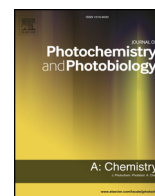




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Ultraviolet photolysis of 1,2-Dimethyldisilane in the gas phase

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ABSTRACT

The formation of MeSiH is the primary process in the photolysis of 1,2-dimethyldisilane at 193 nm that are analogues of carbenes. Gas chromatographic technique was used with a flame ionization detector as an analysis tool to identify the products mixture. The photolysis light at 193 nm was provided by an Oxford KX2 pulsed laser operated with rare-gas halide (known as an excimer laser) as the gain medium to provide ultraviolet (UV) radiation. This work has confirmed that radical processes are not important in the photolysis of 1,2-dimethyldisilane. A method for the determination of rate constants for MeSiH reactions relative to the rate constants of 1,2-dimethyldisilane has been formulated. This has been used to determine some relative rate constants of MeSiH insertions with methylsilanes. The insertion reactions of MeSiH with SiH₄ and Methylsilanes have shown to be fast and closer in reactivity to SiH₂ than to SiMe₂, whereas PhSiH looks to be slightly more reactive than MeSiH.

1. Introduction

The calculation of chemical reaction rate constants is of importance to chemistry and biology. Related studies carried out by our group concentrated on using time resolved spectroscopic studies [1–6]. In the same time and for gaseous reactions, gas chromatography is one of the most common and versatile methods of product analysis. This is because it can provide a separation and quantitative measurements of complex gaseous mixtures.

Silylene can be considered as very reactive intermediates. They have a very important role in the chemical vapor deposition of many thin films that contain silicon compounds. These species have technological importance in microelectronics industry besides the dry etching process of silicon wafers [7,8].

Providing the reaction system is carefully selected, and the conditions are well-defined, product yields can provide a mean of measuring relative rate constants of many chemical intermediate species in the presence of selected substrates.

This technique was employed in this research in order to:

- (i) determine the primary processes and mechanism of the photolysis of 1,2-dimethyldisilane (DMDS) using 193 nm excimer laser,
- (ii) study the rate of trapping of MeSiH by SiH₄, MeSiH₃, and Me₂SiH₂.

2. Material and methods

2.1. Apparatus

A Pyrex glass, static, high vacuum system has been used. The line was pumped by a mercury diffusion pump backed by a single stage rotary oil pump. A pre-calibrated MKS Baratron (type 170 M) was used to measure the pressure. An Edward speedivac gauge model B5 in conjunction with a Pirani gauge head model G6A was employed to monitor the pressure in the line continuously.

Two gas chromatographs were used for the analysis, both of which were equipped with gas sampling valve. Most of the analysis of the runs in this work was carried out using a Perkin-Elmer model 8310 gas chromatograph with flame ionization detector (FID) connected to Hewlett-Packard 3390 integrator. In addition a Perkin-Elmer model F33 gas-liquid chromatography with an FID was also used for some analyses. Several types of columns were employed for analytical purposes, the packing materials and operating conditions of which were dependent on the reaction under investigation. The main columns were of 15% PPG on 80–100 mesh chromosorb W (4.5m), 10% OV101 on chromosorb W-HP 80/100 (4m), Porapak T (4m) and Porapak Q (3m).

Five main cylindrical reaction cells were used for the kinetic runs. Two of these cells were constructed of spectroil quartz tubing of length

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6.5 cm and internal diameter 2.8 cm to be used at high temperature. The two other cells were built from Pyrex glass with silica windows fixed by using black wax. These cells were suitable for possible cleaning of the windows. These windows easily became covered with thin solid films after a number of experiments. One cell was constructed of spectroil quartz tubing and wrapped (except for the window) in “electro-thermal” heating tape and maintained at 343 K during the time of experiments.

The furnace consisted of a horizontal silica tube (4 cm in diameter), wound with nichrome resistance wire as a heater and contained in a box packed with asbestos fiber. The furnace electrical supply was controlled by using a Variac. Temperatures were measured using a chrome-alumel thermocouple, located near the center of the furnace.

The photolysis light was provided by an Oxford KX2 pulsed laser operated with rare-gas halide (known as an excimer laser) as the gain medium to provide ultraviolet (UV) radiation. It was usually used with Ar/F₂ mixtures to provide a wavelength of 193 nm. Discharge efficiencies were around 1–5% and emitted pulses have 0.1 to 1 J of energy in the time range of 10–100 ns. Average powers are normally in the 10 to 100 MW range.

2.2. Source and purity of materials

1,2-Dimethyldisilane, DMDS, was kindly obtained from Professor E. Hengge (University of Graz/Austria), and found to be about 85% pure. The purity was improved to better than 95%, by low temperature distillation using a dry-ice slush technique (DMDS has a vapor pressure of 0.3 mm at 195 K). Unfortunately amongst the remaining traces of other compounds (MeSiH₃, Me₂SiH₂, Me₃SiH, SiH₄, Me₂SiHSiH₃ and MeSiH₂SiHMeSiH₂Me) were two of the main products *viz*, methylsilane and 1,2,3-trimethyltrisilane. This means that correction had to be applied to the yields of these compounds in the photolysis runs.

Other compounds, such as SiH₄ (> 99.9 purity, BOC Ltd. Electra-II grade), MeSiH₃ (99.6% purity, prepared in our lab.), Me₂SiH₂ (99.5% purity, prepared in our lab.), and Me₃SiH (99.8% purity, Fluorochem Ltd.) were degassed by freezing down (77 K) in liquid nitrogen and were used in this work. Electra-II grade Nitrogen (oxygen free, 99.9% purity) was supplied by BOC Ltd.

2.3. Experimental procedure

Samples for photolysis were prepared by putting the required pressure of precursor into the reaction cell then adding the other reacting substrate (if required) and finally making the reaction mixture up with nitrogen to the required pressure. Every precaution was made to reduce the adsorption of the silicon compounds on the walls of the gas line, the reaction cell and the gas sampling loop of the GC by heating. After the photolysis, the mixture of gases in the cell was analyzed by gas chromatography. Kinetic experiments were carried out with mixtures containing 50–100 mTorr precursor with partial pressures of the reacting substrate in the range of 50–2000 mTorr and total pressure ca, 200 Torr (made with nitrogen). An average of 2–10 laser shots was used which was indicated by the amount of the product peaks by GC. The number of shots was chosen as small as possible to keep the conversion low. The procedure for a particular substrate gas was to vary the ratio of precursor to the gas added and monitor the change in the ratio of products produced by gas chromatography.

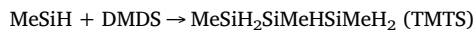
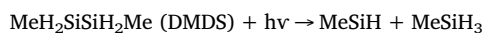
3. Discussion

3.1. Results and discussion

3.1.1. Experiments with DMDS alone

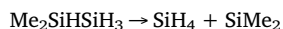
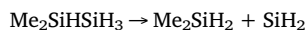
The first set of experiments indicated that the major products were methylsilane (MS) and 1,2,3-trimethyltrisilane (TMTS). The MS peak was identified by comparison of its retention time with that of an

authentic sample. As will be seen, this photolysis provides a relatively clean source of methylsilane (MeSiH). MeSiH reacts with the precursor, DMDS to produce TMTS:



To start with, the measurement of TMTS was a problem. Chromatographic peaks were irreproducible and had rather small yields which made them difficult to analyze. However there were several unrecorded, small peaks in the region where these molecules could be expected. After heating the sample loop of the gas chromatograph the peaks become reproducible. Because of the absence of TMTS authentic sample, TMTS was identified by comparing its retention time with those of other available trimethyltrisilane samples (*ie.* H₃SiSiH₂MeSiH₂Me and HSiMe₂SiMeHSiH₂Me) [9,10]. Its identity was supported by other experiments [11]. The area for this peak was found to increase with the number of shots and decrease in the presence of another substrate under fixed photolysis conditions. TMTS was also observed as one of the main products in the pyrolysis of DMDS by Ring et al. [10]. In the Ring et al. work, the reaction was studied over the temperature range 295–573 K.

Small traces of other compounds such as SiH₄ and Me₂SiH₂ (in addition to MeSiH₃ and TMTS) have also been observed. The most obvious suggestion for the formation of those compounds was due to the presence of about 4% of the 1,1-dimethyldisilane impurity in DMDS. This impurity was identified by comparing its retention time with that of an authentic sample but under different GC conditions [11]. At 193 nm the photodecomposition of this impurity may lead to the formation of SiH₄ and Me₂SiH₂ as follows:



Me₂SiH₂ and SiH₄ were identified by comparison of their retention times with those of authentic samples. Me₂SiH₂ was also detected by gas chromatography in the work of Davidson et al. [9] on the pyrolysis of DMDS. SiH₂ and SiMe₂ probably react with DMDS to give other products (H₃SiSiH₂MeSiH₂Me and HSiMe₂SiMeHSiH₂Me) but these will have rather small yields which makes them difficult to analyze. However there were several unrecorded, small peaks in the region where these molecules could be expected.

Preliminary experiments indicated the formation of an opaque solid film which covered the walls of the cell, particularly when high laser pulse energies were employed. The production of such films reduced the transmission of laser radiation and also could lead to product coming from direct photolysis of the adsorbed material. Usually those compounds if produced were in small yields compared to those produced by the homogenous photolysis of DMDS in the gas phase. Many efforts were made to reduce the effect of this film by using a low pressure of DMDS and low conversion (a few numbers of shots). Regular cleaning of the cell after five runs and leaving it overnight in an oven to 830 K prevented film build up.

DMDS photochemistry was explored by investigating the experimental effects of the number of laser shots, DMDS pressure, total pressure, added oxygen and temperature. In order to assess the effects, The GC peaks ratio [MeSiH₃]/[DMDS] was measured. This ratio gives an indication of the photochemical conversion. TMTS was not identified (and therefore not monitored) at the beginning of the work. The results of these preliminary investigations are shown in Figs. 1–5. A number of points can be extracted from this study:

1) The results in Fig. 1 show the linear dependence of the ratio with the number of shots. This suggests a well behaved reaction with product yields proportional to absorbed photons.

2) Fig. 2 demonstrates that the more DMDS in the cell, the less is the [MeSiH₃]/[DMDS] ratio. A possible explanation is that most of the

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