OF THE YIELD OF PRODUCT V (IN mol PER mol OF THE STARTING PEROXIDE III) ON THE CONCENTRATION OF CsF IN ISOPROPYL ALCOHOL

Initial concentration of $PhMe_2SiOOSiMe_2Ph$ 5×10^{-2} mol l^{-1}

$C(CsF) \times 10^2$ (mol l^{-1})	Yield (mol/mol)
0.038	0.98
0.16	0.87
0.54	0.75
1.0	0.77
20	0.51

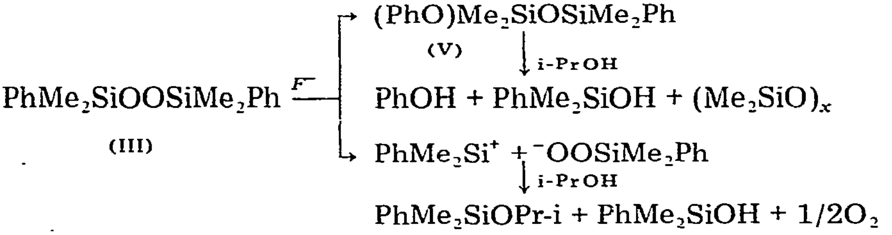
that in the presence of potassium cyanide. The rate constants given in Tables 1 and 2 indicate that the change of the catalyst efficiency is in the order KCN < KF< CsF under identical conditions.

The rearrangement of peroxides I—IV is first order with respect to both the peroxide in the initial concentration range 0.01—0.10 mol l^{-1} and the catalyst in the concentration range 3.8×10^{-4}—2.3×10^{-3} mol l^{-1}. Complete dissociation of potassium and caesium fluorides takes place in alcohol. This is confirmed by experiments carried out in the presence of dibenzo-18-crown-6, addition of which did not change the rate constants. At the same time dibenzo-18-crown-6 added to a solution of potassium cyanide causes an increase in the reaction rate. Probably dibenzo-18-crown-6 shifts the equilibrium to the side of the catalytically active

$$KCN \rightleftharpoons K^+ + CN^-$$

ionic form of the catalyst.

We have established that on increasing the catalyst concentration up to that of the peroxide (Table 3) not only does rearrangement take place but also solvolysis of the starting peroxide occurs with the cleavage of the Si—O bond, to give a silanol, and of the silyloxy compound. The evolution of molecular oxygen according to eq. 6 has been qualitatively established.



$$PhMe_2SiOOSiMe_2Ph \text{ (III)} \xrightarrow{F^-} (PhO)Me_2SiOSiMe_2Ph \text{ (V)} \xrightarrow{i\text{-PrOH}} PhOH + PhMe_2SiOH + (Me_2SiO)_x \quad (5)$$

$$PhMe_2SiOOSiMe_2Ph \text{ (III)} \xrightarrow{F^-} PhMe_2Si^+ + {}^-OOSiMe_2Ph \xrightarrow{i\text{-PrOH}} PhMe_2SiOPr\text{-}i + PhMe_2SiOH + 1/2O_2 \quad (6)$$

On the basis of the analysis of the reaction products, it is assumed that the organosilicon peroxides under the influence of nucleophiles are rearranged intramolecularly or subjected to solvolysis (reaction 6). The contribution of the two competing reactions 5 and 6 depends to a great extent on the concentration of the nucleophile.

Experimental

Peroxides I—IV were prepared by the literature method [4].

Analysis of the reaction products

The rearrangement products were subjected to acid hydrolysis and analyzed by GLC on a Tsvet-4 chromatograph. It was preliminary established that XC_6H_4OH, $(Me_2SiO)_x$ and $XC_6H_4Me_2SiOH$ were formed during hydrolysis of the $(XC_6H_4O)Me_2SiOSiMe_2C_6H_4X$ compounds. Therefore the quantity of the rearrangement product was determined by the quantity of XC_6H_4OH. The solvolysis products of the starting peroxide were also determined by GLC.

Kinetic measurements were carried out by the literature method [1]. The reaction rate was followed iodimetrically by the change in the concentration of peroxide oxygen.

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