Dissociative Excitation of Some Gaseous Organosilicon Compounds by Electron Impact

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Emission spectra induced by electron impact on some gaseous organosilicon compounds were measured by a single photon counting technique. Vinyltrimethylsilane and vinyltrimethoxysilane showed emission bands assigned to decomposition products, CH, H, and Si atom, and trimethylsilylacetylene and Trimethyl(2-propynyloxy)silane produced C₂ in addition to CH, H, and Si atom, indicating that C₂ species was originated from C≡C moiety in the parent molecules. From the comparison of the emission intensity of Si atom produced from each parent molecule, it is concluded that cleavage of Si-C bond is easier than that of Si-O bond. By mixing acrolein molecule into the organosilicon compounds, emission intensity of Si atom decreased, suggesting that acrolein molecule interacted with the organosilicon compounds to suppress the generation of Si atom.

Keywords: Electron impact, Emission spectrum, Organosilicon compounds

1. Introduction

Chemical reactivity of organosilicon compounds have attracted much attention in developing noble processes of microfabrication [1-3] and in potential applications as thin-film photoconductors [4,5] and nonlinear optical materials [6,7], together with in extensive syntheses of a variety of polysilanes and polysiloxanes [8,9]. From some gaseous organosilicon compounds, thin films were synthesized under irradiation with UV and IR laser light using photochemical and photopolymerization reactions [10-17]. Thin films deposited from gaseous organosilicon compounds had chemical structures different from those of the parent molecules and also from those synthesized in the liquid phase. These results clearly showed that a thin-film formation from gaseous organic molecules under irradiation with laser light can afford a unique way to synthesize noble materials.

Recently, we have succeeded to produce sedimentary aerosol particles from gaseous organic molecules under irradiation with N₂ laser

light [18-20]. A gaseous mixture of trimethyl(2-propynyloxy)silane (TMPSi) and acrolein (AC) deposited sedimentary aerosol particles which involved TMPSi in polymer matrix of polyacrolein [21]. Aerosol particles of organosilicon compounds with a size of several tens of nanometer are expected to show unique chemical behaviors and are supposed to become a constituent of microfabrication in direct patterning. To apply the method for practical use, it is necessary to understand chemical behaviors of organosilicon compounds under irradiation with electron beam and UV laser light. In the present paper, in order to investigate the dissociative excitation process by electron impact, decomposition products of some gaseous organosilicon compounds have been detected by measuring emission spectra under irradiation with electron beam, and the collisional effect of AC on the decomposition process has been studied.

2. Experimental

TMPSi was prepared by refluxing a mixture

Fig. 1. Emission spectra induced by electron impact on (A) VTMeSi, (B) VTMSi, (C) TMeSiA, and (D) TMPSi at a pressure of 2 mTorr. Incident electron energy is 80 eV.

of 1,1,1,3,3,3-hexamethyldisilazane (Tokyo Kasei, GR grade, 96%) and 2-propyn-1-ol (Wako, EP grade, 98%) for 12h under nitrogen atmosphere followed by fractional distillation [21]. Fraction at 110°C was used as a pure sample after checking its purity by gas chromatography. TMPSi was stored in a deaerated pyrex glass tube below 10°C to prevent polymerization. Vinyltrimethylsilane (VTMeSi) (Tokyo Kasei, EP grade, 98%), vinyltrimethoxysilane (VTMSi) (Tokyo Kasei, EP grade, 99%), trimethylsilylacetylene (TMeSiA) (Tokyo Kasei, GR grade, 98%), and AC (Merck, 95%, stabilized with 0.2% hydroquinone) were also stored in a refrigerator below 10°C to prevent polymerization. All the samples were degassed by freeze-pump-thaw cycles immediately before use. Each sample vapor of organosilicon compound was introduced into a collision chamber at a background pressure of 6×10^{-7} Torr (1 Torr = 133.3 Pa), and exposed to pulsed electron beam at an incident electron energy of 50 - 100 eV. Acrolein vapor was mixed with an organosilicon

compound just before entering the collision chamber. Sample pressure in the collision chamber was measured with a capacitance manometer (MKS Baratron 227A). Pulse width (50 μ s) of electron beam and timing for triggering a data acquisition system were controlled by a micro-computer. Photons emitted from gaseous decomposition products were detected through a monochromator (Ritsu MC-30N) and the number of photons were counted using a single photon counting technique [22] under irradiation of 3600 shots of electron beam at each wavelength.

3. Results and Discussion

Emission spectra induced by electron impact on gaseous VTMeSi, VTMSi, TMeSiA, and TMPSi at a pressure of 2 mTorr are shown in Fig. 1. At an incident electron energy of 80 eV, Balmer lines of H atom (396, 410, 433, and 486 nm) and 3900 Å and 4300 Å systems of CH were observed with VTMeSi and VTMSi (Figs. 1A and 1B) in addition to 503 and 577 nm bands. The 503 and

577 nm bands disappeared when a filter (UV 35) was used to cut the light shorter than 350 nm, revealing that the actual emitting wavelengths were 251 and 288 nm. These bands can be assigned to the emission bands of silicon atom [23, 24].

Emission spectra of TMeSiA and TMPSi (Figs. 1C and 1D) exhibited Swan bands of C_2 in 450~480 nm and 500~520 nm regions in addition to the bands characteristic of H, CH, and Si atom. This result indicated that C_2 radical was produced from acetylenic moiety of the molecules, but not from ethylenic moiety. C=C double bond adjacent to Si atom was broken by electron impact.

As is shown in Fig. 1, emission intensity of Si atom depended on molecular structure of the parent molecules. At a sample pressure of 2 mTorr, emission intensity of the 251 nm and 288 nm bands normalized to the emission intensity of 431 nm band of CH were 0.46 and 0.32 for VTMeSi, 0.12 and 0.10 for TMeSiA, and 0.06 and 0.05 for VTMSi at an electron energy of 80 eV. At a sample pressure of 1.5 mTorr, the normalized emission intensity of 288 nm band of Si atom was 0.07 for TMPSi and 0.06 for VTMSi at an electron energy of 80 eV. Emission intensity of Si atom decreased in the order of VTMeSi > TMeSiA > TMPSi > VTMSi. The emission intensity of Si atom normalized to the CH band intensity was not sensitive to the incident electron energy between 70~100 eV. In VTMSi, Si band was not observed at an electron energy of 60 eV, but in TMPSi, Si band was detected at an electron energy of 60 eV, but not at 50 eV. From these results, it is concluded that cleavage of Si-C bond is easier than that of Si-O bond being consistent with the value of bond energy, and from the comparison between VTMeSi and TMeSiA, cleavage of Si-C bond adjacent to C=C bond is easier than that of Si-C bond adjacent to C≡C bond.

To investigate the interaction between the organosilicon compounds and acrolein, emission spectra induced by electron impact on gaseous mixtures of organosilicon compounds and AC were measured at an electron energy of 80 eV. The result on a gaseous mixture of VTMeSi (2 mTorr) and AC (1 mTorr) is shown in Fig. 2. In a preliminary experiment, emission spectrum induced by electron impact on pure AC was measured; AC produced H, CH, and C_2 species at electron energies of 50 - 100 eV. The spectrum in Fig. 2 showed the bands characteristic of the emitting species produced from both VTMeSi and AC, except that the emission intensity of Si atom and Balmer lines

Fig. 2. Emission spectrum induced by electron impact on a gaseous mixture of VTMeSi (2 mTorr) and AC (1 mTorr). Incident electron energy is 80 eV.

Fig. 3. Dependence of emission intensity of 288 nm band of Si atom induced by electron impact on gaseous mixtures of VTMeSi/AC (●), VTMSi/AC (△), TMeSiA/AC (▲), and TMPSi/AC (○) against partial pressure of AC. The 288 nm band intensity was normalized to the intensity of 431 nm band of CH. Sample pressure is 2 mTorr for VTMeSi, VTMSi, and TMeSiA, and 1.5 mTorr for TMPSi.

of H atom became weaker. The same spectral behaviors were observed with the gaseous mixtures of the other three organosilicon compounds and AC. The change of the emission intensity of Si atom was measured by varying the partial pressure of AC. As is shown in Fig. 3, AC molecules quenched the emission of Si atom, indicating that AC molecules interacted efficiently with Si atom, and/or Si atom formation process was suppressed by the collisional interaction between the organosilicon compounds and AC. Among the four organosilicon compounds studied in the present paper, VTMeSi was most efficiently quenched by

AC, and TMPSi was quenched least.

In sedimentary aerosol particles deposited from a gaseous mixture of TMPSi and AC under irradiation with N₂ laser light, a considerable amount of elemental silicon was detected together with silicon bonded in an organosilicon polymer [21]. In the case of a gaseous mixture of VTMSi and AC, elemental silicon was detected only little in the aerosol particles [25]. In the aerosol particle formation, organosilicon compound was incorporated into the aerosol particles as polymerized species, and then laser light induced the cleavage of some chemical bonds of polymerized organosilicon compound. More abundance of elemental silicon in TMPSi/AC than in VTMSi/AC under irradiation with N₂ laser light can be explained by the fact that cleavage of Si-C bond is easier than that of Si-O bond, and formation process of elemental silicon in TMPSi/AC is not suppressed effectively by the interaction with AC molecules. These conclusions are consistent with the results observed in the present study under irradiation with electron beam, suggesting that the chemical reactivity of some organosilicon compounds against electron beam is well correlated with the reactivity against UV laser light.

References

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