

ORGANOSILICON COMPOUNDS

XLV*. PYROLYSIS OF TRIALKYLSILANES

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The thermal decomposition of alkylsilanes has received only very limited study, as may be concluded from the fact that only the pyrolysis of ethylsilanes of the type $(C_2H_5)_nSiH_{4-n}$ for $n = 1-3$ has been investigated^{1,2}. Two important facts emerge from the results of this study. Firstly, the fact that the products of ethylsilane pyrolysis were found to contain silane, methylsilane and dimethylsilane, *i.e.* compounds with possibly more Si-H bonds than were present in the starting substance and further derivatives containing a Si-Si bond. This fact is somewhat unexpected in particular in view of values of dissociation energies of the Si-H bonds³⁻⁷ and Si-Si bonds^{7,8} which are undoubtedly lower than the values of dissociation energies of the C-C and C-H bonds and comparable to the dissociation energy of the Si-C bond. The results were obtained when studying pyrolysis of ethylsilanes in a static apparatus after a considerable period of contact and cannot thus provide a description of the reactions taking place during the initial stage of reaction.

In the present paper we attempted to demonstrate that the pyrolysis of silicon hydrides takes place as a homogeneous reaction in gaseous phase. We also intended to use a model different from ethylsilanes to verify the possibility of formation of compounds containing Si-Si bonds and compounds with a higher content of Si-H bonds than are present in the original silicon hydride. For studying the thermal degradation of trialkylsilanes we selected a continuous-flow apparatus as was used for pyrolysis of phenyldimethylsilane¹⁰ in order to be able to work with short periods of contact and to examine pyrolysis products during the initial stage of the reaction. For a detailed study of products of alkylsilane pyrolysis we selected tripropylsilane as it was hoped that the pyrolysis products of this derivative would possess a higher boiling point than those of pyrolysis of triethylsilane and that their condensation from the nitrogen stream in which the reaction took place would occur more readily.

RESULTS AND DISCUSSION

The composition of the tripropylsilane pyrolysis reaction mixture in dependence on the reciprocal steric rate follows from Fig. 1. The results indicate that the main reaction products are polymers and gaseous products which cannot be condensed. Compounds with a higher content of Si-H bonds than tripropylsilane, in our case

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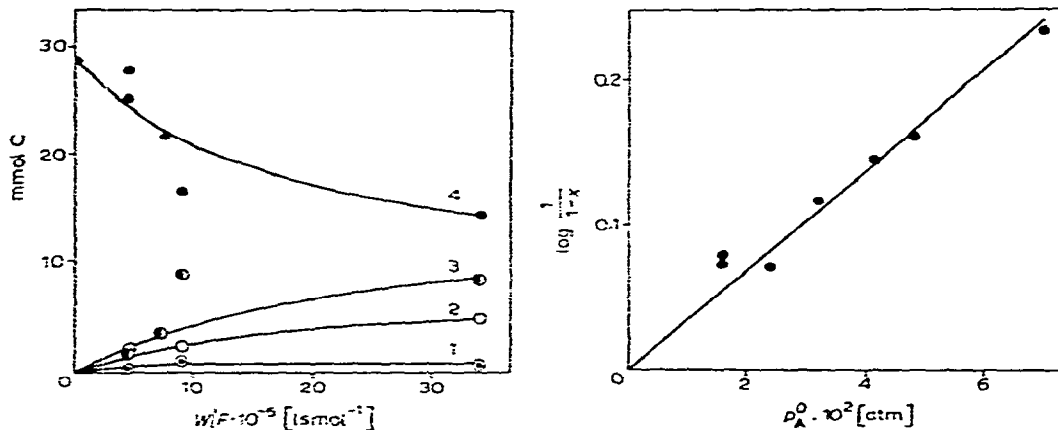


Fig. 1. Dependence of concentration of the individual components of the reaction mixture (in mmoles C) on the reciprocal steric rate (W/F): (1) sum of mmoles C in propylsilane, propylmethylsilane and dipropylsilane; (2) gaseous noncondensable products; (3) polymer; (4) tripropylsilane.

Fig. 2. Dependence of $\log 1/(1-x)$ on the initial partial pressure of triisobutylsilane; 451° ; $W/F = 5.9 \times 10^3$ liter-sec-mole⁻¹; x = conversion expressed in molar fractions.

propylsilane, dipropylsilane and methylpropylsilane, represent only a minute fraction of the reaction mixture. Their concentration referred to the reciprocal steric rate remains constant practically from the beginning of the reaction. These three components are present in practically equivalent ratios which also appear to be independent of the reciprocal steric rate. In addition to the above silanes, the reaction mixture was found to contain trace amounts of dipropylmethylsilane. The polymer products could be divided into two distinct fractions. The first of these contained 53.7% silicon, was insoluble in any solvent and had a melting point above 350° , the second fraction had almost the same silicon content but was soluble in most organic solvents. Elementary analysis of the gaseous products revealed that they contain hydrogen and carbon in a ratio of 2:1. Addition of bromine and subsequent analysis of brominated products showed that we are dealing here with a mixture of propene and ethylene at a ratio of approximately 3:1.

In order to derive the most probable reaction scheme on the basis of these results it was first necessary to decide on the character of the reaction studied. Under the conditions of examining the thermal stability of the silicon hydrides, two reaction types can occur. Firstly, a reaction on the surface of the solid phase can take place (in our case on the walls of the reactor vessel), or else a homogeneous reaction, most likely of the radical type.

As follows from Fig. 2 it is possible at least at the beginning of the reaction to interpret the rate of disappearance of the trialkylsilane (in these experiments triisobutylsilane was used) in the course of thermal degradation as a first-order reaction. This fact made it possible for us to study and uniformly interpret the effect of differently treated reactor surfaces and of the reactor surface: volume ratio on the reaction rate. We used a quartz reactor with untreated surface, a glass (SIAL) reactor with hydrophobic surface achieved with a methylsilicone oil, a reactor after previous severalfold use for pyrolysis and finally a reactor filled to one-third with glass sherds.

TABLE I

THE EFFECT OF REACTOR SURFACE ON THE RATE OF PYROLYSIS OF TRIISOBUTYLSILANE

Pyrolysis of triisobutylsilane was studied at 510–511° at the initial partial pressure of silane of $2.04\text{--}2.06 \times 10^{-2}$ atm and a reciprocal steric rate W/F equal to $5.05\text{--}8.99 \times 10^5$ liter·sec·mole⁻¹.

<i>Treatment of reactor surface</i>	$k \cdot 10^5$ (mol·l ⁻¹ ·s ⁻¹ ·atm ⁻¹) ^a
Glass reactor rendered hydrophobic with silicone oil	3.64
Glass reactor without surface treatment after prolonged usage	3.21
Quartz reactor without surface treatment	3.59
Glass reactor + 100 ml glass sherds	4.37

^a Mean of four measurements.

Data presented in Table I show that the reaction rate changes only within limits of experimental error ($\pm 10\%$). Only in the case of considerably enlarged reactor surface was the reaction rate constant raised by 29%. This difference is insignificant if it is taken into account that the reactor surface was increased by at least an order of magnitude and that the expression of the reaction by first-order kinetics is only a rough approximation valid only over a narrow range of low partial pressures of the starting substance. The results indicate that the thermal decomposition of silicon hydrides proceeds predominantly in the gaseous phase, *i.e.* probably via a radical chain mechanism.

It remains to be decided which bond of the compounds studied is split during the initiation stage of the reaction. This question could be solved theoretically on the basis of knowing the exact dissociation energies of bonds contained in the molecule of the compounds investigated. However, the required data were not available without ambiguity. Thus Tanaka³ and Tannenbaum⁴ computed the dissociation energies of the Si-C_{alkyl} bond for substances of the R_xSiH_(4-x) type ($x = 1\text{--}4$). For their calculation they accepted the assumption that the dissociation energy of the Si-H bond is equal to 72.6 kcal/mole (hence a value similar to 70–76 kcal/mole as obtained by Tanaka by calculation from the heats of combustion of pentamethylcyclopentasiloxanes⁵ as well as to that reported by Pitzer⁶) and that of the C-H bond 98.8 kcal/mole, both of them remaining constant, and that the energy of the C-C bond is the same as in hydrocarbons corresponding to alkyls attached to silicon. Under these conditions they found that the dissociation energy of the Si-C bonds decreases from methyl to isobutyl from 74 to 56 kcal/mole. Recently, Steele, Nichols and Stone⁷ using data from mass spectroscopy, obtained for methylsilane and disilane apparently an erroneous value for the dissociation energy of the Si-H bond as being equal to 94 kcal/mole. It follows from this brief review that the dissociation energies of the Si-C and Si-H bonds are probably similar and are comparable with that of the C-C bond, so that the above data suffering from a considerable experimental error and a number of unconfirmed assumptions cannot be employed for an unequivocal discussion of the problems which of the bonds contained in the trialkylsilane molecule is split during the initiation step of the pyrolytic reaction.

It is known, however, from studies of the heat stability of tetraalkylsilanes that they are split at higher temperatures than are trialkylsilanes containing identical alkyl groups. This qualitative observation leads us to conclude that during the

initiation stage of pyrolysis of silicon hydrides the Si-H bond is homolytically split. This assumption is in agreement with the results of radical additions of silicon hydrides to the multiple C-C bonds, where radical initiators bring about only the cleavage of Si-H bonds.

In view of its low concentration and the low dissociation energy of the Si-Si bond^{7,8} it is not probable that the silyl radical thus formed becomes stabilized by dimerization. A more plausible explanation for the products formed is the reaction between the silyl radical and propyl group of the original hydride.

The fact that the silyl radical splits preferentially the C-H bond rather than the C-C and C-Si bond can be accounted for by the difference in the steric hindrance during attack at the above bonds by the bulky silyl radical and by the different probability of its collision with the individual bonds as follows from the ratio C-Si:C-C:C-H = 1:2:7. The C radical formed in the reaction can split off propene (which was detected in the gaseous products) with the formation of dipropylhydrosilyl radical, whose reaction with the original reactant can serve as an explanation for the formation of dipropylsilane and the basically analogous formation of silanes with a higher content of Si-H bonds. The splitting off of ethylene (also identified in the gaseous products) from the above mentioned C radical can lead to the formation of the transient dipropylhydrosilyl radical, further reactions of which can explain the formation of methyl-dipropylsilane. The hydrogen atom formed by the primary dissociation of the Si-H bond can also react with the hydrogen of the original reactant both at the C-H and Si-H bond.

It must be emphasized that, similarly to tripropylsilane, degradation affects also dipropylsilane and propylsilane, or even methylpropylsilanes, the silanes with a higher Si-H content being far more reactive, as follows from the fact that a steady state is reached with them quite readily (Fig. 1).

On the basis of this assumption it is understandable why compounds with a higher content of Si-H bonds are formed than were present in the starting compound even under the postulate that the cleavage of the Si-H bond requires the least amount

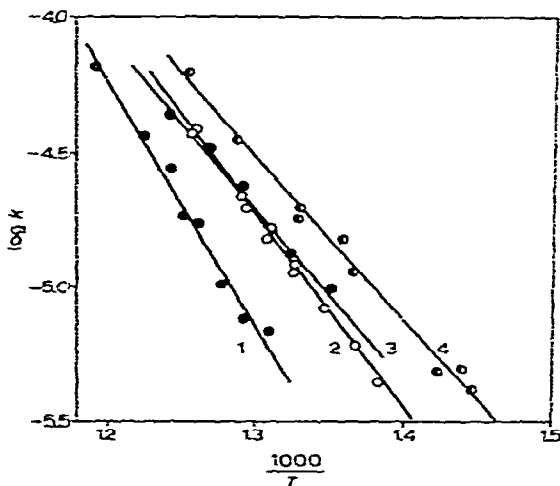


Fig. 3. The effect of temperature on the rate of disappearance of trialkylsilanes during their pyrolysis: (1) methyl-diethylsilane; (2) triethylsilane; (3) triisobutylsilane; (4) triisopropylsilane.

of energy. The polymers found are most probably formed by the decomposition of silanes containing two or more Si-H bonds.

According to these conceptions (if the effect of replacing the alkyl on the dissociation energy of the Si-H bond and on the ease of recombination of the silyl radical is neglected,) pyrolysis of trialkylsilanes should proceed the more readily the more CH_2 , or even better, CH groups there are in the molecule. This view was confirmed experimentally. As shown by Fig. 3 the reactivity of the original silane is most affected by replacement of methyl with ethyl and of ethyl with isopropyl.

EXPERIMENTAL

Compounds used

Solvents, internal standards for chromatography (with the exception of hexamethyldisiloxane), methyldiethylsilane, triethylsilane and tripropylsilane have been described earlier¹⁰⁻¹². Hexamethyldisiloxane, 1,2-dibromoethane and 1,2-dibromopropane are commercial products and were used without further purification. The remaining silicon hydrides used were prepared by reduction of the corresponding chlorosilanes with lithium aluminium hydride. Chlorosilanes were obtained by the reaction of the corresponding Grignard reagent or of alkyllithium with tetrachlorosilane, trichlorosilane or methyldichlorosilane. The preparation of triisopropylsilane serves here as an example.

Triisopropylchlorosilane. A solution of isopropylolithium (0.9 mole) in ether (400 ml) was introduced under the protection of nitrogen atmosphere over a solution of tetrachlorosilane (50.4 g, 0.3 mole) in ether (200 ml) at -50° . After reaction the reaction mixture was slowly heated to room temperature and left to stand overnight. On the next day the salts were filtered off and the product distilled. The yield and melting point are shown in Table 2.

Triisopropylsilane. Triisopropylchlorosilane solution in dioxane (42.5 g, 0.22 mole in 30 ml) was added dropwise to a suspension of lithium aluminium hydride (2.7 g, 0.077 mole) in dioxane (70 ml) at room temperature. The mixture was then boiled for 10 h, cooled to room temperature and decomposed by pouring over a mixture of ice (300 g) with concentrated hydrochloric acid (20 ml). After adding benzene, the aqueous layer was separated, extracted with benzene and after combining the organic layer were extracted with water, a bicarbonate solution and again with water. After drying over magnesium sulphate, the solvents were distilled away. Rectification on a column of 20TP yielded triisopropylsilane. The yield and physical constants are shown in Table 3.

Apparatus

Pyrolysis of trialkylsilanes was studied in a continuous-flow quartz reaction of 350 ml volume. The reactor was placed in a heating mantle which kept the temperature constant to 1° . Silanes were added with a 0.2 ml syringe into the evaporator preheated to the boiling temperature of the compound to be pyrolyzed. The movement of the syringe piston was controlled by a linear feeding device. The products were frozen out in a stream of nitrogen in a freezing pocket provided with a sintered-glass disc over which 10 ml of solvent were placed to a column height of 10 cm. The freezing pocket was cooled in a bath with solid carbon dioxide. The current of nitrogen was

TABLE 2
PREPARATION OF CHLOROSILANES

Starting chlorosilane (mole)	Allyl metal (mole)	Product	Yield (%)	B.p. (°C/mm)
Trichlorosilane (2.5)	Propylmagnesium bromide (1.8)	Propyldichlorosilane	43.9	98--102.5
Methylchlorosilane (1.4)	Propylmagnesium bromide (0.7)	Propylmethylchlorosilane	50.2	95--97
Trichlorosilane (4.0)	Propylmagnesium bromide (1.4)	Dipropylchlorosilane	80.9	148--149
Tetrachlorosilane (0.3)	Isopropyl lithium (0.9)	Trisopropylchlorosilane	89.7	82--85/15
Tetrachlorosilane (0.345)	Isobutyl lithium (1.25)	Trisobutylchlorosilane	83.3	99--103/10

TABLE 3

PREPARATION OF SILANES

Starting chlorosilane	Solvent ^a	Product	Yield (%)	B.p. (°C/mm)	mp ^b	Found	Ref.
Propyldichlorosilane	Ether	Propylsilane	55.1	22.0		1.3757	
Propylmethylchlorosilane	Ether	Propylmethylsilane	75.6	51.5		1.3880	1.3857 ^{b,13}
Dipropylchlorosilane	Ether	Dipropylsilane	35.6	111.2--111.8		1.4097	1.4110 ¹⁴
Diethyldichlorosilane	Ether	Diethylsilane	48.6	54.5--55		1.3920	1.3921 ¹⁵
Trisopropylchlorosilane	Dioxane	Trisopropylsilane	78.9	83.5/50		1.4352	1.4358 ¹⁶
Trisobutylchlorosilane	Dioxane	Trisobutylsilane	9.5	115.5/40		1.4346	1.4332 ^{b,17}

^a Reduction with lithium aluminium hydride was carried out at the boiling point of the solvent. ^b Erroneous value.

maintained by a Cartesian manostat with an accuracy of $\pm 2\%$. Gaseous, non-condensable products were combusted in a stream of a mixture of oxygen with nitrogen over magnesium permanganate at 510–520° and the water and carbon dioxide formed were determined gravimetrically after absorption in anhydrous magnesium perchlorate and soda-lime asbestos. The fact that in a stream of a mixture of nitrogen and oxygen a complete combustion of hydrocarbons takes place was confirmed by analysis of toluene under identical conditions.

Analysis of products condensable at -50° was carried out on commercial Argon Chromatograph (W. C. Pye and Co., Cambridge) and Gas Density Chromatograph S-91-350 (Griffin and George) using columns of Celite and either Apiezon L (20%) or a silicon elastomer (polymethylsiloxane) E 301 (20 or 10%) or else a mixture of Apiezon L and bentonite (each 5%) as liquid phases. Benzene, hexamethyldisiloxane and undecane served as internal standards for a quantitative determination of the concentration of individual components of the reaction mixture.

Qualitative analysis of products of tripropylsilane pyrolysis

Heat decomposition of tripropylsilane (1.225 g, 0.00775 mole) was carried out in a continuous-flow reactor at 505° at a partial pressure of tripropylsilane of 2.6×10^{-2} atm and reciprocal steric rate W/F of 4.95×10^5 liter·sec·mole⁻¹. The products were frozen out in a freezing pocket provided with a sintered-glass disc with 5 ml ethylbenzene in one case and cumene in the other placed on top. At first gas chromatography was applied to determine the boiling points (Table 4) corresponding to the individual chromatographic peaks on the basis of a linear relationship between the boiling point and the logarithm of relative retention times (Fig. 4). Known boiling points were affixed to compounds that might correspond to the individual chromatographic peaks (Table 4). Conditions were then found under which the individual isomers can be separated and chromatographic analysis carried out, its results being shown in Table 4.

TABLE 4

ANALYSIS OF CONDENSABLE PRODUCTS BY MEANS OF GAS CHROMATOGRAPHY

Chromatographic peak	Assumed product	B.p. (°C)		Product found
		Found	References	
1	C ₃ H ₇ SiH ₃ (CH ₃) ₄ Si ^a	23	21.3;760 ¹⁸ 23;760 ¹⁹ 26.64 ²⁰	C ₃ H ₇ SiH ₃
2	C ₃ H ₇ (CH ₃)SiH ₂ (C ₂ H ₅) ₂ SiH ₂	53	53.6 ¹⁵ 55.8;760 ²¹	C ₃ H ₇ (CH ₃)SiH ₂
3	(C ₃ H ₇) ₂ SiH ₂ (C ₂ H ₅) ₂ SiH	108	110.5;769 ²² 108.7 ²³	(C ₃ H ₇) ₂ SiH ₂
4	(C ₃ H ₇) ₂ CH ₂ SiH ^b	124	107.7;760 ²⁴ 125.9;743 ²⁵	(C ₃ H ₇) ₂ CH ₂ SiH

^a Tetramethylsilane was obtained through the kindness of Dr. J. SCHRAML. ^b Dipropylmethylsilane was obtained through the kindness of Dr. J. HETFLÉJŠ.

After chromatography, the solvent and the volatile components were distilled away and the polymer obtained divided into two fractions on the basis of its solubility in ether. The soluble fraction contained 40.98 % C, 6.75 % H and 52.3 % Si, the insoluble fraction contained in addition to carbon and hydrogen 53.7 % Si.

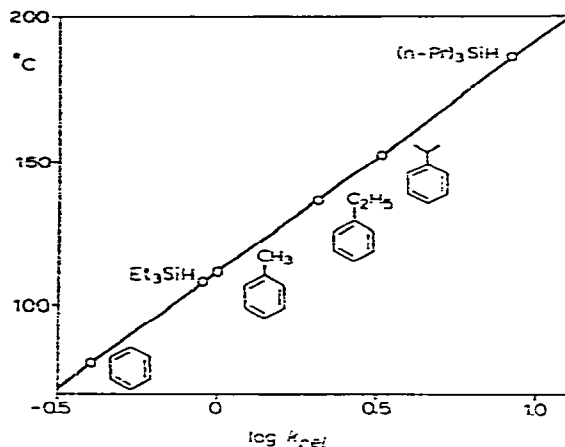


Fig. 4. Linear relationship between temperature ($^{\circ}\text{C}$) and logarithm of retention time (t_{ret}).

Noncondensable, gaseous products were transferred during pyrolysis from the freezing pocket to a solution of bromine in tetrachlorosilane (10 ml) cooled to -10° . The excess bromine was removed after pyrolysis by shaking with a solution of sodium bisulphite. After drying the organic layer with magnesium sulphate, the tetrachloromethane was partly distilled away in a column and the residue was analyzed in a gas chromatograph. Standards were then used to demonstrate that the distillation residue contained 1,2-dibromopropane and 1,2-dibromoethane at a ratio of 3:1.

SUMMARY

It was demonstrated that the pyrolysis of trialkylsilanes in gaseous phase proceeds most likely via a radical chain mechanism. The reaction mixture after pyrolysis of tripropylsilane was analyzed and the results then discussed with a view to the most likely reaction scheme for thermal decomposition of tripropylsilane.

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