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STUDY OF THE MECHANISM OF THE CATALYTIC REARRANGEMENT OF TRIPHENYL(TRIPHENYLSILYLPEROXY)GERMANE

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Summary

The formal kinetics of the rearrangement of triphenyl(triphenylsilylperoxy)-germane in the presence of catalytic amounts of potassium cyanide in THF solution and in a benzene/isopropyl alcohol mixture has been studied. It has been established that the peroxide rearrangement proceeds to form germasiloxane $\text{Ph}_2(\text{PhO})\text{GeOSiPh}_3$ and is a first order reaction with respect to the peroxide. The activation energy value (E) of the process is equal to $13.5 \pm 0.8 \text{ kcal mol}^{-1}$ in the benzene/isopropyl alcohol mixture. The mechanism of the germasiloxane formation is discussed.

Introduction

It is known that the thermal rearrangement of an organometallic peroxide leads to the formation of an isomeric non-peroxide product on heating the starting compound in the temperature range 80–140°C. For example, the peroxides of the type $\text{R}_3\text{SiOOMR}_3$, where $\text{M} = \text{C}, \text{Si}, \text{Ge}$, are rearranged according to the following reaction [1,2]



Germylthallium peroxide is transformed into phenyloxydiphenyl(diethylthalliumoxy)germane [3]



Mixed organoantimonic peroxides are isomerized into a non-peroxide product with the migration of one phenyl group from the antimony atom to the oxygen atom [4]

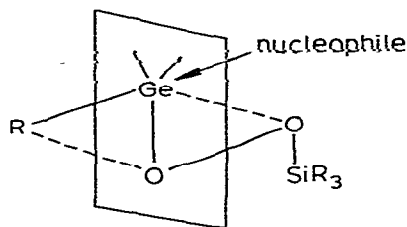


($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$)

Results and discussion

Unlike previous experiments the reaction was carried out in a homogeneous medium. Potassium cyanide was used as a nucleophile. A mixed solvent containing 60 vol. % of benzene and 40 vol. % of isopropyl alcohol and THF were used as solvents. A solution containing potassium cyanide and the peroxide I was kept at a given temperature within the limits of $\pm 0.1^\circ\text{C}$. The reaction rate was followed by the change in the peroxide oxygen concentration. Although the initial concentration of potassium cyanide was 2–3 orders lower than the peroxide concentration, the rearrangement proceeded to a high depth of conversion. Thus, the peroxide rearrangement in the mixed solvent (benzene/isopropyl alcohol) is a first order reaction with a depth of conversion of 70–80%. In THF a noticeable retardation of the reaction was observed only in the latter stages of the peroxide transformation. So it may be concluded that in our case KCN is a real catalyst the concentration of which is not changed in the course of the reaction (mixed solvent) or is changed to a negligible extent (THF). The rearrangement proceeds at a great rate at temperatures 10–50°C. Rate constants and activation parameters of the peroxide rearrangement in the benzene/isopropyl alcohol mixture are listed in Table 1. In comparison with the thermal rearrangement [9] ($E = 27.7 \text{ kcal mol}^{-1}$ in anisole) the activation energy of the catalytic rearrangement sharply decreased ($E = 13.5 \text{ kcal mol}^{-1}$).

The peroxide can be attacked by the nucleophile in various directions. One of the attack directions is the germanium atom which is sterically more available than the silicon one.



(B)

The interaction of the nucleophile with the peroxide leads to a redistribution of

TABLE 1

KINETIC AND ACTIVATION PARAMETERS FOR THE CATALYTIC REARRANGEMENT OF TRIPHENYL(TRIPHENYLSILYLPEROXY)GERMANE ($C_0 = 5 \times 10^{-2} \text{ mole l}^{-1}$) IN A MIXED SOLVENT (60 vol. % of benzene/40 vol. % of isopropyl alcohol). The initial concentration of KCN is $9 \times 10^{-4} \text{ mole l}^{-1}$

Temperature (°C)	$k^a \times 10^2$ ($\text{sec}^{-1} \text{ mole}^{-1}$)	E (kcal mole^{-1})	$\lg k_0$
20.2	14.4	13.5 ± 0.8	9.2 ± 0.5
30	33.0		
40	68.2		
49.8	120		

^a Rate constants have been calculated per unit of the catalyst concentration. E and $\lg k_0$ have been calculated by the least-squares method, and the mean-square error is also given.

electron density and contributes to the migration of the R group from the germanium atom to the oxygen atom. On the basis of structure A and B it may be concluded that both a catalyzed and a non-catalyzed rearrangement are the single-type transformations which occur as a result of the concerted heterolytic bond redistribution in an activated complex.

It is reasonable to assume the following formal scheme of the interaction between the catalyst and the peroxide:



where P is the peroxide I; R is the rearrangement product (II); K , K_1 and K_2 are equilibrium constants; and $\text{P} \cdot \text{KCN}$ and $\text{P} \cdot \text{CN}^-$ are intermediate complexes.

Non dissociated KCN molecules and CN^- ions are the catalytically active forms. Reactions 5–7 are the fast equilibrium stages. The rearrangement of the peroxide I occurs in the complexes $\text{P} \cdot \text{KCN}$ and $\text{P} \cdot \text{CN}^-$. Unlike the molecular form of the catalyst CN^- is more effective. For instance, the rearrangement of peroxide I at 50°C in a mixed solvent (benzene/isopropyl alcohol) proceeds practically at the moment when the reagents are mixed, if 18-crown-6 ether has been added to the reaction mixture in a quantity equal to the initial concentration of KCN.

The reaction rate (w) was determined by the change in the peroxide oxygen concentration. Therefore

$$w = k([\text{P}] + [\text{P} \cdot \text{KCN}] + [\text{P} \cdot \text{CN}^-]) \quad (10)$$

where k is an experimentally determined constant of the reaction rate.

On the other hand, the reaction rate is the sum of the reaction rates 8 and 9

$$w = k_1 K_1 [\text{KCN}] [\text{P}] + k_2 K_2 [\text{CN}^-] [\text{P}] \quad (11)$$

The combined solution of eq. 10 and 11 together with the following transformation gives eq. 12

$$k = \frac{k_1 K_1 [\text{KCN}] + k_2 K_2 [\text{CN}^-]}{1 + K_1 [\text{KCN}] + K_2 [\text{CN}^-]} \quad (12)$$

Taking into consideration that the equilibrium concentrations of KCN and CN^- are of the same order, 10^{-4} mole l^{-1} , eq. 12 may be reduced to eq. 13 if $K_1 [\text{KCN}] \ll 1$ and $K_2 [\text{CN}^-] \ll 1$

$$k = k_1 K_1 \frac{[\text{CN}^-]^2}{K} + k_2 K_2 [\text{CN}^-] \quad (13)$$

An equilibrium concentration of $[\text{CN}^-]$ is unknown to us. It appears to differ

TABLE 2

INFLUENCE OF THE INITIAL KCN CONCENTRATION ON THE RATE CONSTANT OF THE REARRANGEMENT OF THE PEROXIDE I ($C_0 = 5 \times 10^{-2}$ mole l^{-1}) IN THE MIXED SOLVENT; $T = 40^\circ C$

$C_0(KCN)$ (mole l^{-1})	$k \times 10^4$ (sec $^{-1}$)
0.0009	6.1
0.00067	3.4
0.00045	0.7

essentially from the initial concentration of $[KCN]_0$. In any case, dependence of k on a catalyst concentration is rather complex (eq. 13) and confirmed by the data of Table 2. Unlike the mixed solvent (benzene/isopropyl alcohol) in which KCN is rather easily soluble, in THF KCN was solubilized by 18-crown-16, the concentration of the latter being 1×10^{-3} mole l^{-1} . So CN^- ions of the dissociated $[K \cdot 18\text{-crown-6}]^+CN^-$ complex were in a catalytically active form in THF.

The rearrangement of the peroxide I in THF cannot be described by an equation of the first-order reaction (Fig. 1). A decrease in the rate of reaction was observed in this case, probably due to the consumption of the catalyst. A decreasing temperature coefficient of the rearrangement of the peroxide I in THF (Fig. 1) on increasing the temperature from 10 to $50^\circ C$ turned out to be

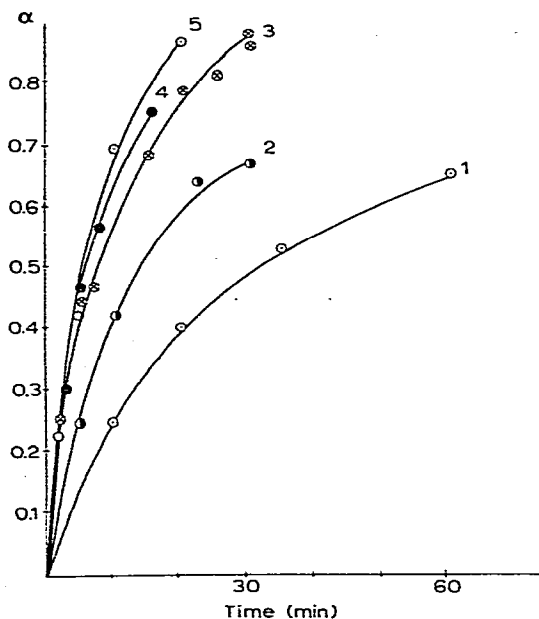


Fig. 1. Dependence of the decomposition degree α of triphenyl(triphenylsilylperoxy)germane ($C_0 = 5 \times 10^{-2}$ mole l^{-1}) on reaction time at various temperatures in THF. Curves 1, 2, 3, 4 and 5 correspond to temperatures of 10, 20, 30, 40 and $50^\circ C$, respectively. The initial concentration of KCN is equal to 3×10^{-5} mole l^{-1} . If the concentration of KCN $> 6 \times 10^{-5}$ mole l^{-1} , the peroxide is instantaneously rearranged at $30^\circ C$.

unexpected and it is difficult to explain this phenomenon.

We have also shown that bis(trimethylsilyl)peroxide and bis(dimethylbenzylsilyl)peroxide are quantitatively rearranged in the presence of catalytic amounts of KCN to form $\text{Me}_2(\text{MeO})\text{SiOSiMe}_3$ and $\text{Me}_2(\text{PhCH}_2\text{O})\text{SiOSi}(\text{CH}_2\text{Ph})\text{Me}_2$, respectively. The formal kinetics of these processes is under investigation.

Experimental

The concentration of KCN in the solutions was determined by a literature method [10].

Kinetic studies

Reactions were carried out in the thermostatted vessel which consisted of two sections. A solution of catalyst of a known concentration in the mixed solvent (benzene/isopropyl alcohol) or THF was placed in one of the sections of the reaction vessel. The solution of peroxide was placed in the other section of the vessel. Then the solutions were mixed. The moment of the first sampling was taken as the beginning of the reaction.

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