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# A KINETIC STUDY OF THE GAS PHASE REACTION BETWEEN TRIMETHYLSILANE AND METHYL CHLORIDE

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## SUMMARY

The kinetics of the gas phase reaction between trimethylsilane and methyl chloride have been investigated between 429 and 494° in packed and unpacked quartz vessels. Methane and trimethylchlorosilane are the only products formed in substantial quantity, and the results are consistent with their being produced in a radical chain reaction propagated in the gas phase with heterogeneous initiation and termination. It is suggested that in the packed vessel initiation is by dissociative desorption of trimethylsilane from singly-occupied surface sites, but in the unpacked vessel a more complex initiation mechanism appears to operate, and it is tentatively suggested that methyl chloride is dissociatively adsorbed, the chlorine atom then reacts with adsorbed trimethylsilane at the surface, and a dimethylchlorosilane molecule and a methyl radical are finally desorbed into the gas phase.

## INTRODUCTION

The ability of silicon hydrides to reduce organic halides to hydrocarbons is well known, and several kinetic and mechanistic studies have been made[1,2]. Photoreduction of alkyl halides in the liquid phase was observed by Haszeldine and Young[3], who proposed a radical chain mechanism involving the following propagation steps:

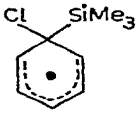
$$R\cdot + R'_3SiH \rightarrow RH + R'_3Si\cdot \qquad (1)$$

$$R'_3Si\cdot + RX \rightarrow R'_3SiX + R\cdot \qquad (2)$$

This propagation sequence, which is generally accepted, neatly illustrates the differences in reactivity between alkyl and silyl radicals resulting from differences in bond strengths to carbon and to silicon; since the Si–H is weaker than the C–H bond, reaction (1) occurs in preference to hydrogen abstraction from RX. On the other hand, silyl radicals abstract halogen selectively from carbon [reaction (2)], since the Si–Hal is stronger than the C–Hal bond. For these reasons also, reaction (2) is more favourable energetically than hydrogen abstraction by silyl radicals. Consequently, the overall reaction proceeds cleanly even up to high percentage conversion.

Photolysis in the gas phase follows a similar course, and relative rate data have been obtained for the reaction of trichlorosilyl radicals with various alkyl halides [reaction (2)][4]. Rate constants for many reactions of type (1) in the gas phase have also been measured[2].

The thermal reaction between silicon hydrides and aryl halides has been extensively studied, mainly by Russian workers, most attention having been directed to the reaction between trichlorosilane and chlorobenzene[5-7]. Reduction is observed, probably proceeding by a mechanism analogous to that for alkyl halides, but there is another concurrent chain sequence, which gives the "condensation" product $PhSiCl_3$ ($HSiCl_3 + PhCl \rightarrow PhSiCl_3 + HCl$). The key step in the condensation is probably the formation of the intermediate (I), which can have no counterpart in the reaction with alkyl halides.



(I)

No kinetic studies of the thermal reactions between silicon hydrides and alkyl halides in the gas phase have been reported, and we describe below an investigation of the reaction between trimethylsilane and methyl chloride.

## EXPERIMENTAL

### Materials

Methylchlorosilanes were re-distilled under nitrogen. Trimethylsilane and dimethylsilane were prepared from the corresponding chlorosilanes by reduction with lithium aluminium hydride, and hexamethyldisiloxane was prepared from trimethylchlorosilane by hydrolysis. These compounds were purified by low-temperature trap-to-trap distillation. Other compounds were obtained commercially, and purified where necessary by trap-to-trap distillation. The purities of all the compounds were checked by IR spectroscopy and GLC analysis and, where appropriate, by mass spectrometry, NMR spectroscopy, or by comparison of b.p.'s, vapour pressures, or refractive indexes with those of authentic samples or with values reported in the literature.

### Apparatus

The kinetic apparatus and associated high-vacuum system were of conventional design, with a quartz static reaction vessel of volume 450 ml, a heated mixing vessel with a jet to facilitate rapid mixing of reactants, and a stainless steel sample valve[8] leading to a GLC column. The reaction vessel was housed in an electric furnace, temperature control being by a Sunvic RT3 controller, and temperature measurement by a chromel/alumel thermocouple. Pressures were measured by a Springham glass spiral manometer, and all stopcocks in contact with reactants and products were greaseless (Fischer–Porter or Springham).

The GLC apparatus consisted of a 2.35 m stainless steel column, packed with 10% w/w squalane on 60–85 mesh Embacel, and a Gow-Mac thermal conductivity detector, which were housed in an air thermostat at 40°. Peaks were recorded on a Kent 1 mV recorder and Chromalog electronic integrator.

## RESULTS

The reaction between methyl chloride and trimethylsilane was investigated between 429 and 494°, with initial pressures of reactants ranging from 10 to 200 mm, the relative pressures being varied by factors of up to 4 on either side of equality. Under these conditions, and up to 50% decomposition, methane and trimethylchlorosilane, in approximately equimolar quantities, accounted for at least 95% of the products. Small quantities of tetramethylsilane, chlorodimethylsilane, and dichlorodimethylsilane were positively identified, as was hexamethyldisiloxane (shown to be largely formed by hydrolysis of trimethylchlorosilane in the GLC sampling valve). A fifth minor product, which had a retention time between those of dimethyldichlorosilane and hexamethyldisiloxane, was not identified.

The order of the reaction was determined by measuring the time required for a constant fraction of reaction to occur at different initial pressures, and confirmed by initial rate measurements. In two series of experiments at 481.5°, with initial pressures between 25 and 200 mm, the total order was found to be $1.90 \pm 0.08$ using the ratio of the concentrations of methane and methyl chloride as the criterion of extent of reaction, and $1.93 \pm 0.06$ using the ratio of the concentrations of trimethylchlorosilane and trimethylsilane as the criterion. Initial rate measurements, also at 481.5°, gave the total order as $2.02 \pm 0.06$, and the orders with respect to trimethylsilane and methyl chloride as $1.69 \pm 0.04$ and $0.32 \pm 0.04$, respectively.

Arrhenius parameters were calculated from a series of runs with fixed initial pressures of 41 mm of each reactant, giving $k\,(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}) = 10^{16.55 \pm 0.68} \exp - (48000 \pm 2000/RT)$.

Addition of 7.5% of toluene reduced the rate of formation of trimethylchlorosilane by 33% at 430°, while addition of 5% of propene reduced the rate by 40% at 445°. In separate experiments, the reaction between trimethylsilane and propene, and the thermolysis of trimethylsilane or methyl chloride alone, were shown to be very slow over the temperature range of this work.

Varying the surface/volume ratio of the reaction vessel by a factor of 15 with a packing of silica tubing increased the rate of formation of trimethylchlorosilane by 42% at 469.8°, and by 129% at 437.5°. The activation energy in the packed vessel was $34 \pm 4\ \mathrm{kcal \cdot mol^{-1}}$.

In similar experiments with methyl chloride and trichlorosilane between 400 and 445°, with initial pressures around 40 mm, methane and silicon tetrachloride were the major products, while the minor products were not identified. The activation energy for the formation of silicon tetrachloride was $46 \pm 2\ \mathrm{kcal \cdot mol^{-1}}$, and addition of 5% of propene at 444.5° reduced the rate by 50%. The rate of formation of methane at 429.5° was about 5.4 times greater than that under comparable conditions in the reaction between methyl chloride and trimethylsilane. Trichlorosilane was found to decompose very slowly under these conditions.

## DISCUSSION

The pronounced inhibition of the reaction between trimethylsilane and methyl chloride by added toluene or propene is good evidence for a radical chain reaction. This evidence, in conjunction with the highly specific formation of methane and trimethylchlorosilane, indicates clearly that the reaction proceeds by the expected propagation steps (3) and (4). The nature of the initiation and termination processes

$$\mathrm{Me\cdot + Me_3SiH \rightarrow CH_4 + Me_3Si\cdot} \qquad (3)$$

$$\mathrm{Me_3Si\cdot + MeCl \rightarrow Me_3SiCl + Me\cdot} \qquad (4)$$

is much less obvious, however, and in this respect this reaction presents several features, and problems, in common with the thermal reaction between trichlorosilane and chlorobenzene[5-7].

The value of 2 for the total order of reaction is significant; there is no realistic bimolecular gas-phase reaction between trimethylsilane and methyl chloride which could lead to the formation of a gaseous free radical, and linear termination must therefore be postulated to account for the observed order. This termination is most likely to be heterogeneous, and in view of the sensitivity of the Arrhenius parameters to changes in surface/volume ratio, initiation is likely to be heterogeneous also. This conclusion is supported by the fractional orders with respect to the individual reactants. For the order with respect to trimethylsilane to exceed one, initiation and termination would have to involve the methyl rather than the trimethylsilyl radical, and this leads us to the following outline scheme:

$$\mathrm{Initiation \rightarrow Me\cdot} \qquad \mathrm{Rate} = R_i$$

$$\mathrm{Me\cdot + Me_3SiH \rightarrow CH_4 + Me_3Si\cdot} \qquad (3)$$

$$\mathrm{Me_3Si\cdot + MeCl \rightarrow Me_3SiCl + Me\cdot} \qquad (4)$$

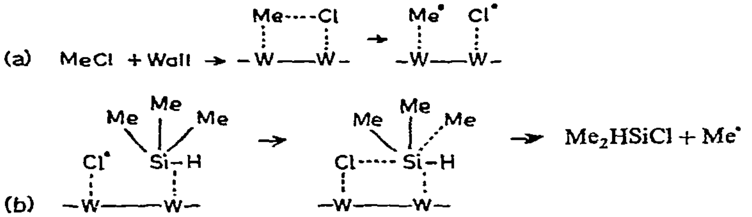
$$\mathrm{Me\cdot + Wall \rightarrow stable\ products} \qquad (5)$$

Steady-state treatment then gives $d[CH_4]/dt = k_3 \cdot R_i \cdot [Me_3SiH]/k_5$. Since the Arrhenius parameters for reaction (3) are known[9] to be $k_3(\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}}) = 10^{11.34} \exp -(7830/RT)$, and since $E_5$ may be assumed to be zero, $E_i = 48.6 - 7.8 = 40.4$ kcal·mol$^{-1}$ and $A_i/A_5 = 10^{16.55-11.34} = 10^{5.2}$. It is noteworthy that the heterogeneous initiation seems to have an $A$ factor $10^5$ times greater than the heterogeneous termination, and also that an almost identical, high $A$ factor was observed in one of the investigations of the reaction between trichlorosilane and chlorobenzene[7].

Some tentative conclusions about the Arrhenius parameters of the reaction between trimethylsilane and methyl chloride in the packed vessel may be drawn from the observed acceleration of the reaction at two temperatures. Since the activation energy was found to be 34 kcal·mol$^{-1}$, $E_i$ is now $34 - 7.8 = 26.2$ kcal·mol$^{-1}$, and if the total order is assumed still to be 2 in the packed vessel, $A$ may be calculated as $10^{12.4}$ cm$^3$·mol$^{-1}$·s$^{-1}$, and hence $A_i/A_5 = 10^{1.1}$. These figures are comparable to those found in another investigation of the trichlorosilane/chlorobenzene reaction $[k = 10^{10.9} \exp -(26500/RT)]$, in which heterogeneous initiation by dissociation of the silicon hydride at the surface was proposed[6]. There are several other examples of the heterogeneous dissociation of organosilicon compounds[10], including trimethylsilane[11], with activation energies between 25 and 30 kcal·mol$^{-1}$, and thus it is reasonable to suggest that in the $\mathrm{MeCl/Me_3SiH}$ reaction in packed vessels the initiation is by dissociative desorption of trimethylsilane from single sites.

In the unpacked vessels the initiation process seems to be more complex.

As a possible explanation of the fractional orders and the high *A* factor observed under these conditions, we suggest that there is dissociative adsorption of methyl chloride on the surface, (–W–W–), followed by transfer of the chlorine atom to a silicon atom adsorbed at a neighbouring site, with displacement of a methyl group from the silicon as in the following scheme:



The observed formation of a small amount of chlorodimethylsilane is consistent with this formulation. If the simple Langmuir adsorption isotherm applies, the dissociative adsorption of the methyl chloride would result in a rate of desorption of order between 0 and 0.5, while if the silyl group were desorbed from a single site with release of methyl atoms, the effective order with respect to trimethylsilane would be between 0 and 1.0. The observed orders for the initiation of 0.32 with respect to methyl chloride and 0.69 with respect to trimethylsilane are entirely consistent with this picture. The rate of initiation would be given[12] by the expression:

$$R_i = \frac{B_S \cdot p_S \cdot B_H \cdot p_H^{0.5}}{1 + B_S \cdot p_S + B_H \cdot p_H^{0.5}}$$

in which *B* denotes a constant and *p* the partial pressure, and the subscripts S and H refer to trimethylsilane and methyl chloride, respectively. Within the pressure range used for the order determinations at 481.5°, this expression would correspond to the observed expression, *viz.* $R_i = k_i \cdot p_S^{0.69} \cdot p_H^{0.32}$, if $B_S$ had a value of ca. $1.4 \times 10^{-2}$ and $B_H$ one of ca. $1.1 \times 10^{-1}$. The high *A* factor for heterogeneous initiation relative to heterogeneous termination would then be attributable to a positive entropy of activation in step (b) of the scheme above; a value of 40.4 kcal · mole$^{-1}$ for $E_i$ would be fairly normal for desorption of a chemisorbed species.

The mechanism proposed shows an analogy with that discussed by Voorhoeve for the Direct Synthesis[13], in which organosilicon compounds are formed by the interaction between methyl chloride and a silicon/copper surface. For that reaction, it was proposed that dissociative adsorption of the methyl chloride on the surface was followed by attachment of methyl groups to silicon at the surface, interaction between adsorbed chlorine atoms and methylsilicon fragments adsorbed on adjacent sites, and finally release of methylchlorosilanes into the gas phase with a positive entropy of activation, giving rise to a high *A* factor[13].

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