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PARTICLE FORMATION OF GAS-PHASE SILICON COMPOUNDS AND AROMATIC COMPOUNDS BY LIGHT OR ELECTRON IRRADIATION

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A number of silicon compounds and aromatic compounds form particles under UV light or electron beam irradiation in the gas phase. Carbonyl compounds, halogen compounds and some aromatic compounds act as initiators for photo-induced particle formation of silicon compounds.

During the course of pulse-radiolytic studies of chlorosilane and benzene in the gas phase, formation of particles was visually observed under electron or photo-irradiation. There have been several reports on light or electron induced particle formation.[1-9] However, the compounds known to form particles by irradiation are still very limited.

We attempted to survey the scope of this interesting phenomenon. Various gas systems (pure and mixed) were irradiated; we observed particle formation of a fair number of compounds and found certain regularities for particle formation among the compounds. We further found that polymers (polysilanes) were produced by photo-irradiation in many of the mixed systems containing silicon compounds.[10]

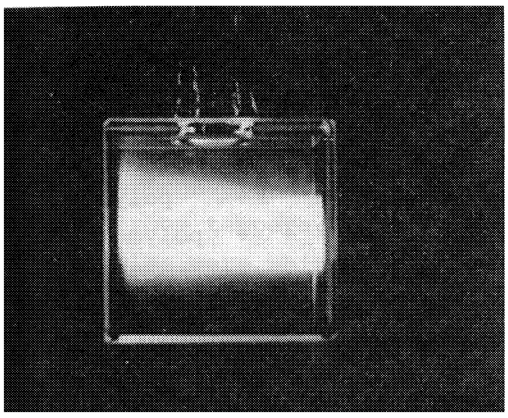

Fig. 1 Scattered light from particles produced by UV-irradiation of trimethylsilane: 800 Torr, benzene: 20 Torr.

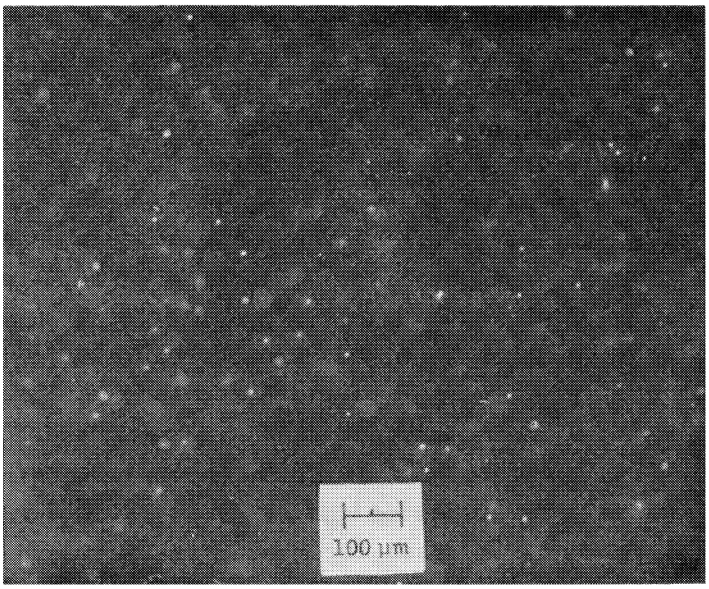

Fig. 2 Magnified photograph of particles produced by UV-light irradiation of the system with trimethylsilane: 800 Torr, benzene: 20 Torr. A flash light and a slit were used to take the photograph.

A mercury free vacuum line was used for sample preparations. Electron irradiation was perfomed by a linear accelerator giving 10 MeV electrons with a pulse width of 5 μs; its peak current being about 0.4 A. Electron beam was led to a cell after it was spread by an aluminum plate (1 mm thick). For survey of particle formation, 20-60 pulses were irradiated. Photo-irradiation was carried out using a full arc from a 500 W xenon lamp or a 500 W high pressure mercury lamp. A lamp-house equipped with a collimetor (50 mm ϕ) was used. In most cases a

Table 1. Particle formation in pure gas systems.

compound (pressure/Torr)	particle formation e[a]	UV	compound (pressure/Torr)	particle formation e	UV
$SiCl_4$ (200)	+	-	C_6H_6 (15-70)	+	+
Cl_3SiH (400-500)	+	-	$C_6H_5CH_3$ (24)	-	+
$(CH_3)_2SiClH$ (130)	+		$C_6H_5C_2H_5$ (7)	-	+
SiH_4 (400-800)	+		C_6H_5F (60)	+	+
$(CH_3)_2SiH_2$ (400-800)	-	-	C_5H_5N[b] (16)	+	+
$(CH_3)_3SiH$ (400-800)	-	-	$(CH_3)_2CO$ (100-150)	-	-
$(CH_3)_4Si$ (600)	-	-	CH_3COOCH_3 (150)	-	-
CH_3I (400)		-	$CH_3COOC_2H_5$ (50)	-	-
C_2H_5Br (400)	+	-	C_2H_5CHO (50)		-

[a]electron beam irradiation. [b]C_5H_5N = pyridine.

Table 2. Particle formation and products in the mixed gas systems.[a]

	e	UV	products(UV)		e	UV	products(UV)
$SiCl_4/C_6H_6$	+	+	polymer	Cl_3SiH/CH_3COOCH_3		+	$CH_3OC_2H_5$[b]
Cl_3SiH/C_6H_6[c]	+	+	polymer	$Cl_3SiH/CH_3COOC_2H_5$		+	$C_2H_5OC_2H_5$[b]
$(CH_3)_2SiCl_2/C_6H_6$		+	polymer	$(CH_3)_3SiH/CH_3COOC_2H_5$	+	+	
SiH_4/C_6H_6	+	+	polymer	$SiCl_4/(CH_3)_2CO$		+	polymer
$(CH_3)_2SiH_2/C_6H_6$		+	polymer	$Cl_3SiH/(CH_3)_2CO$[c]	+	+	polymer,adduct[d]
$(CH_3)_3SiH/C_6H_6$	+	+	polymer	$(CH_3)_2SiCl_2/(CH_3)_2CO$		+	polymer
$(CH_3)_3SiH/CH_3I$		+		$(CH_3)_4Si/(CH_3)_2CO$		+	
$(CH_3)_3SiH/C_2H_5Br$	+	+		$(CH_3)_3SiH/(CH_3)_2CO$	+	+	polymer
$(CH_3)_3SiH/C_2H_5CHO$		+		$(CH_3)_2SiH_2/(CH_3)_2CO$		+	polymer

[a]Pressure of benzene is 0.1-10 Torr; in this range benzene does not form particles alone. Pressures of the other additives are 15-50 Torr. [b]See Ref. 12. [c]When a Pyrex cell was used for photo-irradiation particles were formed in $Cl_3SiH/(CH_3)_2CO$ system but were not formed in Cl_3SiH/C_6H_6 system. [d]Adduct = $(CH_3)_2CHOSiCl_3$.

quartz lens was used for converging light. Although particle formation was observed without the lens, its employment made the observation easier. In runs of pure gas systems, each compound, at a pressure less than 80 % of its saturated vapor pressure, was irradiated in a cubic or a cylindrical quartz cell. In runs of mixed gas systems, 100-800 Torr of a silicon compound and 0.1-50 Torr of an additive compound were irradiated.

The presence of particles was visually verified by observing either scattered irradiation light or scattered light from a monitoring He-Ne laser.

From the results shown in Table 1 and 2, and various other observations the following points are noted:

1) Chlorosilanes, silane and aromatic compounds have a general tendency to form particles by excitation with a few exceptions. As the silicon compounds examined in this work do not absorb light from a xenon or high pressure mercury lamp, particle formation was not observed in pure silicon compounds. We cannot explain at present why alkylbenzenes did not form particles under electron beam irradiation, while they did under photo-irradiation.

2) Benzene[11] forms particles by itself. It also seems to act as an initiator for particle formation when it is irradiated with silicon compounds. In pure benzene particle formation did not occur at pressures below 10 Torr, while in mixed gas systems particle formation occurred at pressures below 10 Torr of benzene. Even in the system of 0.1 Torr of benzene and 400 Torr of trimethylsilane particle formation was observed under photo-irradiation.

3) The carbonyl compounds and halogen compounds tested in this work act as initiators of particle formation with silicon compounds although the former compounds do not form particles by themselves.

4) Silicon compounds form particles in the presence of appropriate inducing reagents, e.g. benzene, carbonyl compounds and halogen compounds. In the silicon compound-initiator systems under light irradiation, we assume that the initiator is first excited by light and subsequent interaction of the activated initiator with a silicon compound results in formation of particles.

Fig. 1 is a photograph of an irradiation cell where particles are formed by xenon light converged by a quartz lens. Once formed, particles survived for about 30 min at room temperature after the light was cut off. During photo-irradiation the particles were whirling; their size became progressively greater with time and seemed to become constant after 20-30 min, while their number increased with time at the beginning, reached a maximum at about 5 min and then decreased gradually. The transmittance of the He-Ne laser beam through the 3 cm cell decreased to 50 % at maximum. As the whirling motion slowed down when the light was cut off, we were able to take a magnified photograph of the particles. Fig. 2 shows such a photograph taken after 1 hour's irradiation. The size of the particles was estimated to be 2-3 μm from the photograph.

The particle formation is dependent on temperature. The particles were formed almost instantly by photo-irradiation at room temperature (halogen compounds systems were exceptional; there was a time lag of about 5 s between the irradiation of light and particle formation), but an induction period of 2-3 s was observed at 50°C, about 40 s at 100°C, and no particle was formed at 150°C. An

interesting phenomenon was observed in the following experiment. The sample was photo-irradiated in an electric oven at 150°C; no particle was observed at this temperature. In 10 s after removal from the oven, particle formation, without photo-irradiation, commenced. From this observation the following suggestion can be made. Light induced nucleation takes place even at high temperature (150°C) but the growth of particles is limited at this temperature, so we cannot observe these particles by scattered light. However, these particles are "living" in the dark, and they grow so large as to scatter light and become visible when the temperature is decreased.

After prolonged photo-irradiation of the silicon compound-initiator systems, liquid and solid polymers were deposited on the cell walls. The solid polymers were insoluble in any organic solvent. The liquid polymers from chlorosilanes may be chlorinated polysilanes, because they changed to white powders on standing in contact with the atmosphere, probably due to hydrolysis of the Si-Cl bond. The liquid polymers from methylsilanes were identified as permethylpolysilanes by analyses of IR, UV, and NMR; their molecular weight distribution were determined as 300-10,000 (max 500-700) by HPLC. It is somewhat curious that disilanes and trisilanes were not produced in methylsilanes-initiator systems.

Detailed studies of the mechanism of particle formation and polymer formation are now under investigation.

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10) It has been known that silicon polymer was formed by vacuum ultraviolet photolysis or by mercury sensitized photolysis of silicon compound. For example, see M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, J. Am. Chem. Soc., 87, 179 (1965); G. G. A. Perkins, E. R. Austin, and F. W. Lampe, J. Am. Chem. Soc., 101, 1109 (1979) and references cited therein.
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