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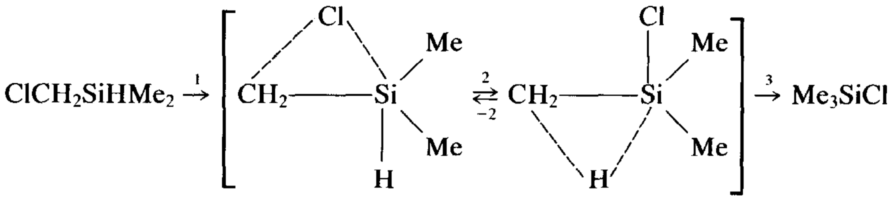
Silicon Mirror Initiated Reactions of Methyl Chloride and Chloromethyldimethylsilane

A silicon mirror surface (deposited from silane decomposition) catalyzes the free radical isomerization of chloromethyldimethylsilane to trimethylchlorosilane and trimethylsilane. This surface also catalyzes the free radical reaction of methyl chloride with silane to produce a mixture of chlorosilanes. It is proposed that these reactions are initiated by free radicals produced at the walls by chlorine atom transfers from the alkyl chloride reactants to the silicon mirror surface. © 1986 Academic Press, Inc.

INTRODUCTION

In a recent kinetic investigation of the gas phase isomerization of chloromethyldimethylsilane (**I**) (see Ref. (*1*)) to trimethylchlorosilane (**II**), it was shown that the isomerization occurs by two parallel first order pathways: a concerted dyotropic rearrangement



Rate = k[**I**]; log k = 12.99 − 52,165 ± 400 cal/2.303RT

SCHEME 1. Dyotropic Rearrangement of (**I**)

and a free radical chain process:

$$\begin{array}{rcl} \mathbf{I} & \xrightarrow[\text{(wall)}]{4} & \cdot CH_2SiHMe_2 + \text{wall-Cl} \\ \cdot CH_2SiHMe_2 + \mathbf{I} & \xrightarrow{5} & Me_3SiH + ClCH_2\dot{S}iMe_2 \\ ClCH_2\dot{S}iMe_2 & \xrightarrow{6} & \cdot CH_2SiMe_2Cl \\ \cdot CH_2SiMe_2Cl + \mathbf{I} & \xrightarrow{7} & Me_3SiCl + ClCH_2\dot{S}iMe_2 \\ 2\ \cdot CH_2SiMe_2Cl & \xrightarrow{8} & \text{products} \end{array} \quad \left.\begin{array}{l} \\ \\ \\ \end{array}\right\}\text{Chain}$$

Rate$_{FR}$ = k_{FR}[**I**]; log k_{FR} = 9.42 − 43,000 ± 1000 cal/2.303RT.

SCHEME 2: Free Radical Induced Isomerization of (**I**)

The free radical process could be quenched by propylene and seemed (from the kinetics), to be initiated by a zero order surface reaction as indicated in Reaction 4.

An attempt to quench the free radical process by conditioning the silica surface of the reaction cell with a silicon mirror deposited from the pyrolysis of silane pro-

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TABLE 1

Effect of Silicon Mirror Surfaces on the Reaction Rate Constant of The Isomerization **I** → **II** (T = 642.5 K)

Series 1[a]				Series 2[a]			
Run No.	P[b] (Torr)	$k_1 \times 10^5$ (sec^{-1})	Y(Me$_3$SiH)[e]	Run No.	P[b] (Torr)	$k_1 \times 10^5$ (sec^{-1})	Y(Me$_3$SiH)[e]
25[c]	160	42.2	(13.0),4,4	30[c]	208	37.3	(17.2),4.9
26	140	23.5	1.6	31	208	23.6	2.0
27	120	15.3	1.3	32	150	15.1	1.2
28	104	14.8	0.9	33	150	13.4	0.84
29	90	13.2	1.2	55[d]	200	5.2	0.60
Uncoated Pyrex reactor runs				Isomerization under propylene inhibition			
23	224	3.13	0.4	—[f]	50–220	1.74 ± 0.05	0
24	184	3.37	0.5				

[a] Runs made over Silicon mirrored surfaces. Reaction mixture compositions were Ar/**I** = 6; T = 642.5 ± 0.2 K.

[b] Total reaction pressures in Torr.

[c] First runs over "new" silicon mirror surfaces.

[d] Twenty one runs were made between runs 33 and 55 effecting a 2.6-fold decrease in k_1. Wall poisoning after the first run is a relatively slow process.

[e] Yields in parenthesis were determined at 15% conversion. All others were determined for the total reaction with conversions around 75%.

[f] The rate constant under propylene inhibition is calculated from the Arrhenius parameters determined in Ref. (*1*), and pertains to the dyotropic reaction with no chain component.

duced very surprising results. Instead of slowing the reaction, as expected, the reaction was significantly accelerated. This silicon metal catalysis is an effect similar to the one reported by Frank and Falconer (*2*). They found that a 100-face of a silicon crystal at 545–695 K promoted the conversion of methyl chloride to other methylchlorosilanes (Me$_x$SiCl$_{4-x}$). The initial step of this clearly complex reaction was thought to involve a chlorine atom transfer from methyl chloride to the silicon surface (like Reaction 4) to generate a catalytic Si—Cl surface site. In this paper we reported additional studies on the catalytic properties of silicon metal films toward reactions of organochlorides.

EXPERIMENTAL

Chloromethyldimethylsilane and silane were prepared by the LiAlH$_4$ reduction of the corresponding chloride. Reactions were carried out in a 400-cm^3 Pyrex reactor immersed in a resistively heated air bath with temperatures maintained to ±0.1°C by a Bayley 124 controller. Silicon mirrored surfaces were produced through the pyrolysis of silane at temperatures above 400°C. Product analyses were made on a $\frac{1}{8}$-in. × 24-ft column packed with 20% squalene on Supercoport.

RESULTS AND DISCUSSION

Initial studies of the catalytic properties of silicon were made on the **I** → **II** isomerization. Neat **I** was reacted at 642 K over silicon mirrored surfaces and the rates of reaction were monitored. The reaction with or without catalysis follows well-behaved first order kinetics. The results of two series of runs, each series initiated with a freshly deposited silicon mirror surface, are listed in chronological order in Table 1. The first runs over a new surface (runs 25 and 30) had reaction rates (as indicated by their first order rate constants) which were more than an order of magnitude faster than runs in the untreated Pyrex reactor (runs 23 and 24), and more than 20 times faster than runs made in the presence of propylene. A systematic decrease in reaction rates for successive runs over a particular surface was also evident and this demonstrates a gradual poisoning of the surface active sites. Yields of trimethylsilane, a minor but significant product of the catalyzed reaction, parallel the rate behavior. Thus, $\mathrm{Me_3SiH}$ yields in the initial stages of the first runs over a silicon mirror surface (13–17%) were much higher than yields in subsequent runs which decreased from 2 to about 0.5%. An obvious explanation of the above is that chlorine atoms are transferred from **I** to the silicon surface to give wall bound chlorine atoms and gas phase $\cdot\mathrm{CH_2SiMe_2H}$ radicals. These radicals then react with **I** to give $\mathrm{Me_3SiH}$ (Reaction 5), and the $\mathrm{ClCH_2\dot{S}iMe_2}$ radical which then initiates the homogeneous chain reactions (Reactions 6 and 7). Trimethylsilane yields averaged only 0.5% in the neat reaction of **I** over silica and were zero in the propylene inhibited reaction. This is consistent with very slow wall initiation in the two-channel reaction and no wall initiation in the exclusively dyotropic rearrangement, respectively.

Further support for catalytic activity of silicon mirror surfaces via chlorine atom "activated" wall abstraction comes from the following two experiments. First the pyrolysis of methyl chloride in argon [$(\mathrm{CH_3Cl/Ar} = 8)$, $P_{\mathrm{total}} = 50$ Torr at 407°C] was studied over a fresh silicon mirror deposited from $\mathrm{SiH_4}$ decomposition. In 100 min only 1% conversion of $\mathrm{CH_3Cl}$ to $\mathrm{CH_4}$ was observed. No reaction was observed under the same conditions prior to the silicon deposition (i.e., in a silica-walled reactor or over a poisoned silicon mirror surface). Second, the pyrolysis of silane–methyl chloride mixtures ($\mathrm{Ar/SiH_4/CH_3Cl} = 1/2/8$, $P_{\mathrm{total}} = 200$ Torr, $T = 407$°C) was examined over fresh silicon mirrors. After 65 min there was a 98% loss of $\mathrm{SiH_4}$ and a concurrent formation of $\mathrm{SiH_2Cl_2}$, $\mathrm{HSiCl_3}$, and $\mathrm{SiCl_4}$ with yields of 2, 20, and 55%, respectively. In addition, 72% of the $\mathrm{CH_3Cl}$ was converted to $\mathrm{CH_4}$. The rate of $\mathrm{SiH_4}$ loss was at least 10 times faster than expected on the basis of the kinetics of neat silane pyrolysis (*3, 4*). These results are consistent with a gas phase methyl–silyl radical chain process propagated by methyl radicals produced at the silicon surface by the chemisorption and subsequent catalytic wall decomposition of $\mathrm{CH_3Cl}$ (Reactions 9 and 10).

$$\mathrm{CH_3\cdot + H_{4-x}SiCl_x \xrightarrow{9} CH_4 + H_{3-x}\dot{S}iCl_x}$$

$$\mathrm{H_{3-x}\dot{S}iCl_x + CH_3Cl \xrightarrow{10} H_{3-x}SiCl_{x+1} + CH_3\cdot}$$

The experimental rate constant of the free radical component of the **I** → **II** isomerization ($k_{\mathrm{FR}} = 10^{9.42} \times e^{-43{,}000\,\mathrm{cal}/RT}\ \mathrm{sec}^{-1}$) can be used in conjunction with the proposed mechanism (Scheme 2) to obtain kinetic information about the wall induced decomposition of **I** (Reaction 4). Thus the free radical reaction rate can be identified with the rate of Reaction 5 (i.e., $\mathrm{Rate_{FR}}\ k_{\mathrm{FR}}[\mathbf{I}] = k_5[\beta][\mathbf{I}]$, where $[\beta] = [\cdot\mathrm{CH_2SiHMe_2}]$, and since first order kinetics in **I** was observed, the β radical steady state concentration must be [**I**] independent. Homogeneous β, β termination (Reaction 8) is the most reasonable termination reaction, therefore Reaction 4 must be a zero order reaction [i.e., full coverage of the surface by **I** at all pressures, and surface reaction of **I** as rate determining], thus, $[\beta_{\mathrm{ss}}] = (k_4/k_8)^{1/2}$.

According to the transition state theory, the rate and rate constant of a zero order wall decomposition can be represented as (5)

$$\mathrm{Rate} = k_4 = C_{\mathrm{a}}\frac{ekT}{h}\left(\frac{f^{\ddagger}}{f}\right) e^{-E_{\mathrm{a}}/RT} \times \frac{S}{V} \times \frac{1000}{N_{\mathrm{AV}}}\ M\ \mathrm{sec}^{-1},$$

where C_{a} is the concentration of absorbed reactant on the walls in molecules/cm^2, $(f^{\ddagger}/f)$ is the ratio of the partition functions for the adsorbed activated complex and reactant, and the other quantities have their usual significance. An identification of experimental Arrhenius parameters with those of Scheme 2 give

$$k_{\mathrm{FR}} = 10^{9.42} \times e^{-43{,}000/RT}\ \mathrm{sec}^{-1}$$

$$= \left[\frac{C_{\mathrm{a}}\,\dfrac{ekT}{h}\left(\dfrac{f^{\ddagger}}{f}\right) e^{-E_4/RT} \times \dfrac{S}{V} \times \dfrac{1000}{N_{\mathrm{AV}}}}{k_8}\right]^{1/2} \times k_5$$

Assuming $k_8 \simeq 10^{9.0\pm0.5}\ M^{-1}\ \mathrm{sec}^{-1}$ [by analogy with iPr· and tBu· recombination rate constants] (*6*), $k_5 = 10^{8.3} \times e^{-7800}$ cal/$RT\ M^{-1}\ \mathrm{sec}^{-1}$ [by analogy with methyl H-abstraction from trimethylsilane] (*7*), $C_{\mathrm{a}} \simeq 10^{15.0\pm0.5}$ molecules/cm^2 [an end on wall interaction of **I** by the chlorine atom with $\sigma_{\mathrm{Cl}} \simeq 2.0$ Å], and $S/V = 1$, one calculates $A_4 \simeq (ekT/h)(f^{\ddagger}/f) \simeq 1.3 \times 10^{16}\ \mathrm{sec}^{-1}$, and $E_4 \simeq 70.4$ kcal. The activation energy is 10 kcal lower than the (C—Cl) bond dissociation energy (*6*) (a reasonable result), and the *A*-factor indicates a "loose" transition state analogous to gas phase bond fission reactions (*6*). Similar high *A*-factors have been found in other wall dissociation reactions (*8*).

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