

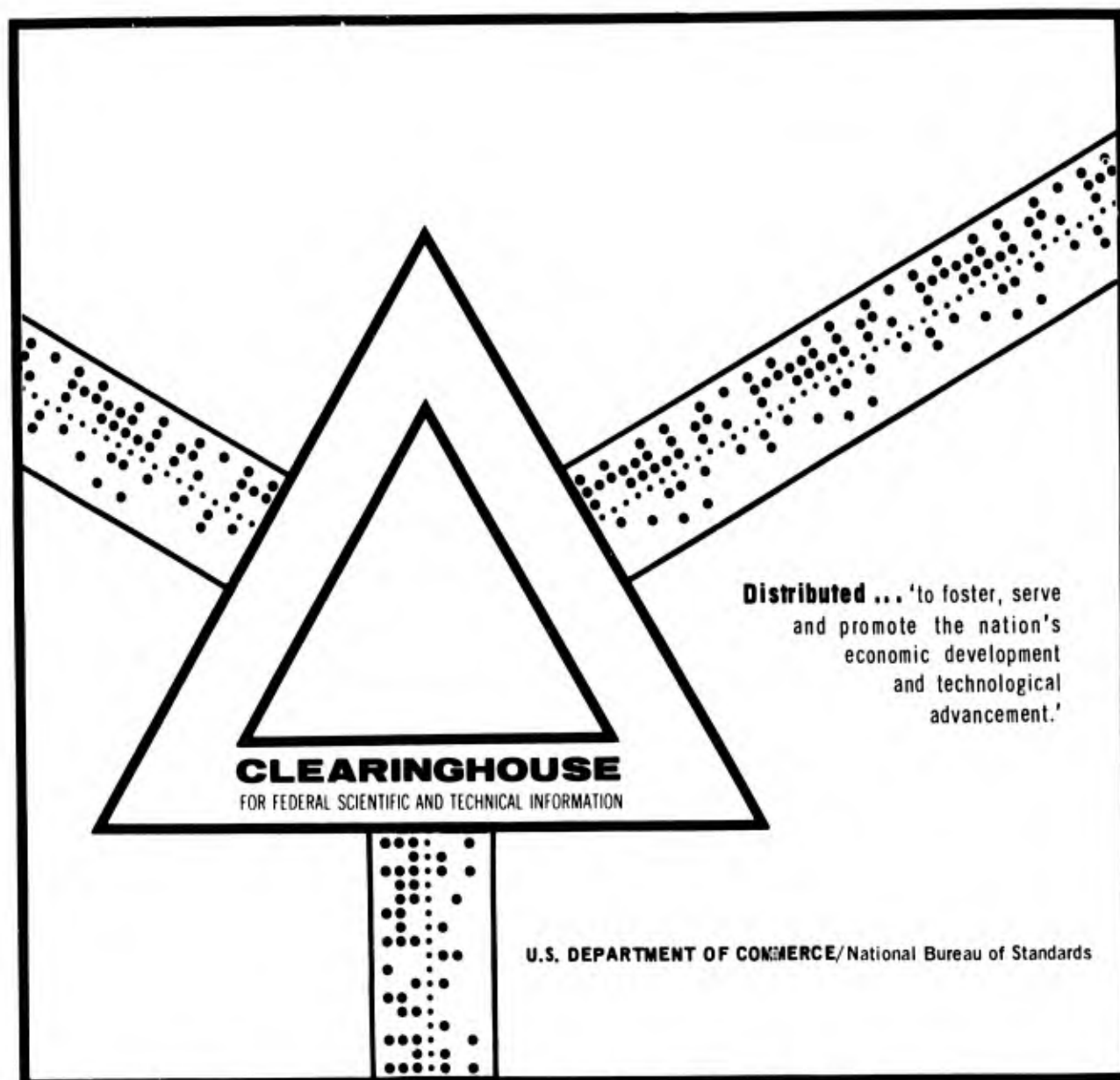
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A KINETIC STUDY OF THE THERMAL DECOMPOSITION
OF SELECTED CYCLOHEXYL AND PHENYLSILANES

Robert W. Coutant, et al

Battelle Memorial Institute
Columbus, Ohio

December 1969



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Aerospace Research Laboratories

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Contract No. AF33(615)-1807
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AEROSPACE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report has been prepared as a part of a research effort at Battelle Memorial Institute, Columbus Laboratories, to better understand the kinetics and mechanisms of decomposition of the arylsilanes. The work was supported by the Aerospace Research Laboratories of the Air Force Office of Aerospace Research at Wright-Patterson Air Force Base, Ohio, through funds supplied under Contract AF 33(615)-1807, "A Kinetic Study of the Thermal Decomposition of Selected Cyclohexyl and Phenylsilanes". Arthur Levy acted as the project director at Battelle and was assisted by Dr. Robert W. Coutant. The work reported herein was done between May 1, 1964, and June 30, 1969, in the Physical and Applied Chemistry Division of the Department of Chemistry and Chemical Engineering at Battelle. This report presents an analysis of results obtained during the program in terms of a generalized approach toward understanding the mechanisms of reaction, and it provides a basis for understanding the parameters important to the utilization of these materials in high-temperature fluids and polymers. Technical administration of the investigation was provided by the Chemical Research Branch, with Dr. Leonard Spialter serving as task scientist.

ABSTRACT

The thermal-decomposition kinetics of the following arylsilanes have been investigated using both static and flow techniques: monophenylsilane, diphenylsilane, triphenylsilane, tetraphenylsilane, diphenyldimethylsilane, and triphenylmethylsilane. The phenylhydrosilanes decompose via a bimolecular second-order redistribution reaction, with no evidence for free-radical formation. On the other hand, the main mode of decomposition of tetraphenylsilane involves elimination of phenyl radicals followed by attack of these radicals on the parent silane. The decomposition of the phenylmethylsilanes also proceeds via a free-radical mechanism, but the main reaction path results in intramolecular cyclization, yielding compounds containing the dibenzosilole nucleus. Reasons for these three basically different modes of reaction are discussed in terms of substituent size and degree of (p $\rightarrow$ d) π bonding between the phenyl rings and silicon.

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SECTION I

INTRODUCTION

There is much interest by both Government agencies and industry in the production of polymers and fluids having high thermal stability.⁽¹⁾ Organosilanes and, in particular, the arylsilanes have received much attention as building blocks for these polymers and fluids because of the inherently high thermal stability of the silanes. Much of the work done with these materials has centered around testing of the stabilities of individual polymers or compounds with somewhat arbitrary definition of stability.⁽¹⁾ Little has been done to define the chemistry and kinetics of thermal decomposition of the monomers used to prepare these compounds or to attempt to relate the monomer stability to that of the polymeric material. That is, preparation of thermally stable compounds has largely been a case of trial and error. The purpose of the current work is to define the kinetics and mechanisms of thermal decomposition of selected arylsilanes so as to provide a basis for better understanding of the factors involved in determining the thermal stability of polymers and fluids derived from these materials.

This report covers work done during the period of May 1, 1964, through June 30, 1969. An Interim Technical Report⁽²⁾ covering the first 12 months of this period was issued in October, 1965. The results of earlier work [Contracts No. AF 33(616)-5217 and AF 33(616)-7236] on the kinetics of decomposition of cyclohexyl and phenylsilanes have been reported as ARL Technical Reports. (3, 4)

SECTION II

SUMMARY

The kinetics of thermal decomposition of several arylated silanes have been determined using both static and flow techniques. Three distinctly different modes of decomposition have been found. The phenylhydrosilanes decompose via a four-center activated complex in a rearrangement-type reaction. The main mode of decomposition of tetraphenylsilane is by phenyl radical elimination followed by radical attack on the parent silane. With the phenylmethylsilanes, a free-radical mechanism also occurs, but the main reaction path results in intramolecular cyclization to form compounds containing the dibenzosilole nucleus. The reasons for these different types of reaction are discussed in terms of electronic and steric effects for the various compounds studied.

SECTION III

EXPERIMENTAL

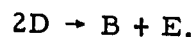
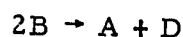
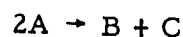
APPARATUS AND PROCEDURES

Three different types of apparatus and procedures were used to obtain information on the kinetics of thermal decomposition of the arylsilanes. These procedures involved a batch sealed-vial technique and plug- and stirred-flow reactor technique.

Standard sealed-vial techniques were used to generate data on product distributions and rates of pyrolysis for long-term (100-300 min) reaction conditions. The procedure for these experiments involved loading of a weighed amount of the silane into a Pyrex or Vycor vial, sealing off the vial under vacuum, and heating the sample for the desired length of time in a tube furnace. Thermal gradients within the furnace were reduced through the use of an aluminum liner. Reacted samples were analyzed by gas chromatography, mass spectrometry, and infrared spectrometry.

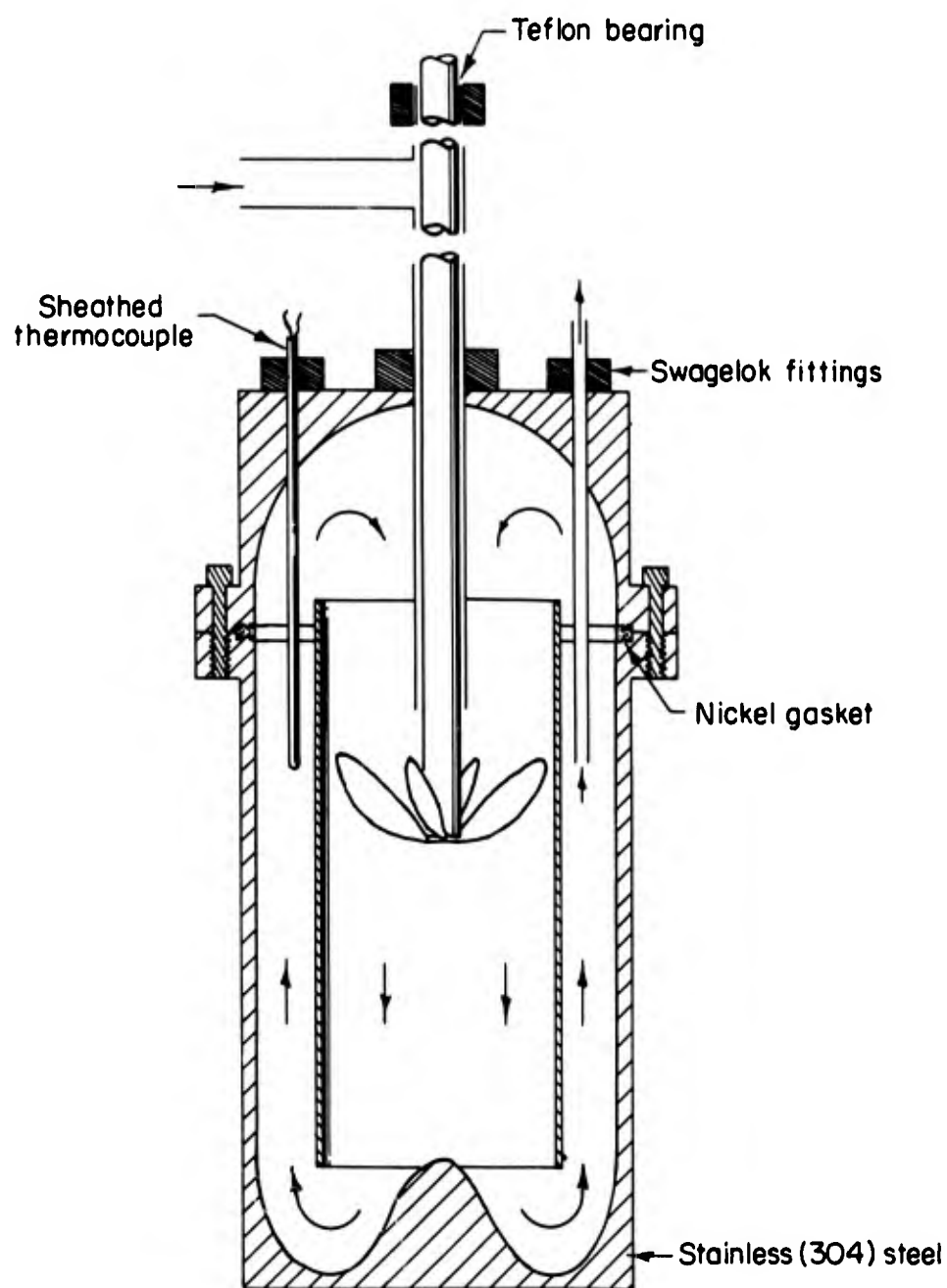
The bulk of the kinetics data was obtained using flow techniques. Initially, a conventional tube reactor, hereinafter referred to as the Pyrex reactor, was used in flow experiments. Operation of the apparatus consisted of passing a metered stream of helium through a constant-temperature source of the silane, then into the reactor, and, finally, into a gas-chromatography unit for analysis. The helium flow was metered by a Croxton-type differential manometer with interchangeable capillaries. Both the source container and the reactor were set into heated metal blocks to minimize thermal gradients. The reactor consisted of a coil of Pyrex tubing (12 mm in diameter by 12.5 ft long) wound about a stainless steel core. All intervening gas lines were heated by heating tapes, and temperatures throughout the system were monitored with a series of thermocouples. The gas stream was coupled to the gas-chromatography unit through a gas-sampling valve.

Some difficulties associated with analysis of the data were encountered in the use of this reactor because of the complex nature of many of the reactions studied. For example, the pyrolysis of the phenylhydrosilanes can be represented as the following series of reactions:



The differential rate equations for these reactions form a set of nonlinear simultaneous equations that cannot be solved explicitly. Approximate solutions can be made, but these lead to considerable uncertainty in derived rate constants. A stainless steel stirred-flow reactor that allows circumvention of many of these problems was designed, constructed, and used for the bulk of the experiments described in this report. A drawing of this reactor is given in Figure 1.

This apparatus offers several advantages over the conventional tube reactor. Thermal gradients within the reactor are reduced because of continuous back mixing



2 cm = 1 inch

A-49080

FIGURE 1. Stirred-flow reactor

throughout the reactor. Under conditions of good back mixing found with this type of reactor, the kinetic equations can be treated rigorously in differential form, thus bypassing many of the difficulties of data analysis associated with complex reactions in straight tube reactors. In the current design, particular attention was given to the flow characteristics of the reactor. The high-pitch propeller fits closely into the draft tube and provides efficient gas circulation throughout the chamber, which is contoured to limit dead space. The relatively large volume (530 cc) of the reactor allows for use of a wider range of reaction times than could be specified with reasonable accuracy with the previous tube reactor. In turn, the availability of longer reaction times allows some study of the rate of formation of products as well as the rate of disappearance of the reactant.

Under conditions of good mixing, the rate of change of the number of moles of reactant in the stirred-flow reactor is

$$V \left(\frac{dC}{dt} \right) = FC_0 - FC - kVC^n + V \sum_i k_i C_i^{n_i} \quad (1)$$

where V is the volume of the reactor, F is the flow rate, C_0 is the concentration of the reactant in the input stream, C is the concentration in the reactor, k is the specific rate constant, n is the order of the reaction, and the last term represents the sum of all of the secondary-reaction fluxes that contribute to C . In most experiments, reactions were carried out at low extents of conversion, and these secondary fluxes were negligible. However, to illustrate the use of this term, any diphenylsilane produced in the pyrolysis of triphenylsilane may in turn pyrolyze partially to yield some triphenylsilane. In cases where this back reaction was appreciable, the last term in Eq (1) was used to correct the observed rate of triphenylsilane decomposition. In practice, C is measured at steady-state conditions ($dC/dt = 0$), and the ratio V/F is written τ , the residence time. Thus, Eq (1) may be written as

$$C^n \tau = \frac{1}{k} \left(C_0 - C + \tau \sum_i k_i C_i^{n_i} \right) \quad (2)$$

and a plot of $C^n \tau$ versus $C - \tau \sum_i k_i C_i^{n_i}$ should yield a straight line with a slope of $-1/k$ and an intercept on the abscissa of C_1/k . The order of the reaction, n , may be found by taking the logarithm of Eq (2):

$$\log \frac{C_0 - C + \tau \sum_i k_i C_i^{n_i}}{\tau} = \log k + n \log C \quad (3)$$

A plot of $\log (C_0/\tau - C/\tau + \sum_i k_i C_i^{n_i})$ versus $\log C$ should yield a straight line with a slope equal to n . Both graphical procedures and least-squares analysis of the data were used to obtain the kinetics parameters k and n .

THE SILANES

The di-, tri-, and tetraphenylsilane used on this program were supplied by M&T Chemicals, Inc. The phenylmethylsilanes were obtained from Peninsular Chem-research, Inc. Monophenylsilane was synthesized by reduction of phenyltrichlorosilane with lithium aluminum hydride. All silanes were analyzed by gas chromatography and were further purified by sublimation or preparative gas chromatography. All starting materials used in the pyrolysis experiments were at least 99 percent pure.

ANALYSES

Starting materials and reaction products were analyzed by gas chromatography. In most cases, the columns used were stainless steel loaded with 10 percent SE-30 on 60-80 mesh Chromosorb W. Different loadings of the SE-30 were used in some cases, but loading generally was not a critical factor. In some of the initial work on diphenylsilane and monophenylsilane, copper columns were used, but these gave anomalous results suggesting that these materials may have reacted with copper oxide on the inner surface of the columns; these anomalous results are illustrated below. Certification of the identities of reaction products was made by mass spectrometry and, in some cases, by infrared spectrometry.

SECTION IV

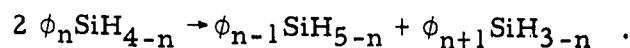
RESULTS AND DISCUSSION

Some initial studies of the thermal stability of monophenylsilane, diphenylsilane, triphenylsilane, and tetraphenylsilane were conducted under an earlier contract [AF 33(616)-7236] and are reported in an ARL Technical Report.⁽²⁾ In the current work, data on the kinetics of pyrolysis of these materials were extended. The results discussed below include those obtained in the earlier contract so that a complete discussion of these materials can be presented at this time.

The various materials studied on this program are divided into several groups according to the chemistry and kinetics of pyrolysis. The results for these groups therefore are presented as subsections of this part of the report.

THE PHENYLHYDROSILANES

The phenylhydrosilanes, monophenylsilane, diphenylsilane, and triphenylsilane, undergo rearrangement with respect to phenyl and hydride groups when they are pyrolyzed. The reaction may be represented as



The reaction is relatively "clean" for a pyrolysis reaction. No detectable high-molecular-weight materials, benzene, or hydrogen are formed as long as the extent of reaction is kept low enough to keep an appreciable amount of SiH_4 from forming and as long as the temperature is low enough that $\phi_4\text{Si}$ formed does not decompose. The reaction is similar to the aluminum chloride catalyzed rearrangement of the phenylhydrosilanes in benzene solution.⁽⁵⁾ The pyrolysis reaction, however, does not appear to be heterogeneous. Changes in surface-to-volume ratio of the reaction vessel or in the nature of the reaction vessel (Pyrex, Vycor, or stainless steel) do not appear to affect the kinetics of the reaction. The kinetic data indicate that the reaction is second order with respect to the parent silane.

Monophenylsilane

Monophenylsilane was pyrolyzed in the Pyrex reactor at temperatures ranging from 342-389°C. Additional pyrolyses were also carried out using the sealed-vial technique at 320°C. Analyses for unreacted monophenylsilane were carried out using both copper and stainless steel chromatography columns. Data obtained with the copper column showed somewhat more scatter than those obtained with the stainless steel column. In addition, vapor pressures obtained by extrapolation of the kinetic data to zero percent conversion coincided with the literature data⁽⁶⁾ only where the stainless steel column was used. For a comparison of the effect of column construction on analyses, the values of rate constants calculated from the two classes of data are shown in the Arrhenius plot in Figure 2. The data obtained with the stainless column are probably more accurate; these data yield an activation energy of 39.9 kcal/mole and a frequency factor of $10^{14.7}$ liter/mole min.

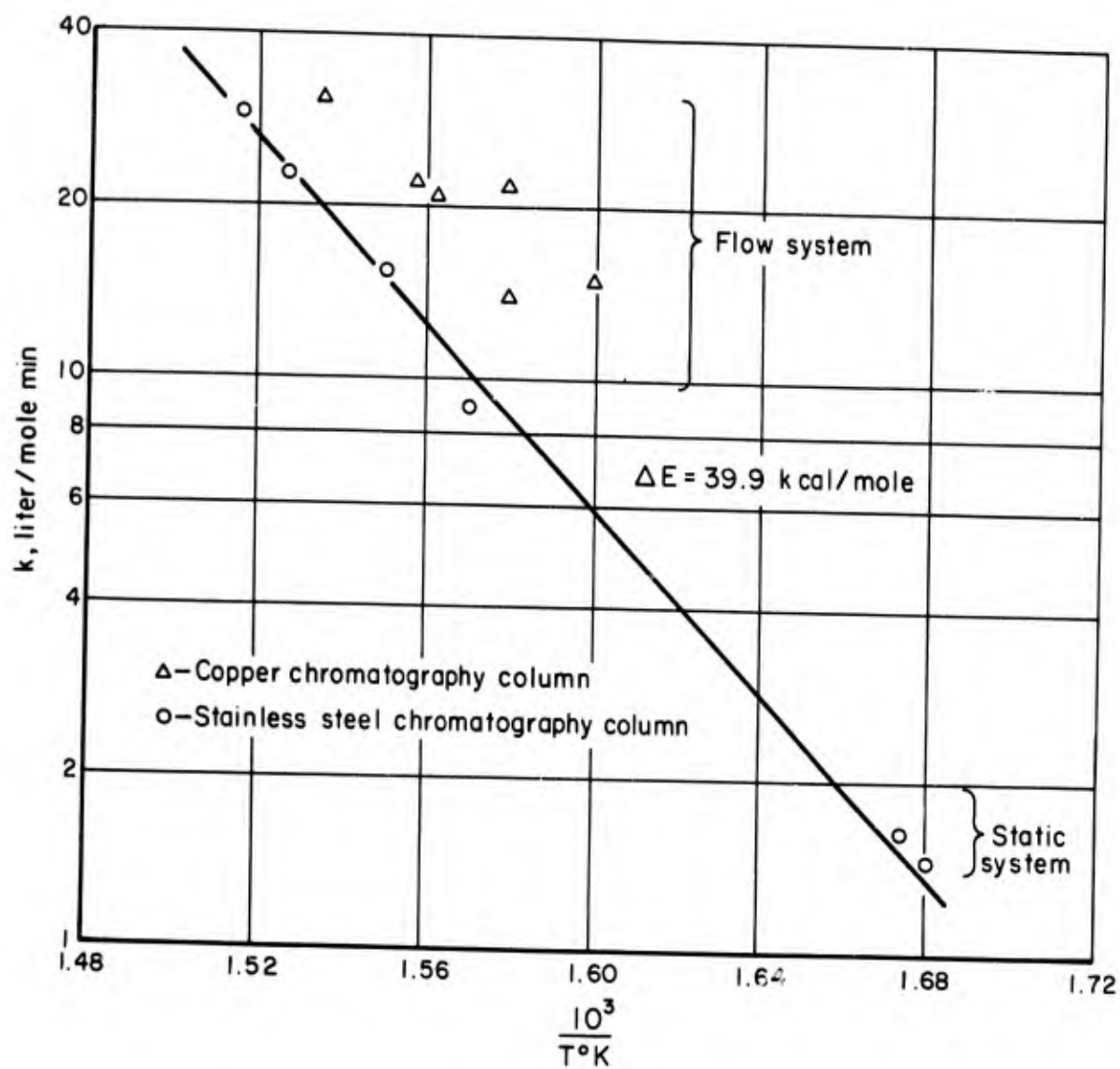


FIGURE 2. Arrhenius plot for monophenylsilane decomposition

Diphenylsilane

Diphenylsilane was pyrolyzed in the Pyrex reactor at temperatures of 385-425°C and in sealed vials at 350°C. As in the case of monophenylsilane, chromatographic analyses for diphenylsilane were greatly affected by the material of construction of the column. Analyses for diphenylsilane were carried out using both types of columns. In certain of these experiments, there was also a small residual amount of air, which is believed to have affected some of the kinetic data. Of those data for diphenylsilane (see Figure 3), only points marked with x's are considered to be representative of the decomposition of diphenylsilane in the absence of air. The data shown in Figure 3 indicate an activation energy of 58 kcal/mole and a frequency factor of $10^{19.8}$ liter/mole min.

Triphenylsilane

The bulk of the work done on triphenylsilane was carried out under the previous contract.⁽⁴⁾ This earlier work was done using only the sealed-vial techniques and the Pyrex flow reactor. In the current work, triphenylsilane was pyrolyzed at 525°C in the stainless steel stirred-flow reactor. The rate constant determined with the stirred-flow reactor is in good agreement with the value gained by extrapolation of the previous work with the Pyrex reactor and suggests that the kinetics of pyrolysis of triphenylsilane are not affected by the construction material of the reactor. Complete results for the thermal decomposition of triphenylsilane are shown in Figure 4. The low-temperature points showing considerable uncertainty in the rate constants were derived from sealed-vial experiments; the one point at highest temperature was obtained with the stirred-flow reactor, and data were obtained with the Pyrex tube reactor at intermediate temperatures. The activation energy for this reaction is 70.1 kcal/mole and the frequency factor is $10^{21.6}$ liter/mole min.

Mechanism of Reaction

The kinetic data indicate that the pyrolysis reactions of the phenylhydrosilanes are second-order bimolecular reactions. A trend toward increasing activation energy and increasing frequency factor is seen with these materials as the number of phenyl groups attached to the silicon is increased. This trend is illustrated in Table I. The frequency factors for diphenylsilane and triphenylsilane are higher than one might expect for bimolecular reaction and indicate extraordinarily high entropies of activation for diphenylsilane and triphenylsilane.

TABLE I. Kinetic parameters for pyrolysis of the phenylhydrosilanes

Silane	ΔE , kcal/mole	A, liter/mole-min
ϕ SiH ₃	39.9	$10^{14.7}$
ϕ_2 SiH ₂	58	$10^{19.8}$
ϕ_3 SiH ₃	70.1	$10^{21.6}$

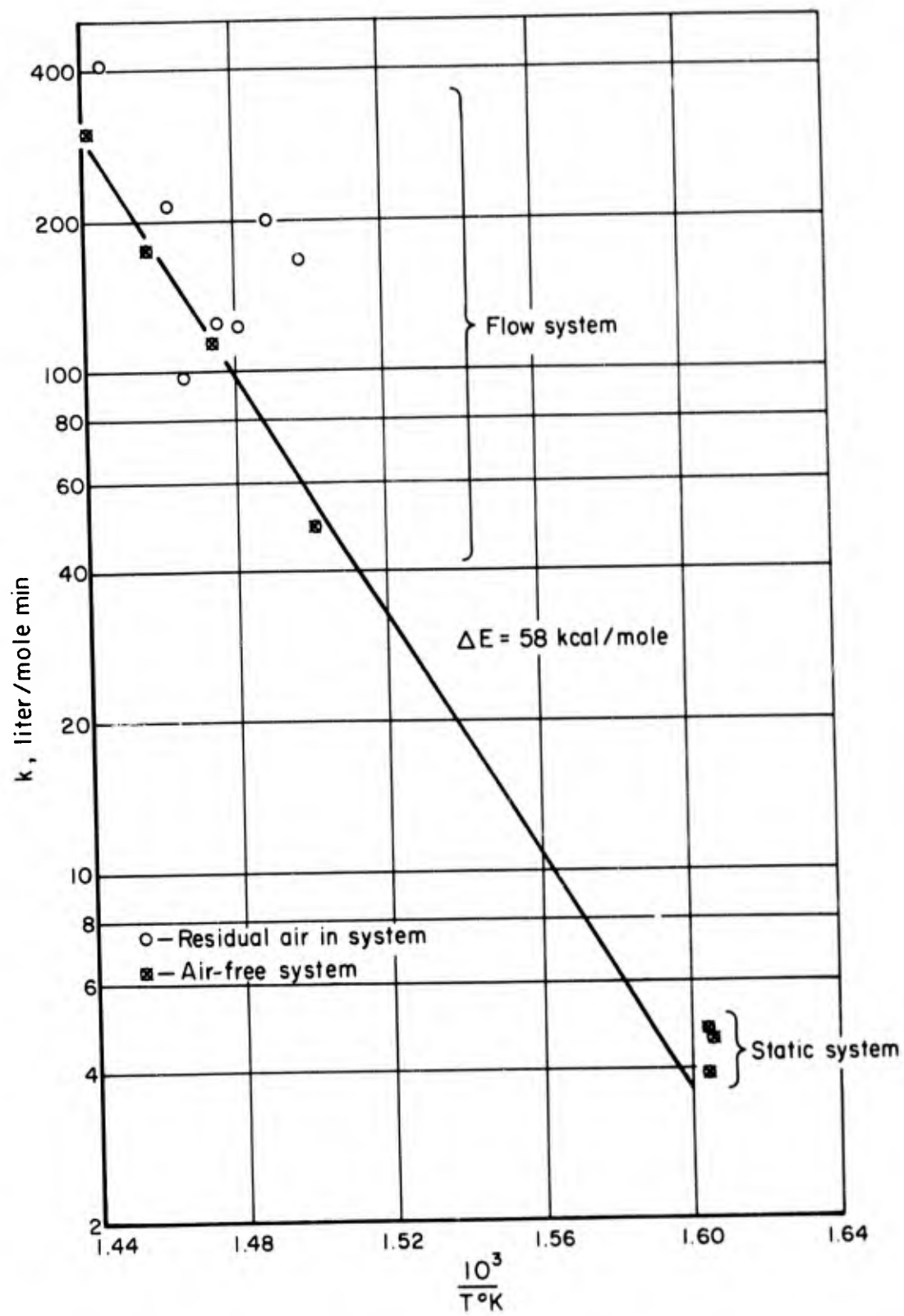


FIGURE 3. Arrhenius plot for diphenylsilane decomposition

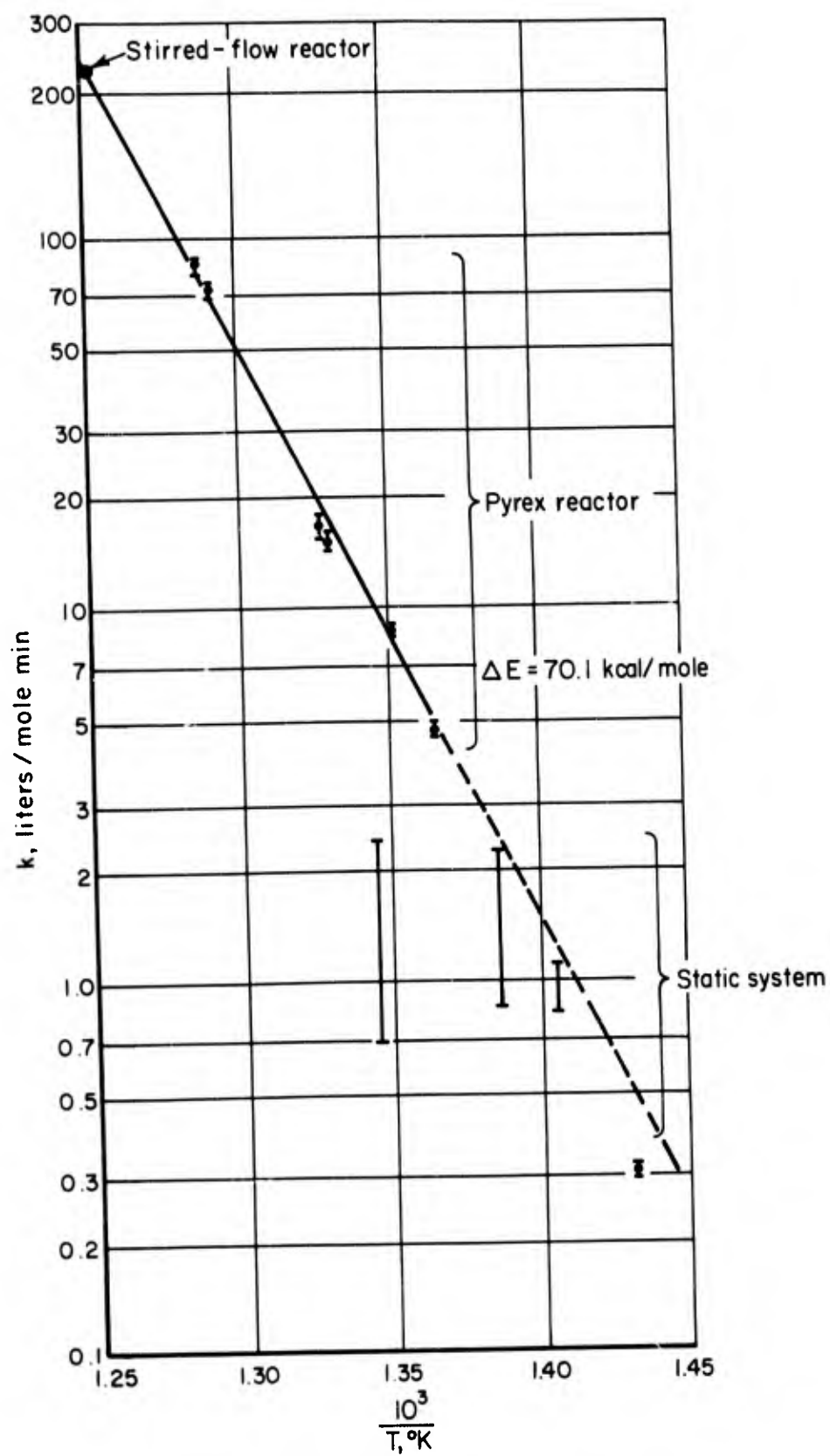


FIGURE 4. Arrhenius plot for triphenylsilane pyrolysis

Two alternate mechanisms may be proposed which satisfy the observed kinetic order of reaction of the phenylhydrosilanes: (1) a second-order collisional activation followed by a series of rapid free-radical reactions and (2) formation of a four-center activated complex that decomposes directly to the observed products. If the reaction were of the first type, a more complex set of reaction products resulting from radical attack on both the parent and product silanes might be expected. For example, in the pyrolysis of tetraphenylsilane or the phenylmethylsilanes, both of which are discussed later in this report, product distributions are very complex and indicate the formation of phenyl, silyl, and hydrogen radicals during the overall reaction. Also, the strong trend in activation energies observed with the phenylhydrosilanes would not be expected if the main route of reaction were by free-radical formation. On the other hand, with a four-center type of mechanism, the increasing activation energy with increasing molecular size might, in part, be attributed to the increased steric hindrance to formation of the activated complex as more phenyl groups are bonded to the silicon. The activation energy for triphenylsilane, 70.1 kcal/mole, is nearly that required for the activation of tetraphenylsilane to form phenyl radicals, 77.7 kcal/mole (see later discussion). This fact, along with the very high frequency factor for triphenylsilane, suggests that extensive bond rupture occurs during the activation of triphenylsilane.

TETRAPHENYLSILANE

The thermal decomposition of tetraphenylsilane was studied at temperatures between 530 and 663°C using both sealed-vial techniques and the stirred-flow reactor. The chemistry of pyrolysis of this material is distinctly different from that of the phenylhydrosilanes; the reaction occurs via a free-radical mechanism, with the resultant formation of a broad spectrum of reaction products. The main products noted are hydrogen, benzene, triphenylsilane, ortho-, meta-, and para-biphenyl-triphenylsilane, and, under conditions of long-term pyrolysis, diphenyldibenzosilole.

Analysis of the rate data for the decomposition of tetraphenylsilane indicated that the reaction order is best represented as 3/2. An Arrhenius plot of the calculated rate constants is shown in Figure 5. The activation energy for the process is 77.7 kcal/mole and the frequency factor is 10^{19} liter^{1/2}/mole^{1/2}min.

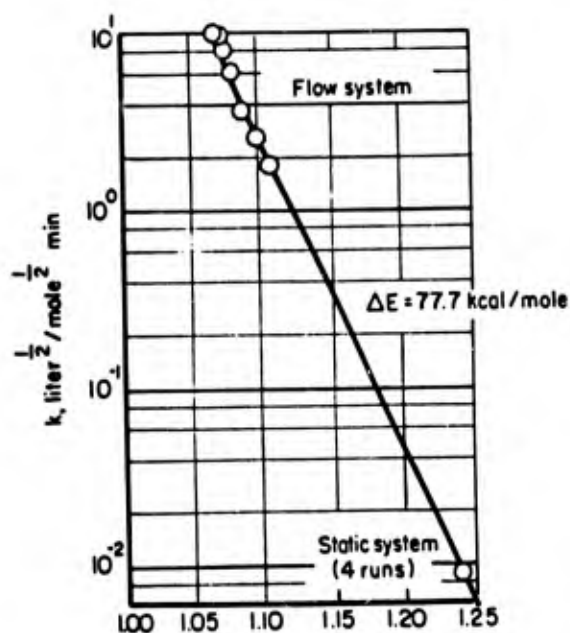
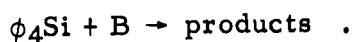
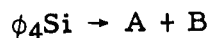
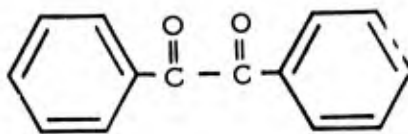


FIGURE 5. Arrhenius plot for tetraphenylsilane decomposition

Free Radical. The product distribution and order of reaction for tetraphenylsilane indicate a free-radical type of mechanism:

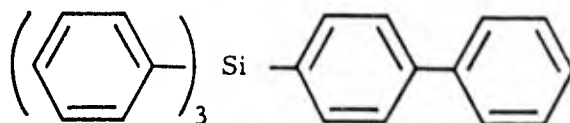


To clarify the second step of this mechanism further, several experiments were run in which phenyl radicals were added to the system. This was accomplished by heating benzil with tetraphenylsilane under conditions which allowed decomposition of the benzil to form phenyl radicals and carbon monoxide. In these experiments, the temperature was not high enough to cause decomposition of the tetraphenylsilane. In a typical experiment, 4.44×10^{-4} moles of tetraphenylsilane and 8.9×10^{-5} moles of benzil were heated to 448°C for 100 minutes in an evacuated sealed vial having a volume of 47 cc.



BENZIL

Chromatographic analysis of the products showed approximately a 60 percent yield of biphenyltriphenylsilanes with the ortho-, meta-, and para-isomers in a ratio of approximately 1:4:2.



P-BIPHENYLYLTRIPHENYLSILANE

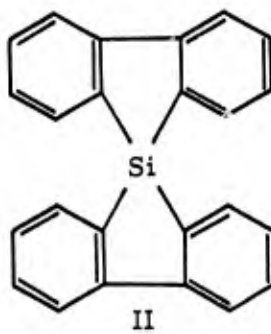
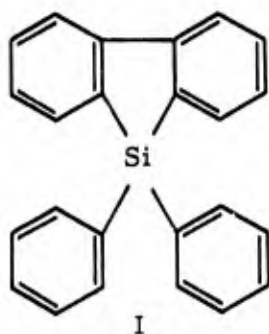
These results are very similar to those obtained in the pyrolysis of tetraphenylsilane. It is concluded, therefore, that the primary step in the decomposition of tetraphenylsilane involves the elimination of a phenyl radical. This then is followed by a series of rapid radical reactions to give the observed products.

The other radical formed in the primary step is probably the triphenylsilyl radical, which may either abstract hydrogen-yielding triphenylsilane or combine with any of the various molecular species in the system. Triphenylsilane is observed in the reaction products, and it is assumed that this material decomposes as cited above to form the lower members of the phenylhydrosilane series and, ultimately, hydrogen. The benzene that is observed in the reaction products may result either from abstraction of hydrogen by phenyl radicals or by direct elimination. Evidence for the latter type of reaction has not been observed directly in these thermal decomposition reactions, but it was observed to occur as a slow reaction in the mass spectrometer during analysis of some phenylsilanes. In these cases, direct elimination of benzene was indicated, during the flight of ionized species to the mass spectrometer detector, by the presence of metastable peaks in the spectra. Although there is no direct evidence for the occurrence of the elimination reaction in the thermal system, the possibility of such cannot be ignored.

The energy of activation for tetraphenylsilane is essentially the same as that obtained for the pyrolysis of tetramethylsilane⁽⁷⁾, 78 kcal/mole. Thermochemical considerations⁽⁸⁾ yield a Si-C bond energy of 69-76 kcal/mole, and bond dissociation energies of 79-95 kcal/mole have been obtained by electron impact⁽⁹⁾. The observed energy of activation is therefore consistent with published values of the bond energy. The frequency factor for tetraphenylsilane is high, but this may be partially accounted for by the multiplicities of equivalent phenyl groups available in the dissociation step and equivalent sites for attack by the phenyl radical.

Internal Cyclization. A distinctly different type of thermal reaction which is apparently the main mode of decomposition of the phenylmethylsilanes also was observed with tetraphenylsilane. This is an internal cyclization reaction with the resultant formation of compounds containing the dibenzosilole nucleus. With tetraphenylsilane, this cyclization reaction is of minor importance - compounds such as

5,5-diphenyldibenzosilole (I) and 5,5'-spirobi(dibenzosilole) (II) being formed in appreciable quantities only under conditions of long-term pyrolysis.



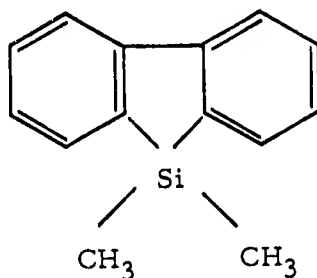
These products do, however, appear to be more stable than the triphenylbiphenylsilanes and other relatively simple structures which are formed via the main pyrolysis path of tetraphenylsilane. For example, when a sample of 5,5'-spirobi(dibenzosilole) was analyzed in the mass spectrometer using a 70-volt ionization source, only a single peak at mass 332 was observed. Under these relatively extreme conditions, there was no fragmentation of the basic molecular unit. This degree of stability suggests rather interesting possibilities for the dibenzosilole as a high-temperature fluid. These siloles might also serve as basic structural units in high-temperature polymers.

PHENYLMETHYLSILANES

The phenylmethylsilanes decompose via a free-radical mechanism, but their main mode of decomposition is distinctly different from that of tetraphenylsilane.

Diphenyldimethylsilane

The pyrolysis of diphenyldimethylsilane was studied at temperatures ranging from about 560 to 670°C using the stirred-flow reactor and sealed-vial techniques. The sealed-vial experiments were used to determine the overall chemistry of the pyrolysis of diphenyldimethylsilane and the distribution of products formed. At low extents of conversion of the silane, the main product formed is 5,5-dimethyldibenzosilole,



5,5-DIMETHYLDIBENZOSILOLE

with only minor amounts of other materials being detected by gas chromatography. Under conditions of long-term pyrolysis, an array of products is formed including triphenylmethylsilane, trimethylsilyldimethylphenylsilylbenzene, bis(dimethylphenylsilyl) benzene, and corresponding compounds containing the dibenzosilole nucleus. Identification of these compounds was made by mass spectrometry. A number of low-molecular-weight compounds were also observed including toluene, phenyltrimethylsilane, and phenyldimethylsilane. Complete identification of all of the reactions products was not attempted because of the extreme complexity of the product distribution. The observed reaction products suggest a very complex set of free-radical reactions, with hydrogen, methyl, and various silyl radicals contributing to the overall reaction.

Because of this complexity, studies with the stirred-flow reactor were limited to examination of the initial phases of decomposition of diphenyldimethylsilane and formation of 5,5-dimethyldibenzosilole. Some difficulty still was encountered in obtaining reliable rate data for the decomposition of diphenyldimethylsilane because of the fact that the overall decomposition rate was extremely sensitive to the "condition" of the walls of the stainless steel reactor. After the reactor was cleaned or exposed to air while at temperature, apparent rates of decomposition were always lower than when the walls were well conditioned by extended periods of operation of the reactor. This indicates the importance of radicals to the overall decomposition rate. However, the apparent rate of formation of the dibenzosilole product was not affected by wall condition, indicating that this compound is formed directly from the parent silane rather than as a result of reaction with radical species. Because of the dependence of rate of decomposition on wall condition, special operational procedure was adopted to ensure good conditioning of the walls. As a part of this procedure, the reactor was not held at temperature without a flow of helium through it, and the silane was circulated through the reactor along with helium for 4 to 5 hours prior to a run. Use of this procedure resulted in a self-consistent set of data for the decomposition of the silane.

Arrhenius plots for the decomposition of diphenyldimethylsilane and for the formation of 5,5-dimethyldibenzosilole are shown in Figures 6 and 7. For the decomposition process, the activation energy and frequency factor are 37 ± 2 kcal/mole and $107.3 \pm 0.5 \text{ min}^{-1}$, respectively. For the formation of the dibenzosilole compound, the activation energy and frequency factor are 39.7 ± 1.5 kcal/mole and $107.5 \pm 0.4 \text{ min}^{-1}$, respectively. The implications of this apparent agreement and the significance of the unusually low frequency factors are discussed below.

Triphenylmethylsilane

Pyrolysis of triphenylmethylsilane was carried out in the stirred-flow reactor at temperatures of 580 to 645°C. The reaction of this material was very similar to that of diphenyldimethylsilane; the main product was phenylmethyldibenzosilole,

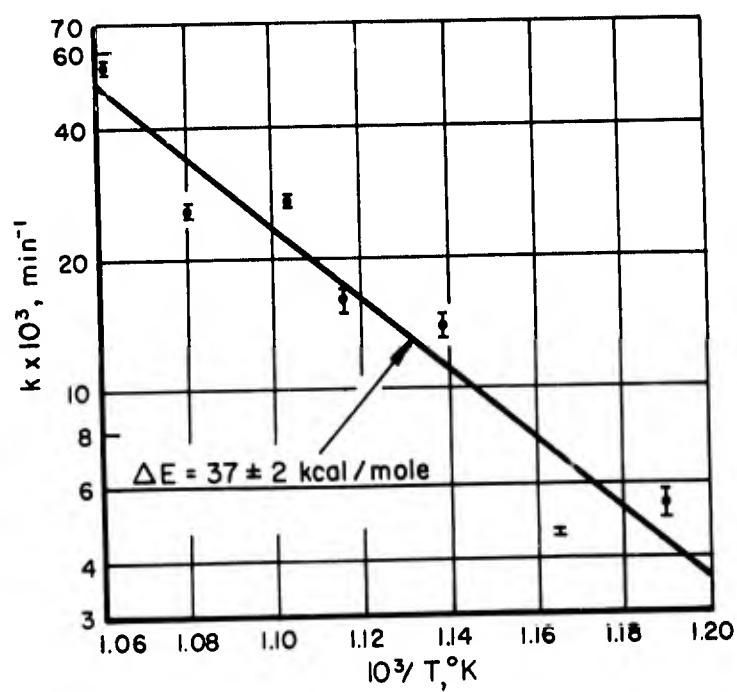


FIGURE 6. Arrhenius plot for pyrolysis of diphenyldimethylsilane

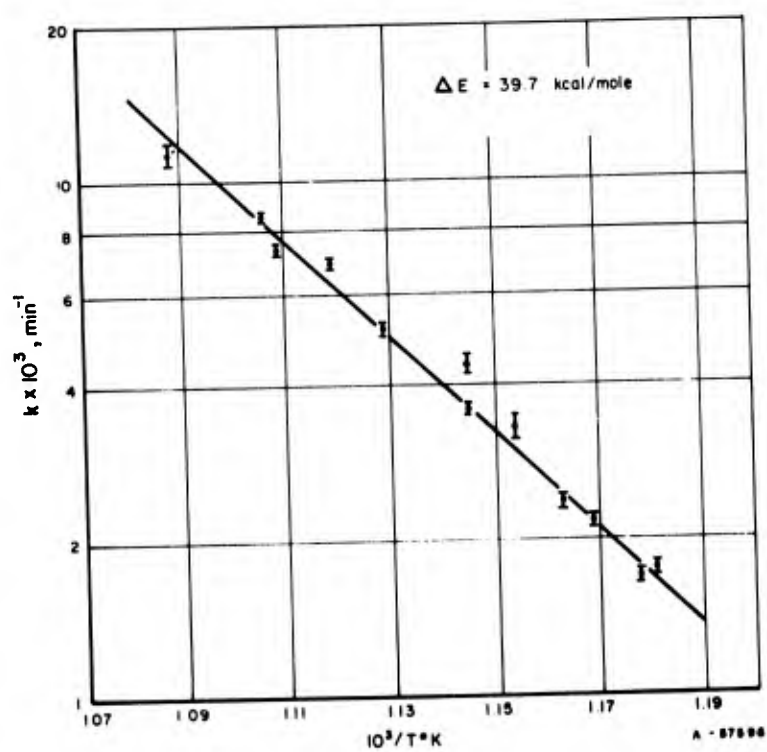
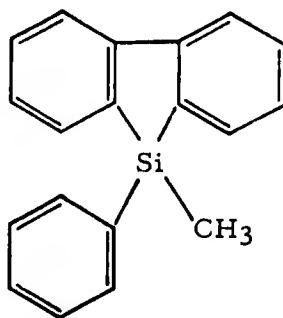


FIGURE 7. Arrhenius plot for formation of 5, 5-dimethyldibenzosilole



PHENYLMETHYLDIBENZOSILOLE

and the decomposition rate of the parent silane was very sensitive to wall conditioning. Procedures similar to those used with diphenyldimethylsilane were needed to obtain good data for the decomposition reaction.

Arrhenius plots for the decomposition of triphenylmethylsilane and the formation of phenylmethyldibenzosilole are shown in Figures 8 and 9. The observed activation energy and frequency factor for the decomposition reaction are 37 ± 3 kcal/mole and 107.7 ± 0.7 min⁻¹, respectively. The activation energy and frequency factor for the formation of the dibenzosilole compound are 43.9 ± 1.3 kcal/mole and 108.24 ± 0.3 min⁻¹, respectively. These kinetic parameters are in reasonably good agreement and, considering the difficulties involved in obtaining good data for the phenylmethylsilanes, may be considered in agreement with the values found for diphenyldimethylsilane. Discussion of the implications of these data is given below.

Mechanism of Reaction

The good agreement between the kinetic parameters for the decomposition of the phenylmethylsilanes and for the formation of the corresponding dibenzosilole compounds indicates that the same chemical process which determines the rate of formation of the dibenzosilole structure controls the overall rate of decomposition of the parent silane. The other types of products noted are formed as a result of rapid radical-molecule and radical-radical secondary reactions.

A possible mechanism by which the phenylmethylsilanes may decompose is illustrated in Figure 10. It is hypothesized that the first step in the decomposition involves the elimination of a hydrogen atom from either the ortho or para positions of the phenyl group. In this step, ortho elimination is statistically favored by a factor of 2:1. Only the ortho elimination can lead to the formation of the dibenzosilole structure, and it is suggested that the para-radical is involved in secondary reactions with the parent silane to yield some of the other products that are noted.

The frequency factors noted for these materials are unusually low, implying considerable decrease in entropy upon activation of the silane. The low frequency factor may not be unreasonable, however; in the parent molecules, the phenyl groups are free to rotate about the Si-C bond. In the dibenzosilole structure, such rotation is not possible. If it is assumed that the slow step is Reaction (3) in Figure 10, the decrease in rotational entropy and the effect of this factor on the frequency factor may be estimated as follows:

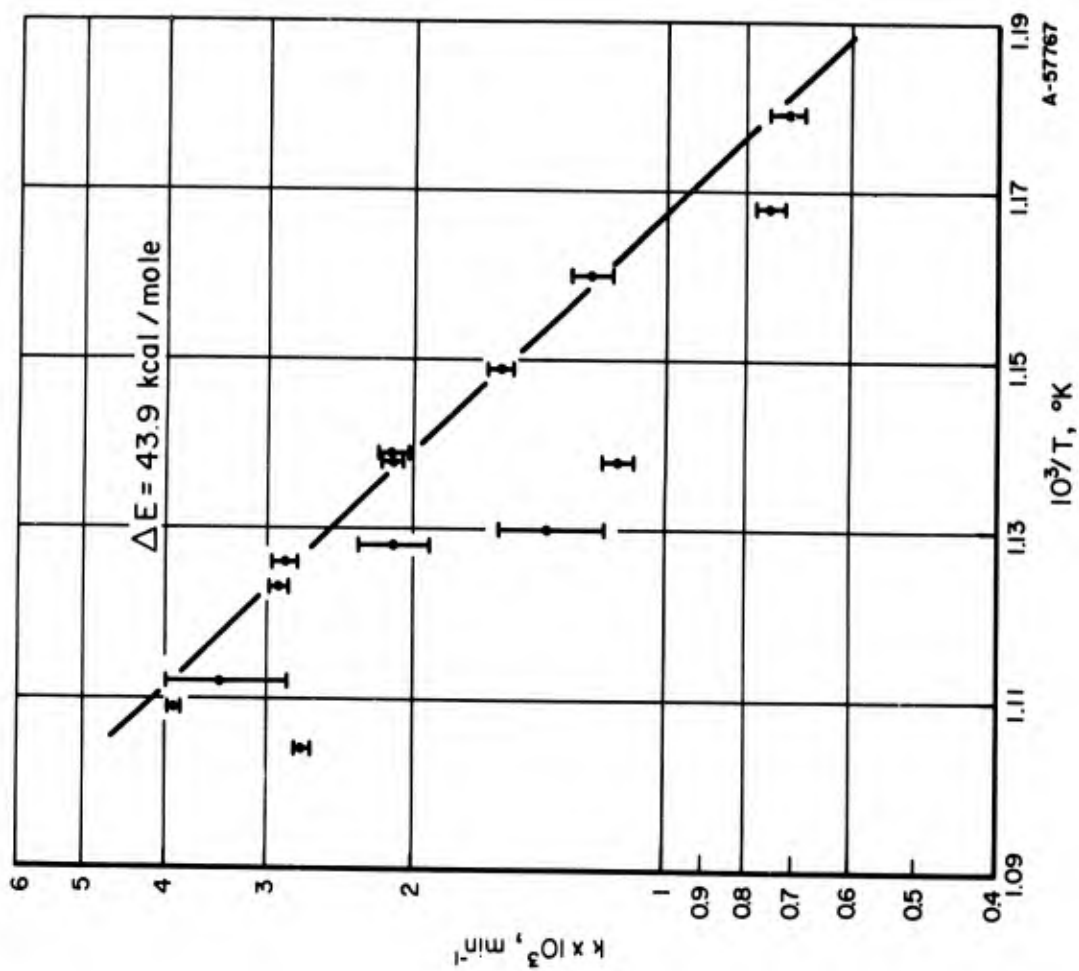


FIGURE 9. Arrhenius plot for formation of phenylmethyldibenzosilole

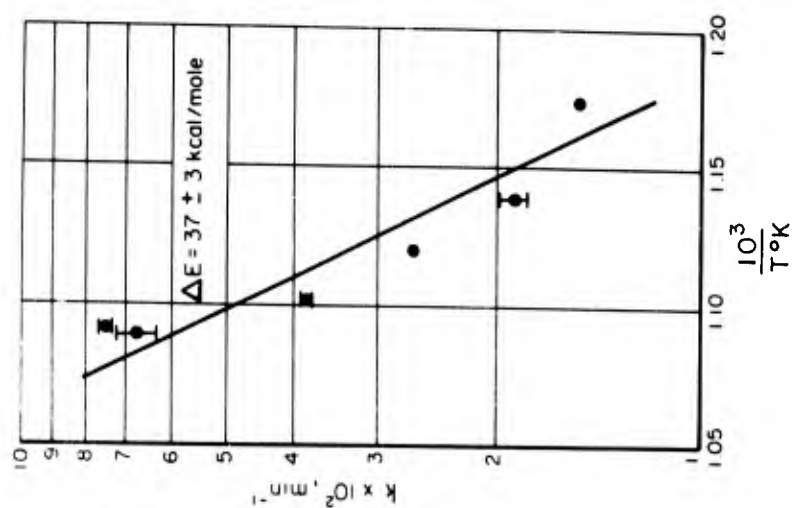


FIGURE 8. Arrhenius plot for decomposition of triphenylmethylsilane

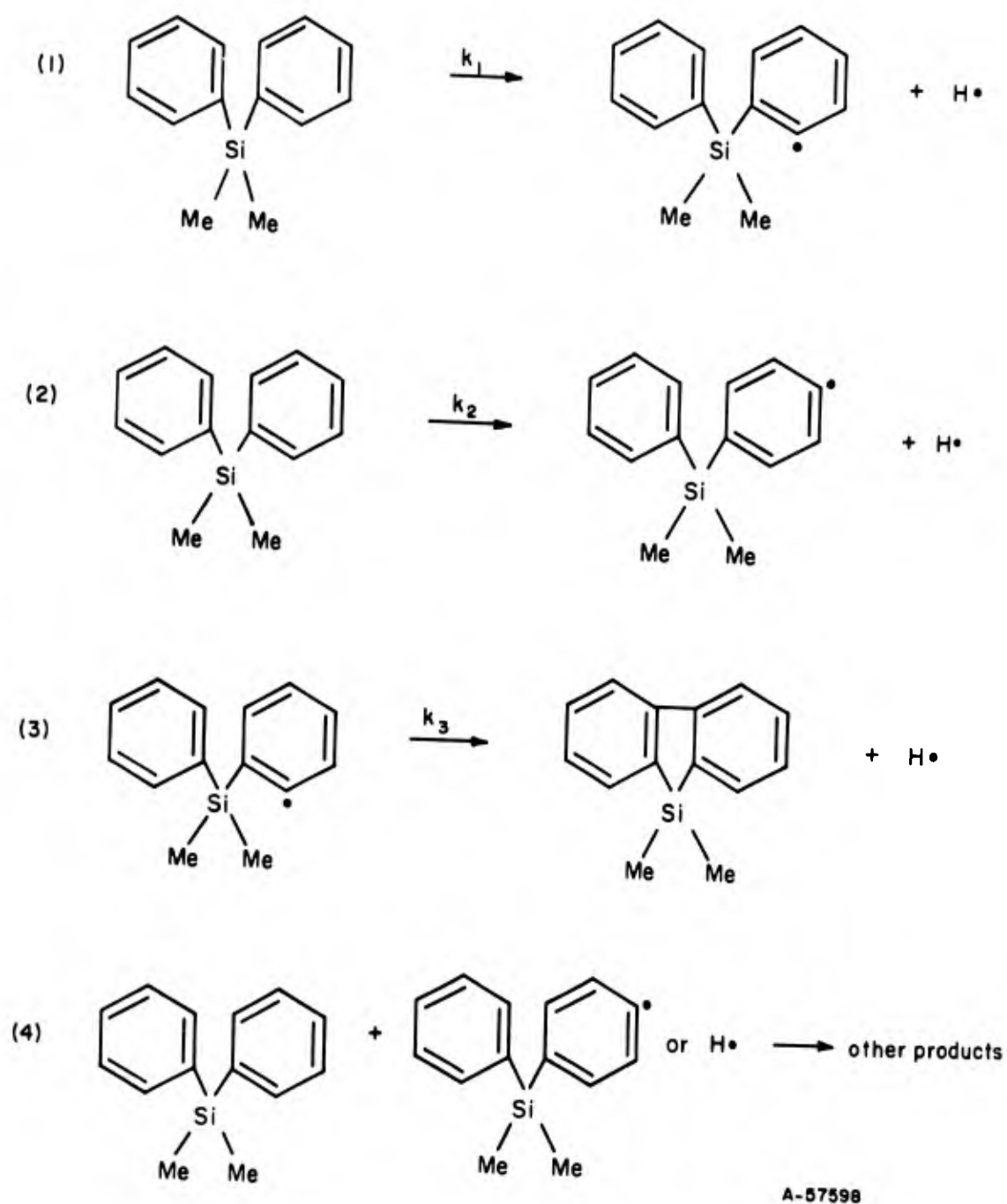


FIGURE 10. Possible mechanism for diphenyldimethylsilane

The rotational entropy of phenyl groups in diphenyldimethylsilane may be estimated using classical statistical mechanics:

$$S_{\text{rot}} = R(\ln pf + 1) ,$$

where pf is the rotational partition function for the phenyl group. Since the phenyl group is free to rotate only about the Si-C bond axis, the partition function is given by the equation for a rigid linear molecule,

$$pf = \frac{8\pi^2 I k T}{\sigma h^2} ,$$

where I is the moment of inertia, k is Boltzman's constant, h is Planck's constant, T is the absolute temperature, and σ is multiplicity of equivalent rotational states ($\sigma = 2$ for the phenyl group). The moment of inertia can be calculated from the structural parameters of the phenyl group, as given in Figure 11.⁽¹⁰⁾

$$\begin{aligned} I &= \sum mr^2 \\ &= 145.98 \text{ g-cm}^2 . \end{aligned}$$

The total rotational entropy of the two phenyl groups is twice that for each group, or 33.25 e. u. At least this much entropy must be lost upon formation of the activated complex in the formation of 5,5-dimethyldibenzosilole. Hence, the estimated frequency factor is

$$\begin{aligned} A &= \frac{kT}{h} e^{-33.25/R} = 10^{5.96} \text{ sec}^{-1} \\ &= 10^{7.74} \text{ min}^{-1} . \end{aligned}$$

This estimated frequency factor is in good agreement with the experimental values.

COMPARISON OF REACTIONS

The arylsilanes studied in this program are similar in structure, and yet the type of pyrolysis reaction observed depends critically on the details of the individual molecular structures. The differences in structure and reaction type may be conveniently expressed in terms of a set of substituted triphenylsilanes, as shown in Figure 12.

When $R=H$, the small size of the hydrogen apparently allows for formation of a pentacoordinate transition state, as illustrated in Figure 13. Formation of this hydrogen-bridged transition state is probably enhanced by $(p \rightarrow d)\pi$ bonding between the phenyl ring and the silicon. The variation in activation energy with number of phenyl groups attached to the silicon may be due to a combination of steric requirements for the formation of the transition state and increased Si-H bond strength. As the number of phenyl groups is increased, greater bond separation and, hence, more energy may be required for activation because of steric requirements. Also, the more phenyl groups attached to the silicon, the stronger the SiH may be because of polarization of the molecule. Weakening of the phenyl-silicon bond may also

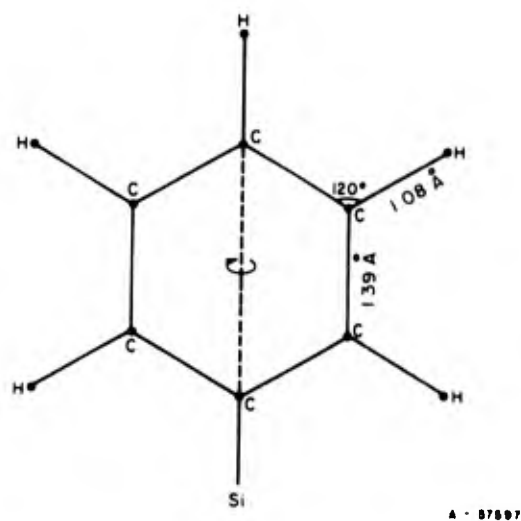


FIGURE 11. Phenyl group structure

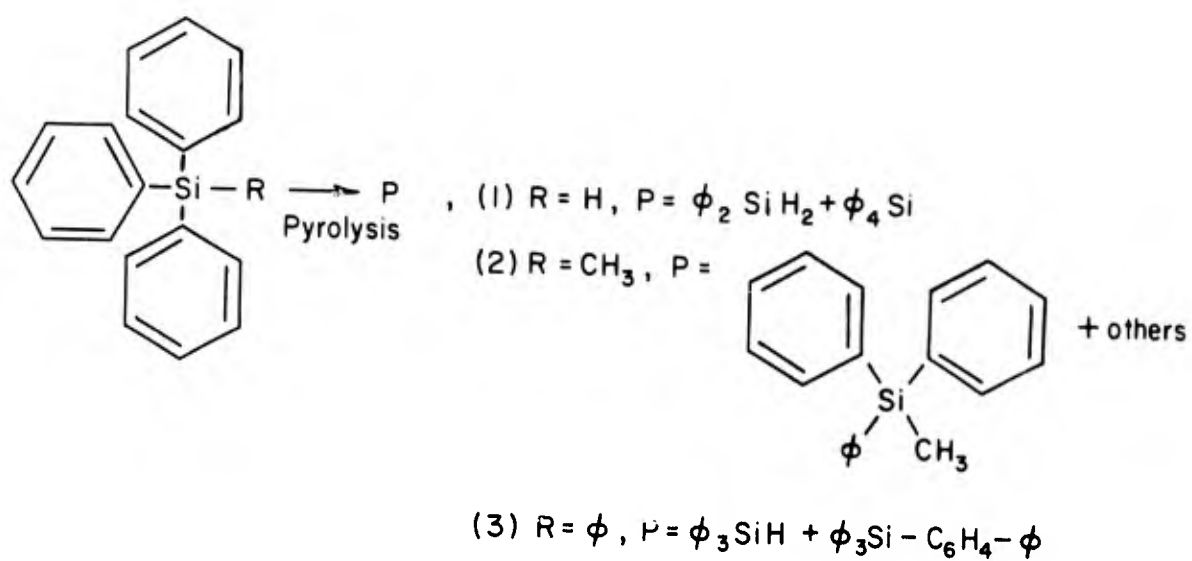


FIGURE 12. Summary of observed types of silane pyrolysis reactions

account for the observed trend in frequency factors for the phenylhydrosilanes; a higher degree of vibrational freedom would be expected as the phenyl-silicon bond is weakened.

With $R=CH_3$, the size of the substituent should hinder formation of an intermolecular bridge structure. An alternate mode of decomposition therefore must occur. It is interesting to note that a redistribution type of thermal reaction has been observed in the case of pyrolysis of phenyltrimethylsilane.⁽¹¹⁾ Of course, the cyclization type of reaction is not possible with this molecule, since there is only one phenyl group. The cyclization reaction is a relatively low-energy reaction which results from $(p \rightarrow d)\pi$ interaction between the phenyl ring and the silicon, as is suggested in Figure 14. It might also be noted in regard to the reaction scheme suggested in Figure 14 that this reaction scheme has some formal similarity to an analogous cyclization caused photochemically in perchlorotriphenylmethyl.⁽¹²⁾ Because of the low frequency factor, the net rate of this type of reaction with the phenylhydrosilanes is less than the rate of rearrangement under the conditions employed.

With tetraphenylsilane, the cyclization reaction is observed, but the elimination of phenyl radicals occurs more readily. This may be due to the electronic homogeneity of the molecule. That is, in the case of triphenylmethylsilane, the methyl group probably enhances $(p \rightarrow d)\pi$ bonding because of the electron-withdrawing character of the methyl-silicon relative to the phenyl group. But, with tetraphenylsilane, there is no enhancement of $(p \rightarrow d)\pi$ bonding, because all four substituents on the silicon are identical.

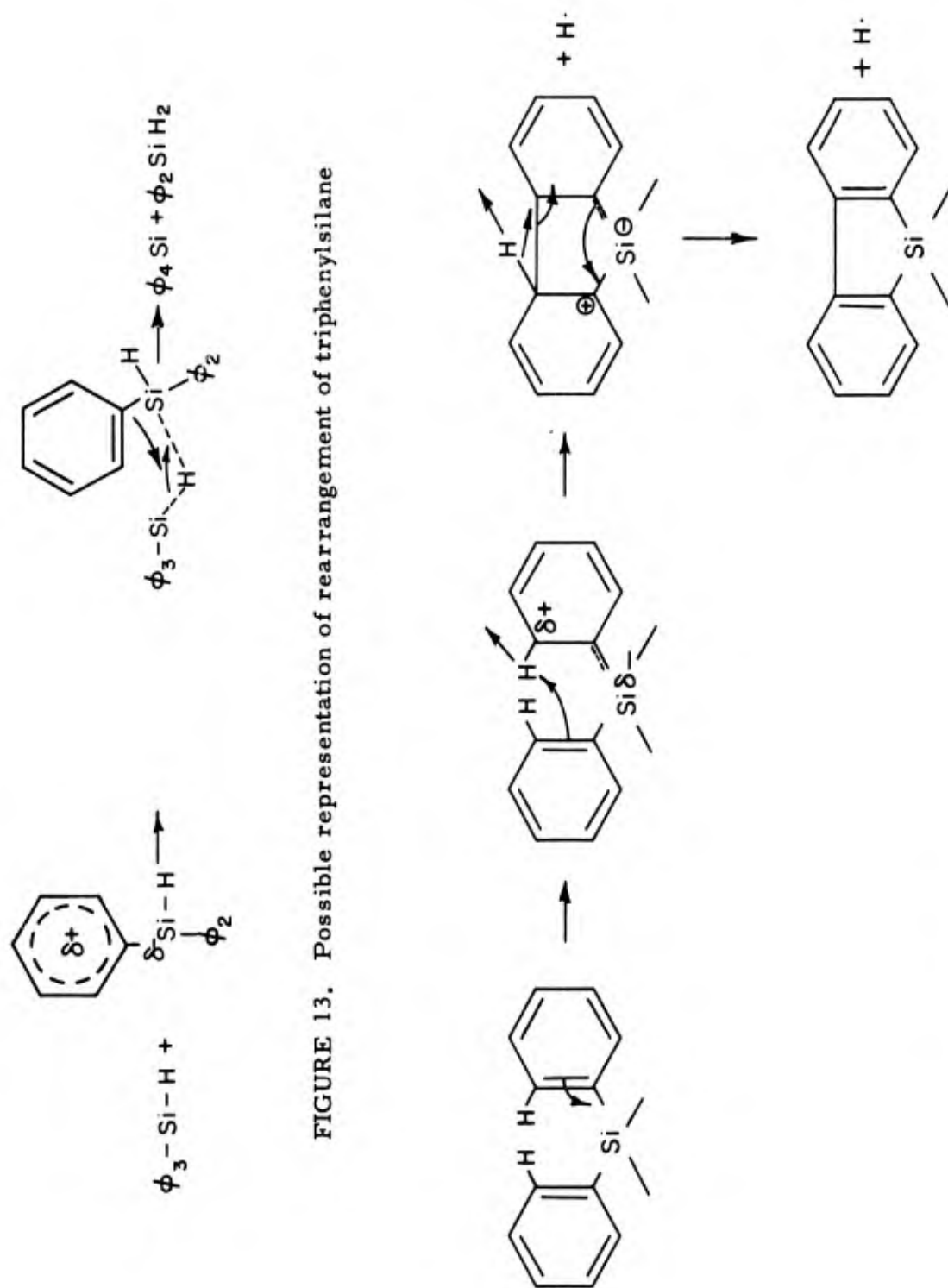


FIGURE 13. Possible representation of rearrangement of triphenylsilane

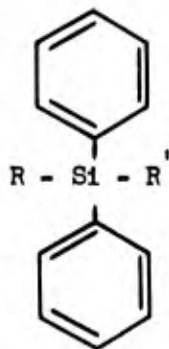
FIGURE 14. Possible stepwise representation of mechanism for formation of dibenzosilole structure

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

The arylsilanes studied in this program have been shown to be relatively stable materials, with temperatures of 300-650°C being required to obtain appreciable decomposition rates. The results indicate variation in both rate and mechanism of decomposition with types of substituents on the silicon, but these variations can be explained in terms of steric and electronic effects.

The least stable materials studied, mono- and diphenylsilane, would be unlikely candidates for use as structural units in high-temperature polymers or fluids because of their chemical reactivity toward air and water. Hence, a more realistic decomposition-temperature range for materials having polymer application might be 450-650°C. The results indicate that polymer structures having free phenyl groups, e. g.,



may have a tendency for phenyl-radical elimination and subsequent radical attack on the polymer chain. This tendency might be reduced by utilization of substituents on the silicon to enhance (p → d)π bonding between the silicon and phenyl groups, thus encouraging the formation of the stable dibenzosilole unit during thermal decomposition. However, a better approach might be to base the polymer structure on structural units already containing the dibenzosilole nucleus. Both mass spectra and kinetic results obtained in this program indicate that the dibenzosilole structure is quite stable.

Methods for incorporation of highly arylated structures, such as molecules containing the dibenzosilole nucleus, need to be considered further. Further consideration also needs to be given to synthesis of possible monomers containing the dibenzosilole nucleus. Conventional wet-chemical procedures such as the Wurtz-type reactions can be used, but yields are generally low (10-15 percent). Pyrolysis of the parent phenyl silane is a possibility; under certain conditions, yields as high as 35-40 percent have been achieved. However, more information is needed to judge the efficacy of the pyrolysis method for large-scale production of these compounds.

SECTION VI

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13. ABSTRACT The thermal-decomposition kinetics of the following arylsilanes have been investigated using both static and flow techniques: monophenylsilane, diphenylsilane, triphenylsilane, tetraphenylsilane, diphenyldimethylsilane, and triphenylmethylsilane. The phenylhydrosilanes decompose via a bimolecular second-order redistribution reaction, with no evidence for free-radical formation. On the other hand, the main mode of decomposition of tetraphenylsilane involves elimination of phenyl radicals followed by attack of these radicals on the parent silane. The decomposition of the phenylmethylsilanes also proceeds via a free-radical mechanism, but the main reaction path results in intramolecular cyclization, yielding compounds containing the dibenzosilole nucleus. Reasons for these three basically different modes of reaction are discussed in terms of substituent size and degree of (p → d)π bonding between the phenyl rings and silicon.		

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