Chapter 6

PHOTOCHEMICAL SYNTHESIS AND MAGNETIC FIELD EFFECT ON ULTRAFINE PARTICLES INVOLVING ORGANOSILICON AND ORGANOMETAL COMPOUNDS

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ABSTRACT

From gaseous mixtures involving organosilicon and organometal compounds, ultrafine and fine particles were synthesized in the gas phase using photochemical reactions of gaseous molecules.

Under UV light irradiation at 313 nm with a medium pressure mercury lamp, a gaseous mixture of trimethyl(2-propynyloxy)silane (TMPSi) and carbon disulfide (CS₂) produced sedimentary spherical aerosol particles involving organosilicon compound under a magnetic field of up to 5 T. From measurement of monitor (He-Ne laser) light intensity scattered by aerosol particles as formed under UV light irradiation, it was shown that the nucleation process during aerosol particle formation was accelerated with increasing partial pressure of TMPSi and by application of a magnetic field. Analysis of FT-IR and X-ray photoelectron spectra (XPS) of the sedimentary particles revealed that excited CS₂ molecules reacted with TMPSi at C≡C bond to initiate the nucleation reaction, and that under a magnetic field, incorporation of TMPSi molecules into the aerosol particles decreased, resulting in a greater abundance of sulfur atoms in C-S bonding than in >C=S bonding. Chemical reactions between TMPSi and CS₂ that were responsive to the magnetic field were discussed briefly.

From a gaseous mixture of iron pentacarbonyl (Fe(CO)₅) and cobalt tricarbonyl nitrosyl (Co(CO)₃NO), both the crystalline deposits and the spherical particles were produced. By decreasing a partial pressure of Fe(CO)₅ to 0.5 Torr, only the spherical aerosol particles were produced. Chemical composition of the particles was rich in Co species, and under a magnetic field, atomic ratio of Fe to Co atom increased with increasing magnetic field of up to 5 T. Magnetic field effect on the chemical composition of the particles was entirely different from that of the crystalline deposits. This was discussed based on chemical reactions between Fe(CO)₅ and Co(CO)₃NO.
By controlling the convectional flow of a ternary gaseous mixture of Fe(CO)$_5$, allyltrimethylsilane (ATMeSi), and CS$_2$ during UV light irradiation at 313 nm, linearly aggregated particles (i.e., particle wires) were formed efficiently at the vicinity of the front edge of a substrate placed at the bottom of an irradiation cell. When the partial pressure of CS$_2$ was increased to 5 times higher than that of Fe(CO)$_5$, particle wires as long as 500 $\mu$m with a mean diameter of 0.4 $\mu$m were formed efficiently. The formation of particle wires is characteristic of the sedimentary particles produced by the photochemical method in the gas phase. Experimental details to form long particle wires were discussed briefly.

**INTRODUCTION**

Nanostructured materials provide the critical building blocks for nanotechnology and biotechnology. Ultrafine particles and nanoparticles can be used as building blocks of nanowire and nano-devices in addition to digital dots in high density recording materials. Synthesis, surface chemical modification, and assembly of nanoparticles, and fabrication of nanostructures have been studied extensively [1-3]. Monodispersed semiconductor and metal nanocrystals were produced via chemical precipitation of supersaturated species in solution and micelles. In the gas phase, vaporization and ablation of solid materials using resistive heating, electron beam, laser light, and microwave were frequently used to produce fine particles from solid materials.

From gaseous mixtures, spherical fine and ultrafine particles were synthesized using photochemical reactions of reactive molecules such as carbon disulfide (CS$_2$) [4-8] and 2-propenal (acrolein) (AC) [9, 10]. This photochemical method has been applied to gaseous mixtures involving organosilicon and organometal compounds [11-15], and some characteristics of the particles have been elucidated [16, 17].

The photochemical method to produce spherical aerosol particles in the gas phase has some technical advantages as follows.

1) Chemical structure of the particles can be controlled by choosing the wavelength and intensity of the exciting light. In cases where two-photon excitation of gaseous molecules is required to initiate the nucleation reaction (such as of AC), photochemical sensitization is effective to increase the product yield of the particles. Some organometal compounds produce magnetic particles via multiphoton process.

2) The particle size can be controlled by regulating the photochemical reaction rate and the reaction time. As a typical example, particles deposited from a gaseous mixture of Fe(CO)$_5$ and CS$_2$ reduced their mean diameter to 58 nm from 220 nm by shortening the irradiation time of UV light from 120 s to 1 s [14].

3) Magnetic field influences the chemical reactions during aerosol particle formation, resulting in a change of chemical compositions of the spherical particles. Magnetic field accelerates or decelerates the chemical reaction rate, resulting in a change of the particle size.

4) The particles can be connected in each other by a chemical bond, leading to the formation of linearly aggregated particles. This technique can be developed to produce particle-wires applicable to build a nano-device.
In this chapter, the study on the synthesis of aerosol particles involving some organosilicon and organometal compounds was reviewed. In the first section, aerosol particle formation process from a gaseous mixture of trimethyl(2-propynyloxy)silane (TMPSi) and CS$_2$ was studied. From chemical analysis of the particles produced under a magnetic field, it was elucidated how the magnetic field affected the chemical reactions during the nucleation and propagation processes of particle formation [18, 19].

In the second section, spherical particles were produced from iron pentacarbonyl (Fe(CO)$_5$) / cobalt tricarbonyl nitrosyl (Co(CO)$_3$NO) gaseous mixture [20]. The chemical characteristics of both the crystalline deposits and the spherical particles were elucidated, and experimental conditions to produce only spherical particles were studied. The magnetic field effects on the chemical compositions of both the crystalline deposits and the particles were studied in detail.

In the last section, a ternary gaseous mixture of Fe(CO)$_5$, allyltrimethylsilane (2-propenyltrimethylsilane) (ATMeSi), and CS$_2$ was irradiated with UV light [21, 22]. Morphology and chemical compositions of the deposits were compared to those produced from a binary gaseous mixture of Fe(CO)$_5$/ATMeSi and Fe(CO)$_5$/CS$_2$. From the ternary gaseous mixture, particle wires were efficiently produced. The advantages of producing particle wires were discussed briefly.

**EXPERIMENTAL**

1. **Materials and Preparation of Gaseous Mixtures**

TMPSi was prepared by refluxing a mixture of 1,1,1,3,3,3-hexamethyldisilazane (Tokyo Kasei, GR grade, 96%) and 2-propyn-1-ol (Wako, EP grade, 98%) for 12 h under nitrogen atmosphere followed by fractional distillation. 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. ATMeSi (Tokyo Kasei, G. R. grade), Fe(CO)$_5$ (Kanto, 95%), Co(CO)$_3$NO (Gelest, 95%), and CS$_2$ (Kanto, >99%, G. R. grade) were degassed by freeze-pump-thaw cycles in the dark and purified by vacuum distillation immediately before use.

To prepare a gaseous mixture, each vapor was introduced successively into a cylindrical or cross-shaped Pyrex cell (inner diameter 35 or 20 mm) equipped with a couple of quartz windows through a vacuum line equipped with a capacitance manometer (Edwards Barocel Type 600).

The background pressure of the irradiation cell was less than $1 \times 10^{-4}$ Torr (1 Torr = 133.3 Pa), and the leakage into the evacuated cell from the atmosphere was carefully controlled to be less than 1 Torr in a day. The partial pressures of Fe(CO)$_5$, Co(CO)$_3$NO, ATMeSi, and CS$_2$ in the irradiation cell were determined from the diagnostic band intensities of FT-IR spectra at 645 cm$^{-1}$ for Fe(CO)$_5$, 2108 cm$^{-1}$ for Co(CO)$_3$NO, 1259 cm$^{-1}$ for ATMeSi, and 1531 cm$^{-1}$ for CS$_2$.

The partial pressure of CS$_2$ was also determined from its UV absorption intensity in the 280 - 350 nm region.
2. Light Irradiation on Gaseous Mixtures

To initiate nucleation reactions during aerosol particle formation, gaseous samples prepared from TMPSi and CS₂ were irradiated with a medium pressure mercury lamp (Ushio UM-452, 450W) through UV31 and UVD33S filters (energy, 3.5 mJ/s·cm²) to excite only CS₂ molecules at 313 nm or with nitrogen gas laser light (Lumonics HE-440, 337.1 nm, pulse width 10 ns) at an energy of 1.8 mJ/pulse effective on the area of 3 cm² at a repetition rate of 12 Hz. For the Fe(CO)₅/Co(CO)₃NO gaseous mixtures, UV29 and UV-D33S filters were used to excite both Fe(CO)₅ and Co(CO)₃NO molecules at 313 nm and 365 nm (energy, 5.4 mJ/s·cm²). Light intensity at 365 nm was 1.6 times stronger than the one at 313 nm. Absorbance of 1 Torr of Fe(CO)₅ and of Co(CO)₃NO is 0.28 and 0.06, respectively, at 313 nm, and 0.06 and 0.23, respectively, at 365 nm in 10 cm light path length. For the ternary Fe(CO)₅/ATMeSi/CS₂ gaseous mixtures, UV29 and UV-D33S filters were also used to excite both Fe(CO)₅ and CS₂ molecules at 313 nm (energy, 8.8 mJ/s·cm²). Absorbance of 1 Torr of CS₂ is 0.07 at 313 nm in 10 cm light path length. In some cases, aerosol particles were produced in a helium-free superconducting magnet (Toshiba TM-5SP) or in an electromagnet (Tokin SEE-10D) under light irradiation.

3. Measurements

The nucleation process during aerosol particle formation was investigated by measuring monitor (He-Ne laser) light intensity scattered by aerosol particles formed under UV light irradiation. Light intensity scattered perpendicularly to the incident direction of the monitor light was measured with a combination of a photomultiplier tube (Hamamatsu R212 or 1P28, or EMI 6256S) and a lock-in amplifier (SRS SR-530) through a Y-52 (or R-62) filter as shown in Figure 1.

Figure 1. Experimental setup for measuring monitor (He-Ne laser) light intensity scattered by aerosol particles as formed under UV light irradiation. a: exciting light source (Hg lamp, N₂ gas laser, or Nd:YAG laser), b: electromagnet (or helium-free superconducting magnet), c: Pyrex cell, d: He-Ne laser, e: lens, f: glass filter (Y-52), g: sector, h: photo-interrupter, i: high-voltage power supply, j: photomultiplier tube, k: lock-in amplifier, l: personal computer.
The aerosol particles were deposited on a glass plate and/or Cu substrate at the bottom of the irradiation cell. To investigate a morphological change of the deposits, scanning electron microscope (SEM) images were recorded with a JEOL JSM 6060 or Topcon ABT-32 scanning electron microscope. Chemical compositions of the deposits were analyzed by scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS) using a Philips XL30 CP/EDAX scanning electron microscope. X-ray photoelectron spectra (XPS) were measured with a Gammadata Scienta ESCA 310 electron spectrometer using monochromatized Al Kα or Mg Kα radiation for electron excitation. To investigate chemical structures of the particles, FT-IR spectra of sedimentary aerosol particles embedded in KBr pellets were measured with a Nicolet NEXUS 470 or 670 FT-IR spectrometer. Raman spectra of the sedimentary particles were measured with a Bio Tools chiral Raman RL-1 spectrometer.

**RESULTS AND DISCUSSION**

1. Fine Particles Involving Organosilicon Compounds

1.1. Aerosol Particle Formation from a Gaseous TMPSi/AC Mixture

Trimethyl(2-propynyloxy)silane (TMPSi) which has a C≡C bond has the longest wavelength absorption peak at a wavelength shorter than 200 nm. ArF laser photolysis (at 193 nm) of gaseous TMPSi was dominated by polymerization at the triple bond and resulted in the chemical vapor deposition of polytrimethylsiloxy-substituted polyhydrocarbon [23], whereas IR laser-photosensitized (SF6) decomposition (at 10.6 μm) of TMPSi vapor produced transient (CH3)2SiO species which subsequently polymerized into solid polydimethylsiloxane films [24].

On the other hand, N2 laser light irradiation (at 337.1 nm) on a gaseous TMPSi and AC mixture resulted in the production of spherical aerosol particles with a mean diameter of ~0.5 μm [11] (Figure 2(a)). XPS analysis of the sedimentary particles showed that two Si 2p bands assignable to elemental silicon and silicon bonded in an organosilicon polymer were detected at 99.3 and 101.7 eV in a relative abundance of 0.45 and 0.55, respectively (Figure 2(b)). The existence of considerable amount of elemental silicon suggested that during the parent aerosol particle formation of polyacrolein by a two-photon process [10], TMPSi molecules were incorporated into the aerosol particle formation process and under irradiation with N2 laser light, cleavage of Si-C bonds of TMPSi molecule took place to form Si-Si bond between neighboring TMPSi molecules, followed by cleavage of some Si-O bonds adjacent to Si-Si bonds eventually to produce elemental silicon in the aerosol particles.

The elemental silicon may be widely distributed in the polyacrolein matrix of the aerosol particles with amorphous structure. The production of elemental silicon reflected the highly reactive characters of two-photon excited AC and TMPSi molecules during the aerosol particle formation.
1.2. Aerosol Particle Formation from a Gaseous TMPSi/CS₂ Mixture

A gaseous TMPSi/CS₂ mixture could produce aerosol particles via one-photon process of CS₂ molecules. It is well recognized that CS₂ is polymerized under UV light irradiation to produce a thin film and/or aerosol particles. Chemical structure of the aerosol particles produced from pure CS₂ vapor was described as (CS₂)ₙ polymer [25, 26], a blend of C
polymer and S polymer [27], (CS)_k polymer [4, 5, 28, 29], or a mixture of (CS2)_k and (C3S2)_k [30]. These different views were based on IR spectral analysis and theoretical calculation on the structure. In this section, chemical structure of the CS2 particles was determined to be (-C-S-)n from XPS analysis. Based on chemical structure analyzed from FT-IR and XPS spectra, particle formation process from a gaseous mixture of TMPSi and CS2 was studied extensively.

1.2.1. Aerosol Particle Formation from Pure CS2 Vapor

CS2 molecule has absorption bands in the 270 - 350 nm region [31]. Lower excited states come from the electron configuration (\(\pi_g\))^3(\(\pi_u\)). The molecular geometry is linear (of D\(_{\infty h}\) symmetry) in the ground state, and is bent (of C\(_{2v}\) symmetry) in lower excited states [32]. The \(^1\Lambda_u\) and \(^3\Lambda_u\) states in the linear molecule split into the \(^1\Lambda_2\) and \(^1\Lambda_2\) states, and the \(^3\Lambda_2\) and \(^3\Lambda_2\) states, respectively, by the Renner-Teller interaction. The longest wavelength absorption (called Kleman’s R system) corresponds to the transition to the B\(_2\) spin component of the \(^3\Lambda_2\) state [33,34]. The transition to the \(^1\Lambda_2\) state is observed as strong bands (V system) in the 290-330 nm region, whereas the transition to the \(^1\Lambda_2\) state is electronically forbidden: only the hot bands are observed in the 334-350 nm region (T system) [32]. N\(_2\) laser light (337.1 nm) can excite CS\(_2\) to the \(v'_2 = 3\) and 5 levels of the \(^1\Lambda_2\) state from the \(v''_2 = 1\) and 2 levels, respectively [32].

Under irradiation with N\(_2\) laser light (at an energy of 1.8 mJ/pulse for 3 h), aerosol particles of reddish-brown color were produced from pure CS2 vapor (50 Torr) [35]. FT-IR spectrum of the deposited aerosol particles was similar to that of the (CS2)_k polymer deposited from gaseous CS2 under light irradiation at 313 nm [26]. The XPS analysis was performed on the sedimentary aerosol particles deposited on a Cu sheet [35]. The XPS spectrum of S 2p photoelectrons had three S 2p\(_{3/2}\) bands at the binding energy of 162.0, 163.7, and 167.9 eV, assigned to sulfur in \(>\text{C}=\text{S}\) or Cu-S bonding, sulfur in (-C-S-)n bonding (and partly in elemental sulfur), and sulfur in sulfidic and/or S-O- moiety, respectively. The population of sulfur in each band was 22, 72, and 6 %, respectively. The particles contained sulfur atoms in a (-C-S-)n bonding (and partly in elemental sulfur) as a major contribution (72%) [36-38]. In the C 1s spectrum of the aerosol particles, carbon belonging to the (-C-S-)n bonding was detected at 285.5 eV. The atomic ratio of S to C atom pertinent to the C-S bonding was evaluated using the experimentally determined stoichiometry of atoms to be 0.72:0.81 for the particles. The value which was very close to unity clearly supported that the major chemical species of polymeric particles was (-C-S-)n polymer as suggested previously [28]. The chemical structure of the sedimentary aerosol particles produced from CS2 was strongly suggested to be highly crosslinked (-C-S-)n polymer.

1.2.2. Aerosol Particle Formation Process of Gaseous TMPSi/CS2 Mixture

Under UV light irradiation at 313 nm with a medium pressure mercury lamp for 4 h, a gaseous mixture of TMPSi (10 Torr) and CS2 (50 Torr) initiated the nucleation reaction via photo-excited CS2 molecules, and produced sedimentary aerosol particles of yellowish brown color with a mean diameter of 0.61 \(\mu\)m (Figure 3) and with a product yield of \(~0.2\) mg (~0.3%) [18]. Under the same experimental conditions, pure CS2 (50 Torr) produced sedimentary aerosol particles of reddish brown color with a mean diameter of 0.60 \(\mu\)m and
with a product yield of ~0.1 mg (~0.2%). A slight change in color of the sedimentary particles and the increase of the product yield deposited from the gaseous mixture strongly suggested that TMPSi which did not absorb light was incorporated into the nucleation and propagation reactions during aerosol particle formation. In order to study the nucleation and propagation processes, the monitor (He-Ne laser) light intensity scattered by aerosol particles which were formed under UV light irradiation was measured [18]. The results are shown in Figure 4.

Figure 3. (a) SEM image of sedimentary particles deposited from a gaseous mixture of TMPSi (10 Torr) and CS$_2$ (50 Torr) under light irradiation at 313 nm, and (b) particle size distribution therefrom. Original magnification of SEM, 5500×.

With increasing partial pressure of TMPSi from 0 to 15 Torr at a fixed partial pressure of CS$_2$ (50 Torr), the scattered light intensity increased and fluctuation of the scattered light intensity with an interval of ~10 min was more pronounced. Fluctuations of the scattered light intensity with long and short periods were frequently observed in the nucleation processes involving CS$_2$ molecules [4-6]. The fluctuation of long period (~10 min) is due to the convection of entire gaseous sample and the fluctuation of short period (~ 2 min) is believed to be due to the temporal and local pressure change of reactant gaseous molecules caused by the formation and sedimentation of the aerosol particles. Scattered light intensity depends on both the particle size and the number of particles.

In cases where the particle size distribution is not dependent on irradiation time of exciting light as in the present experimental conditions, scattered light intensity after reaching its initial maximum value is proportional to the total number of aerosol particles with various particle sizes. In Figure 4, with increasing partial pressure of TMPSi, the induction period to detect scattered light became shorter (from 200 s to 100 s, and further to 75 s, and to 60 s at 0, 5, 10, and 15 Torr of TMPSi, respectively).

During the induction period, nuclei of particles grow to a detectable size. Hence, the induction period is a measure of relative rate of nucleation and propagation reactions. Shortening of the induction period and the stronger intensity of scattered light with increasing partial pressure of TMPSi clearly showed that in addition to CS$_2$ molecules, TMPSi molecules contributed to the nucleation and propagation processes during aerosol particle formation.
Figure 4. He-Ne laser light intensity scattered by aerosol particles produced from gaseous mixtures of TMPSi and CS$_2$ (50 Torr) under light irradiation with a medium pressure mercury lamp at 313 nm. Respective partial pressures of TMPSi were: (a) 0, (b) 5, (c) 10, and (d) 15 Torr.

Chemical processes in the gaseous phase were investigated by measuring FT-IR spectra of a gaseous mixture of TMPSi (5 Torr) and CS$_2$ (10 Torr) [18]. Upon UV light exposure, the $\nu$(C=S) band intensity (absorbance, $A$) at 1521 cm$^{-1}$ of CS$_2$ decreased. The ratio of $A$ to the initial absorbance before light irradiation, $A_0$, was evaluated in pure CS$_2$ and in the gaseous mixture.

The value, (-ln $A/A_0$) was plotted against cumulative irradiation time (Figure 5), and the depletion rate of CS$_2$ (assuming the pseudo first order decay) was determined to be $2.1 \times 10^{-4}$ s$^{-1}$ in the gaseous mixture and $9.7 \times 10^{-6}$ s$^{-1}$ for pure CS$_2$ vapor. The depletion of CS$_2$ was accelerated by $\approx 20$ times due to the presence of TMPSi. For a gaseous mixture of TMPSi (10 Torr) and CS$_2$ (50 Torr), the depletion of TMPSi bands (3324, 2968, and 1260 cm$^{-1}$ bands) was also measured. In a typical experiment under UV light irradiation for 4 h, TMPSi and CS$_2$ respectively depleted by $\approx 6\%$ (0.6 Torr) and $\approx 1.2\%$ (0.6 Torr), i.e., almost equal amount in each other.
Chemical compositions of the sedimentary particles were analyzed from FT-IR and XPS spectra. The XPS analysis was performed on the sedimentary particles deposited from a gaseous mixture of TMPSi (10 Torr) and CS₂ (50 Torr) [18]. The stoichiometry of atoms was \( \text{Si}_{1.0} \text{ C}_{8.2} \text{ O}_{3.4} \text{ Si}_{0.57} \) (Cu_{1.8}). The Cu signal was from the uncovered substrate, and analysis of the signal indicated that some fraction of the O and also of the C signals could originate from oxidation of the substrate and surface contamination with hydrocarbons present prior to particle deposition. Stoichiometry of atoms clearly showed that Si atoms, hence chemical species originating from TMPSi molecule were involved efficiently in the sedimentary particles with molar ratio of 1:1 to those from CS₂ molecule, in agreement with the result obtained from the depletion of the gaseous molecules. Si 2p spectrum showed a major band at 101.6 eV, which was assigned to silicon atoms in trimethylsilyl group bonded to oxygen atom. The S 2p spectrum is shown in Figure 6(a).

Considering the splitting due to spin-orbit coupling of the S 2p band, the spectrum was resolved into four bands. The results are summarized in Table 1, together with the results for C 1s spectrum. The particles contained sulfur atoms in a C-S bonding (and partly in elemental sulfur) as a major (~35 %) contribution. About 46 % of sulfur was assigned to sulfur in >C=S or Cu-S bonding [36-38].
In the C 1s spectrum of the sedimentary aerosol particles, carbon belonging to the C-S bonding was detected at 285.5 eV. The binding energies (284.5 and 287.7 eV) of components of the C 1s spectrum were compatible with carbon contained in C-C and C-H bonds (major components) and C-O and C=O bonds (minor components). The atomic ratio of S to C atom pertinent to the C-S bonding was evaluated to be ~1:3. For the particles deposited from pure CS$_2$, the value was very close to unity [35]. This implied that contribution from carbon contained in -CH$_2$-CH$_2$- and -CH$_2$-CH=CH-CH$_2$- bonds was significant to the band at 285.5 eV.

As revealed by XPS analysis, the particles deposited from the gaseous mixture of TMPSi and CS$_2$ contain sulfur atoms in >C=S bonding as well as in C-S bonding. The sedimentary particles deposited from pure CS$_2$ contain sulfur atoms predominantly (~72 %) in C-S bonding [35].
Table 1. XPS characterization of aerosol particles produced from a gaseous mixture of TMPSi (10 Torr) and CS₂ (50 Torr) under a magnetic field of 0 and 3T

<table>
<thead>
<tr>
<th>Magnetic field</th>
<th>0 T</th>
<th>3 T</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line designation</td>
<td>Binding energy/eV</td>
<td>Population</td>
<td>Binding energy/eV</td>
</tr>
<tr>
<td>S 2p₃/₂</td>
<td>162.0</td>
<td>0.46</td>
<td>162.0</td>
</tr>
<tr>
<td></td>
<td>163.6</td>
<td>0.35</td>
<td>163.5</td>
</tr>
<tr>
<td></td>
<td>165.2</td>
<td>0.13</td>
<td>165.3</td>
</tr>
<tr>
<td></td>
<td>168.1</td>
<td>0.06</td>
<td>168.1</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.5</td>
<td>5.53</td>
<td>284.5</td>
</tr>
<tr>
<td></td>
<td>285.5</td>
<td>0.91</td>
<td>285.5</td>
</tr>
<tr>
<td></td>
<td>286.4</td>
<td>0.49</td>
<td>286.4</td>
</tr>
<tr>
<td></td>
<td>287.7</td>
<td>0.74</td>
<td>287.7</td>
</tr>
<tr>
<td></td>
<td>288.2</td>
<td>0.53</td>
<td>288.3</td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.6</td>
<td>0.57</td>
<td>101.3</td>
</tr>
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<td></td>
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<td>102.6</td>
</tr>
</tbody>
</table>

Formation of >C=O bonding is clearly due to the interaction of CS₂ with TMPSi molecule. Under UV light irradiation at 313 nm, excited CS₂ molecules react with both CS₂ [4-6, 25-30, 39] and TMPSi molecules in the ground electronic state.

\[
CS₂ + hν \rightarrow CS₂^* 
\]

\[
CS₂^* + CS₂ \rightarrow (CS₂)_2^* \rightarrow (CS)₂ (or 2CS) + S₂
\]

\[
CS₂^* + TMPSi \rightarrow (CS₂·TMPSi)
\]

\[
\text{R: -CH₂-O-Si(CH₃)₃}
\]

\[
\text{H} \text{C} \equiv \text{C-} \text{S-S} \text{R} + \text{CS₂} \rightarrow \text{H} \text{C} \equiv \text{C-S-S-R} \text{R} \quad \text{or} \quad \text{H} \text{C} \equiv \text{C-S-S-R} \text{R}
\]

\[
\text{H} \text{C} \equiv \text{C-S-S} \text{R} + (\text{CS₂}) \rightarrow \text{H} \text{C} \equiv \text{C-S-S-R} \text{R} \quad \text{or} \quad \text{H} \text{C} \equiv \text{C-S-S-R} \text{R}
\]

\[
\text{H} \text{C} \equiv \text{C-S-S} \text{R} + n \text{TMPSi} + n \text{CS₂} \rightarrow \text{H} \text{C} \equiv \text{C-S-S-R} \text{R} 
\]

Considering the acceleration of nucleation reaction with increasing partial pressure of TMPSi, reaction (3) is more efficient than reaction (2) in the gaseous mixture. Transient species, (CS₂·TMPSi), can react with CS₂, (CS₂)₂, and TMPSi (reactions (4) - (6)) to initiate polymerization reactions. These reactions may compete with each other to produce complex
chemical structures of the aerosol particles. Thus, the C-S and C=S structures are involved in
the sedimentary aerosol particles, and TMPSi molecules can accelerate the nucleation
reaction during aerosol particle formation through polymerization reaction at the C≡C triple
bond, resulting in the formation of ultrafine particles which are rich in organosilicon
compounds.

1.3. Magnetic Field Effect on Aerosol Particles Produced from a Gaseous
TMPSi/CS₂ Mixture

Magnetic field affected the chemical reactions during aerosol particle formation, resulting
in a change in the reaction rate, particle size, chemical compositions of the particles, and
thermal convection of entire gaseous mixture.

1.3.1. Magnetic Field Effect on Particle Formation Process

Under UV light irradiation at 313 nm with a medium pressure mercury lamp, a gaseous
mixture of TMPSi (10 Torr) and CS₂ (50 Torr) produced sedimentary aerosol particles under
a magnetic field of up to 5 T without any morphological change [19]. Magnetic field effects
on the nucleation process during aerosol particle formation were studied by measuring the
He-Ne laser light intensity scattered by the aerosol particles, as formed in an electromagnet;
the results for a gaseous mixture of TMPSi (5 Torr) and CS₂ (50 Torr) are shown in Figure 7.
By application of a magnetic field of 0, 0.27 and 0.51 T, the induction period to detect
scattered light became shorter from 60 s to 40 s, and further to 30 s, indicating that the
magnetic field accelerated the nucleation reaction between TMPSi and CS₂. Under UV light
irradiation at 313 nm, pure CS₂ vapor also produced sedimentary aerosol particles under a
magnetic field. In contrast to the results of the gaseous mixture in Figure 7, the induction
period to detect scattered light was almost constant, regardless of magnetic field strength [19].
The above two results strongly suggested that a magnetic field influenced the nucleation
reactions only between TMPSi and CS₂ molecules but not between CS₂ molecules
themselves.

Magnetic field accelerated the nucleation and propagation reactions of the gaseous
mixture as discussed above. To investigate the effect on the particle size, sedimentary aerosol
particles were produced in a superconducting magnet using a small cylindrical cell with inner
diameter of 20 mm [19]. With decreasing diameter of the irradiation cell (from 35 mm to 20
mm), particles became smaller and the mean diameter of the sedimentary particles reduced to
0.33 μm from 0.61 μm. This is due to the fact that aerosol particles generated under UV light
irradiation travel along the cylindrical cell wall due to convection of the entire gaseous
sample. Throughout the entire travel period, aerosol particles continue to grow and finally
collide with the substrate accommodated at the bottom of the irradiation cell within one cycle
of the convection. In a cylindrical cell with a smaller diameter, the convection period is
shorter resulting in a shorter propagation time, and hence smaller particle size. The mean
diameter of sedimentary particles produced under a magnetic field of 1, 3, and 5 T was 0.36,
0.39, and 0.41 μm, respectively. The mean diameter increased with increasing magnetic field,
this being consistent with the fact that the chemical reaction between TMPSi and CS₂ was
accelerated by application of a magnetic field.
1.3.2. Magnetic Field Effect on Thermal Convection of Gaseous Mixture

During the measurement of the scattered light intensity, it was found that the convection of aerosol particles formed from the gaseous mixture was influenced considerably by application of a magnetic field.

As a method for monitoring any changes in convection, the sedimentation patterns of the aerosol particles after 4 h light irradiation in an electromagnet were observed. The results for a gaseous mixture of TMPSi (10 Torr) and CS$_2$ (50 Torr) are shown in Figure 8, compared to the result for pure CS$_2$ vapor (50 Torr).
Figure 8. Sedimentation pattern of aerosol particles deposited from a gaseous mixture of TMPSi (10 Torr) and CS$_2$ (50 Torr) over 4h light irradiation at 313 nm by application of a magnetic field of (a) 0, (b) 0.27 and (c) 0.51 T, and (d) deposited from pure CS$_2$ vapor (50 Torr) by application of a magnetic field of 0.51 T.

The sedimentation pattern from the gaseous mixture, which was directly along the incident light path (being perpendicular to the magnetic field), was distorted and curved to the right (when viewed from the top of the irradiation cell) with increasing magnetic field. When the direction of the applied magnetic field was reversed, the distortion of the sedimentation pattern was the same, i.e., the pattern curved to the right. In contrast to this result, the sedimentation pattern from pure CS$_2$ vapor was not distorted by application of a magnetic field of 0.51 T, maintaining a straight sedimentation pattern as observed without a magnetic field. The distortion of the sedimentation pattern is well explained based on thermal convection, because the magnetic field accelerated the reaction rate of particle formation from the gaseous mixture accompanying a larger heat release, which eventually caused more pronounced thermal convection of the gaseous mixture. A non-uniform temperature distribution in space between two magnetic poles of the electromagnet enhanced the distortion of thermal convection. The distortion from the straight and uniform sedimentation pattern due to the application of a magnetic field was previously observed with gaseous mixtures of glyoxal and acrolein [40] and glyoxal and CS$_2$ [41].

1.3.3. Magnetic Field Effect on Chemical Compositions of Particles

Sedimentary particles were produced from a gaseous mixture of TMPSi (10 Torr) and CS$_2$ (50 Torr) in a superconducting magnet, and chemical structures of the particles were analyzed from FT-IR and XPS spectra [19]. FT-IR spectra of the sedimentary particles produced under a magnetic field of up to 5 T are shown in Figure 9. Compared to the v(C=S) band intensity at 1066 cm$^{-1}$, strong bands characteristic of trimethylsilyl group (such as the δ(SiCH$_3$) band at 1252 cm$^{-1}$, the ρ(SiCH$_3$) band at 845 and 865 cm$^{-1}$, and the v(Si-O) band at 1100 cm$^{-1}$) decreased their intensities with increasing magnetic field.
Figure 9. FT-IR spectra of sedimentary particles deposited from a gaseous mixture of TMPSi (10 Torr) and CS₂ (50 Torr) under light irradiation at 313 nm for 4h by application of a magnetic field of (a) 0, (b) 1, (c) 3 and (d) 5 T.

Furthermore, with the application of a magnetic field of 5 T, the $\nu$ (C=S) band intensity at 1066 cm$^{-1}$ decreased, whereas the $\nu$ (C-S) band intensity at 818 cm$^{-1}$ increased. These results indicated that incorporation of TMPSi molecules was suppressed, and the chemical structure of C=S bonding was influenced by the magnetic field.

XPS analysis was performed on sedimentary particles produced under a magnetic field of 3 T. The stoichiometry of atoms was S$_{1.0}$ C$_{5.7}$ O$_{2.0}$ Si$_{0.18}$ (Cu$_{0.7}$). Compared to the values without a magnetic field, S$_{1.0}$ C$_{8.2}$ O$_{3.4}$ Si$_{0.57}$ (Cu$_{1.8}$), Si atoms, hence, chemical species originating from TMPSi molecules, were less involved when a magnetic field of 3 T was applied.

The XPS spectrum of S 2p photoelectrons is shown in Figure 6(b), and the results are summarized in Table 1. Compared to the results in the absence of a magnetic field, sulfur assigned to sulfur in -C-S- bonding increased to 50 % (from 35 %), and sulfur assigned to sulfur in >C=S or Cu-S bonding decreased to 26% (from 46 %). These results were consistent with FT-IR spectral change shown in Figure 9 where the $\nu$(C=S) band intensity decreased, whereas the $\nu$(C-S) band intensity increased by application of a magnetic field of 5 T.
1.3.4. Magnetic Field Effect on Nucleation Reactions

The nucleation and propagation processes were described using reactions (1) – (6) as discussed in section 1.2. Following these chemical pathways, magnetic field effects discussed above were interpreted as follows.

1) Acceleration of the nucleation reaction by a magnetic field indicated that reaction (3) was accelerated by application of a magnetic field. As was evidenced from the result on pure CS$_2$ vapor, reaction (2) was not responsive to a magnetic field.

2) Without a magnetic field, contribution of TMPSi and CS$_2$ molecules to the sedimentary particles was 1: (1~2) in molar ratio. This result strongly suggested that reaction (6) followed reaction (3) effectively. However, when a magnetic field was applied, incorporation of TMPSi molecules decreased. This was attributed to a change in chemical reactivity of the transient chemical species, (CS$_2$· TMPSi), i.e., the transient species favored reactions (4) and (5) than reaction (6) under a magnetic field.

3) XPS and FT-IR analyses showed that chemical structures pertinent to C-S bonding were more abundant than those involving C=S bonds under a magnetic field. This strongly suggested that reaction (4) was more accelerated than reaction (5), resulting in a greater production of C-S chemical bonds, because reaction (4) added only one C=S chemical bond, in contrast to reaction (5), which added two C=S bonds. Between the two chemical structures in reaction (4), a polymerization reaction through chemical species (4b) was favored under the magnetic field, because polymerization reaction through chemical species (4a) resembled to the polymerization reaction of pure CS$_2$ vapor, which was not accelerated by application of a magnetic field.

At later stages in particle growth, two C=S bonds (coming closer to each other) can form a C-S····S-C structure, as was suggested in the nucleation reaction of pure CS$_2$ vapor [26].

The formation of a network structure through C-S····S-C chemical bonding is thought to be much less in aerosol particles produced from the gaseous mixture of TMPSi and CS$_2$ (where incorporated TMPSi molecules break the successive bond formation between CS$_2$ molecules) than in particles produced from pure CS$_2$ vapor. This is partly responsible for the fact that many C=S bonds are detected in sedimentary particles produced from the gaseous mixture.

The radical pair mechanism responsible for the magnetic field effect frequently observed for chemical reactions in solutions and micelles [42-45] could not be applied for the nucleation reaction during aerosol particle formation. Also, the magnetic field effect on intramolecular relaxation of the excited state of gaseous CS$_2$ molecule [46-49] could not explain the present experimental results.

The present observation of the magnetic field effect strongly suggested that somehow a new mechanism took place either on collisional intermediate species in the gas phase or on chemical species at gas-solid interface on a small surface area of nanometer size.
2. Fine Particles Involving Organometal Compounds

2.1. Aerosol Particle Formation from a Gaseous Fe(CO)₅/Co(CO)₃NO Mixture

In this section, aerosol particles involving Fe and Co species were synthesized from a gaseous mixture of Fe(CO)₅ and Co(CO)₃NO by using the photochemical method. Morphology of crystalline deposits was changed into spherical particles by controlling the partial pressure of Fe(CO)₅, and magnetic field effect on chemical compositions of the products was investigated by measuring SEM-EDS and XPS.

2.1.1. Chemical Composition and Formation Process of Crystalline Deposits

Under UV light irradiation with a medium pressure mercury lamp at 313 and 365 nm for 30 min, a gaseous mixture of Fe(CO)₅ (2.3 Torr) and Co(CO)₃NO (1.7 Torr) produced crystalline deposits with sizes of 13~25 μm (mean size 18 μm) and of ~5 μm in addition to a small amount of spherical sedimentary particles with a mean diameter of 0.42 μm as shown in Figure 10 [20]. Morphological change of the crystalline deposits was studied by changing UV light irradiation time. During light irradiation for 2 min, only sedimentary particles with a mean diameter of 0.26 μm were detected. The sedimentary particles had a tendency to coagulate in each other. After light irradiation for 5 min, crystalline deposits with a size of 5-10 μm were observed in addition to spherical particles with a mean diameter of 0.27 μm. During prolonged light irradiation up to for 30 min, crystalline deposits with sizes of ~18 μm were formed in addition to crystalline deposits of ~5 μm in size and sedimentary particles. It is clear that crystalline deposits grow up separately from spherical particles under prolonged light irradiation.

The morphology of the deposits was compared to the one of deposits produced from pure Fe(CO)₅ and Co(CO)₃NO vapors (Figure 11). Fe(CO)₅ vapor (1.0 Torr) produced two kinds of morphologically different deposits, i.e., hexagonal rod with a mean size of 2.8 × 2.4 μm and crystalline particles with a mean size of 0.46 μm [13], composed of Fe₂(CO)₉ and Fe₃(CO)₁₂, respectively [50, 51]. Co(CO)₃NO vapor at a pressure of 2 Torr produced coagulated sedimentary particles with a mean diameter of 82 nm [20]. From the morphological similarity, the crystalline deposits produced from the gaseous Fe(CO)₅/Co(CO)₃NO mixture may originate mainly from Fe(CO)₅.

From SEM-EDS analysis, incorporation of Co(CO)₃NO into the crystalline deposits was investigated. The population of Fe, Co, C, and O atoms in the crystalline deposits produced from a gaseous mixture of Fe(CO)₅ (2.4 Torr) and Co(CO)₃NO (1.3 Torr) was 24.8, 1.9, 23.6, and 49.7 at%, respectively. The atomic ratio of Co atom to Fe atom was 1 : 13, showing that Co(CO)₃NO molecules were actually incorporated into the formation process of the crystalline deposits.

Chemical processes in the gas phase were investigated by measuring FT-IR spectrum of a gaseous mixture of Fe(CO)₅ (2.3 Torr) and Co(CO)₃NO (1.7 Torr). The spectra of Fe(CO)₅ vapor (2 Torr) and Co(CO)₃NO vapor (2 Torr) are shown in Figure 12(A). Upon UV light exposure, FT-IR bands of Fe(CO)₅ and Co(CO)₃NO decreased their intensities both in pure vapor and in the gaseous mixture.
Figure 10. SEM images of deposits produced from a gaseous mixture of Fe(CO)$_5$ (2.3 Torr) and Co(CO)$_3$NO (1.7 Torr) under light irradiation with a medium pressure mercury lamp for (a) 2, (b) 5 and (c) 30 min. Original magnification of SEM, (a) 13000×, (b) 4000×, (c) 1300×.
After allowing for complete sedimentation of the formed aerosol particles, the band intensity (absorbance, $A$) of $\delta$(Fe-C-O) band at 645 cm$^{-1}$ of Fe(CO)$_5$ [52, 53] and of $\nu$(C≡O) band at 2108 cm$^{-1}$ of Co(CO)$_3$NO [54, 55] was measured, and the value, $A/A_0$, was plotted against cumulative irradiation time (Figure 12(B)). In pure vapor, Fe(CO)$_5$ molecules were almost completely consumed in 10 min, whereas in the gaseous mixture, they still remained by ~17% even after 60 min. On the other hand, Co(CO)$_3$NO molecules were consumed by only ~20% during 60 min under light irradiation both in pure vapor and in the gaseous mixture. Assuming the pseudo first order decay, the depletion rate was estimated; depletion of Fe(CO)$_5$ molecules was decelerated by $\approx$6 times due to the presence of Co(CO)$_3$NO, showing that the incorporation of Co(CO)$_3$NO molecules decelerated the formation of Fe$_2$(CO)$_9$, and formed the Fe-(C=O)-Co bond.

Figure 11. SEM images of deposits produced from (a) pure Fe(CO)$_5$ vapor (1.0 Torr) and (b) pure Co(CO)$_3$NO vapor (2.0 Torr) under light irradiation with a medium pressure mercury lamp for (a) 10 min and (b) 1 h. Original magnification of SEM, (a) 4500×, (b) 45000×.
2.1.2. Magnetic Field Effects on Morphology and Chemical Compositions of Crystalline Deposits and Sedimentary Particles

Magnetic field effect on the morphology of crystalline deposits produced from a gaseous mixture of Fe(CO)$_5$ (2.4 Torr) and Co(CO)$_3$NO (1.3 Torr) in a superconducting magnet was investigated from SEM images. SEM images of crystalline deposits are shown in Figure 13.
In the absence of an external magnetic field, crystalline deposits with a size of ~5 \( \mu \text{m} \) were produced. Under a magnetic field of 3 T, the crystalline deposits grew vertically onto a substrate placed at the bottom of the irradiation cell and had a shape like a rose petal. At 5 T, the deposits became larger and more dense and had a hexagonal shape lying down on the substrate. The morphological change of the deposits strongly suggested that formation process of the crystalline deposits was accelerated by application of a magnetic field.

SEM-EDS analysis was performed on the spherical particles and on the crystalline deposits separately, and the results are tabulated in Table 2. The atomic ratio of Fe to Co atom was 13 for the crystalline deposits and 1.8 for the particles. Co species were relatively rich in the particles.

Different chemical compositions between the crystalline deposits and the particles supported for the suggestion that the crystalline deposits were formed independently from the spherical particles. This was further supported from different magnetic field effects on the crystalline deposits and on the particles tabulated in Table 2. With increasing magnetic field, Co species increased in the crystalline deposits, whereas Fe species increased in the particles.

Magnetic field effect on the chemical compositions is explained using the following chemical reactions. Under UV light irradiation, \( \text{Fe} \left( \text{CO} \right)_5 \) and \( \text{Co} \left( \text{CO} \right)_3 \text{NO} \) evolve CO and/or NO groups to produce reactive species (reactions (7) - (9)) [56-58].

Figure 13. SEM images of deposits produced from a gaseous mixture of \( \text{Fe} \left( \text{CO} \right)_5 \) (2.4 Torr) and \( \text{Co} \left( \text{CO} \right)_3 \text{NO} \) (1.3 Torr) under light irradiation with a medium pressure mercury lamp for 60 min under a magnetic field of (a) 0, (b) 3, and (c) 5 T. Original magnification of SEM, (a) 1000×, (b) 7000×, (c) 5000×.
Fe(CO)$_5$ + hv $\rightarrow$ Fe(CO)$_4$ + CO  \hspace{1cm} (7)

Co(CO)$_3$NO + hv $\rightarrow$ Co(CO)$_3$ + NO \hspace{1cm} (8)

Co(CO)$_3$NO + hv $\rightarrow$ Co(CO)$_2$NO + CO \hspace{1cm} (9)

In the gaseous mixture, Fe(CO)$_4$ reacts with Fe(CO)$_5$ and Co(CO)$_3$NO to form the crystalline deposits involving Fe-(C=O)-Co bond (reactions (10) and (11)).

Fe(CO)$_4$ + Fe(CO)$_5$ $\rightarrow$ Fe$_2$(CO)$_9$ \hspace{1cm} (10)

Fe(CO)$_4$ + Co(CO)$_3$NO $\rightarrow$ FeCo(CO)$_7$ NO \hspace{1cm} (11)

Co(CO)$_3$ may react with Fe$_2$(CO)$_9$ to form any chemical species involving Fe and Co atoms (reaction (12)).

Co(CO)$_3$ + Fe$_2$(CO)$_9$ $\rightarrow$ Chemical species involving Co and Fe atoms  
(such as Fe$_2$Co(CO)$_{12}$) \hspace{1cm} (12)

As for the particle formation, Co(CO)$_3$ reacts with Co(CO)$_3$NO to form any reactive species such as Co$_2$(CO)$_6$NO to initiate the nucleation reaction (reaction (13)). These dicobalt species may react with Fe(CO)$_5$ and/or Fe(CO)$_4$ to form chemical species involving Co and Fe atoms (reaction (14)).

Co(CO)$_3$ + Co(CO)$_3$NO $\rightarrow$ Co$_2$(CO)$_6$NO \hspace{1cm} (13)

Co$_2$(CO)$_6$NO + Fe(CO)$_5$ and/or Fe(CO)$_4$ $\rightarrow$ Chemical species involving Co and Fe atoms. \hspace{1cm} (14)

Judging from the magnetic field dependency of the chemical compositions analyzed by SEM-EDS (Table 2), reactions (12) and (14) may be accelerated by the magnetic field to result in the increase in atomic abundance of Co atom in the crystalline deposits and Fe atom in the sedimentary particles. Acceleration of reaction (12) may be responsible also to the morphological change of the crystalline deposits.

<table>
<thead>
<tr>
<th>Magnetic field</th>
<th>0 T</th>
<th>3 T</th>
<th>4 T</th>
<th>5 T</th>
</tr>
</thead>
<tbody>
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<td>Particles</td>
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<td>1.7</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Crystalline deposit</td>
<td>13</td>
<td>12</td>
<td>12</td>
<td>8.6</td>
</tr>
</tbody>
</table>

**Table 2. Atomic ratio of Fe to Co atom in sedimentary particles and in crystalline deposits produced from a gaseous mixture of Fe(CO)$_5$ (2.4 Torr) and Co(CO)$_3$NO (1.3 Torr) under a magnetic field**
2.1.3. Formation and Chemical Structure of Spherical Aerosol Particles

As discussed above, a gaseous mixture which contained more Fe(CO)$_5$ vapor (2.3 Torr) than Co(CO)$_3$NO vapor (1.7 Torr) produced both the crystalline deposits and the sedimentary spherical particles. The crystalline deposits were rich in Fe species and were produced after the deposition of the particles.

These experimental results strongly suggested that in order to produce the particles predominantly by suppressing the formation of the crystalline deposits, a decrease in the partial pressure of Fe(CO)$_5$ was effective. Hence, a gaseous mixture which contained only 0.4 Torr of Fe(CO)$_5$ was prepared. Under UV light irradiation for 7 min and even for 60 min, a gaseous mixture of Fe(CO)$_5$ (0.4 Torr) and Co(CO)$_3$NO (2.4 Torr) produced only sedimentary aerosol particles with a mean diameter of 0.31 and 0.39 \( \mu \text{m} \), respectively as shown in Figure 14. Monitor (He-Ne laser) light scattered by the aerosol particles was detected only for the first 20 min (Figure 15), showing that aerosol particles were formed during the first 20 min. The crystalline deposits were not formed until 60 min under the present experimental conditions.

SEM-EDS analysis was performed on the sedimentary particles. Because the signals from uncovered Cu substrate were intense, signals from Fe and Co atoms became relatively weak. The results under a magnetic field of 0 and 3 T are tabulated in Table 3. The atomic ratio of Fe to Co atom was increased to 0.78 (1 : 1.3) from 0.68 (1 : 1.5) by application of a magnetic field of 3 T, revealing that chemical composition of the particles was rich in Co species, and that chemical reaction (14) was accelerated during aerosol particle formation by application of a magnetic field as in the case where both the crystalline deposits and the particles were produced.

Table 3. Atomic abundance of Fe and Co atoms in sedimentary particles produced from a gaseous mixture of Fe(CO)$_5$ (0.4 Torr) and Co(CO)$_3$NO (2.6 Torr) under a magnetic field of 0 and 3 T

<table>
<thead>
<tr>
<th>Atomic line</th>
<th>Magnetic field</th>
<th>0 T</th>
<th>3 T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At %</td>
<td>Ratio</td>
<td>At %</td>
</tr>
<tr>
<td>Fe K</td>
<td>0.52</td>
<td>1</td>
<td>0.62</td>
</tr>
<tr>
<td>Co K</td>
<td>0.76</td>
<td>1.5</td>
<td>0.79</td>
</tr>
<tr>
<td>C K</td>
<td>29.7</td>
<td></td>
<td>23.6</td>
</tr>
<tr>
<td>O K</td>
<td>16.5</td>
<td></td>
<td>13.2</td>
</tr>
<tr>
<td>Cu K</td>
<td>52.6</td>
<td></td>
<td>61.8</td>
</tr>
</tbody>
</table>
Figure 14. SEM images of sedimentary aerosol particles produced from a gaseous mixture of Fe(CO)$_5$ (0.4 Torr) and Co(CO)$_3$NO (2.4 Torr) under light irradiation for (a) 7 and (b) 60 min. Original magnification of SEM, (a) and (b) 8,500×.

Figure 15. He-Ne laser light intensity scattered by aerosol particles produced from a gaseous mixture of Fe(CO)$_5$ (0.4 Torr) and Co(CO)$_3$NO (2.4 Torr) under light irradiation with a medium pressure mercury lamp.
FT-IR spectrum of the sedimentary aerosol particles is shown in Figure 16(a). The spectrum showed strong bands at 1955, 2025, 2052, 2100, and 2198 cm\(^{-1}\) assigned to terminal CO stretching vibration of Co and Fe species [52-55, 59], and bands in the 1250 ~ 1650 cm\(^{-1}\) region (at 1384, 1470, 1495, and 1633 cm\(^{-1}\)) which were characteristic of the deposits from Co(CO)\(_3\)NO (Figure 16(c)) and assignable to C-O bond coordinated to a metal atom. In the spherical particles, IR bands ascribed to bridging C=O (at 1825 cm\(^{-1}\) in Figure 16(d)) and terminal NO (at 1822 cm\(^{-1}\) in Figure 12A(b)) [55] disappeared almost completely. Chemical structure is suggested to be entirely different from that of the crystalline deposits shown in Figure 16(b) which are mainly composed of Fe\(_2\)(CO)\(_9\) structure involving Fe-(C=O)-Co bond. In the particles, Co species are more abundant than Fe species. Co atoms can be connected directly or via a bridging >C=O group as in the structure of Co\(_2\)(CO)\(_8\) [60-62]. Disappearance of the IR band of the bridging >C=O group and appearance of the bands in 1250 ~ 1650 cm\(^{-1}\) region ascribed to C-O bond coordinated to a metal atom strongly suggest that (1) Fe atom in Fe(CO)\(_4\) which is produced from Fe(CO)\(_5\) via photodecomposition [56, 57] coordinates the O atom in Co-(C=O)-Co structure to form Co-C-O-Fe structure and to result in the shift of the C-O stretching vibrational frequency to 1250 ~ 1650 cm\(^{-1}\) region, and/or (2) under UV light irradiation, two CO groups in such chemical species as Co\(_2\)(CO)\(_6\)NO (reaction (13)) form \(\alpha\)-diketone structure, and O atom in the diketone structure coordinates to Fe atom in Fe(CO)\(_4\) to show the v(CO) band at 1500~1530 cm\(^{-1}\) [63].

On oxidized aluminum surface, Co\(_2\)(CO)\(_8\) was reported to produce carbonate species [64]. Monodentate carbonate of Co showed asymmetric CO stretching band at 1540~1420 cm\(^{-1}\) and symmetric CO stretching band at 1390~1330 cm\(^{-1}\). The Cu substrate used in the present experiment is significantly oxidized, hence the carbonate structure may be produced from CO groups during photochemical surface reaction in the presence of Co and Fe atoms. Judging from the spectrum in Figure 16, the CO bands due to several chemical structures may contribute to the 1250 ~ 1650 cm\(^{-1}\) region, and the chemical structures discussed above may be formed during the particle formation.

Depletion of the gaseous molecules was measured from the intensity change of FT-IR bands of gaseous molecules, and molar ratio of Co(CO)\(_3\)NO to Fe(CO)\(_5\) molecules depleted over 60 min was evaluated to be \(~1.8\). This value was close to the atomic ratio in the sedimentary particles analyzed by SEM-EDS.

A gaseous mixture containing a little more Fe(CO)\(_5\) (0.5 Torr) and a little less Co(CO)\(_3\)NO (1.9 Torr) produced only sedimentary aerosol particles under UV light irradiation. FT-IR spectrum of the particles was essentially identical to the spectrum in Figure 16, and SEM-EDS analysis revealed that atomic ratio of Fe to Co atom was 1 : 1.3. The different atomic ratio of Fe to Co atom depending on the initial partial pressures of a gaseous mixture strongly suggested that the chemical structure of the aerosol particles was composed of several chemical structures involving Co and Fe atoms.
Figure 16. FT-IR spectra of (a) sedimentary particles deposited from a gaseous mixture of Fe(CO)$_5$ (0.4 Torr) and Co(CO)$_5$NO (2.4 Torr), (b) crystalline deposits produced from a gaseous mixture of Fe(CO)$_5$ (2.3 Torr) and Co(CO)$_5$NO (1.7 Torr), (c) sedimentary particles deposited from pure Co(CO)$_5$NO vapor (2.0 Torr) and (d) crystalline deposits produced from pure Fe(CO)$_5$ vapor (1.0 Torr). Light irradiation time, (a) 7, (b) 30, (c) 60, (d) 10 min.
2.2. Aerosol Particle Formation from a Gaseous Fe(CO)\textsubscript{5} / ATMeSi / CS\textsubscript{2} Mixture

Carbon disulfide (CS\textsubscript{2}) reacts with transition metal complexes to exhibit \(\pi\)-CS\textsubscript{2} coordination, to form \(\sigma\)-bonded complex through a S atom, and to form complexes with bridging CS\textsubscript{2} group [65]. A gaseous mixture of Fe(CO)\textsubscript{5} and CS\textsubscript{2} produced spherical aerosol particles under UV light irradiation [13, 14]. Chemical analysis by SEM-EDS and FT-IR spectrum of the sedimentary aerosol particles strongly suggested that the major chemical structure was similar to the one of Fe\textsubscript{2}(CO)\textsubscript{9} but two Fe atoms in the particles were connected by \(\sigma\)-coordinated bridging CS\textsubscript{2} [14].

Fe(CO)\textsubscript{5} can also react with vinylsilanes to form iron tetracarbonyl \(\pi\)-coordinated vinylsilanes [66]. From a gaseous mixture of Fe(CO)\textsubscript{5} and allyltrimethylsilane (2-propenyltrimethylsilane) (ATMeSi), crystalline deposits with a size of \(\sim\)5 \(\mu\)m were produced under UV light irradiation in addition to a small amount of spherical aerosol particles with a mean diameter of 0.5 \(\mu\)m [21]. To produce the spherical aerosol particles which involve both organometal compound and organosilicon compound more efficiently, addition of CS\textsubscript{2} molecules to the gaseous mixture is preferable.

In this section, a ternary gaseous mixture of Fe(CO)\textsubscript{5}, ATMeSi, and CS\textsubscript{2} was prepared, and sedimentary aerosol particles were produced under UV light irradiation. Chemical structure of the particles was studied from FT-IR and SEM-EDS analyses, and magnetic field effect on the particle size was also studied. Under a regulated convectional flow, the ternary gaseous mixture could produce linearly aggregated particles (i.e., particle wires). Participation of ATMeSi and CS\textsubscript{2} molecules to efficient production of the particle wires was discussed briefly.

2.2.1. Chemical Structure and Formation Process of Sedimentary Particles

Under UV light irradiation with a medium pressure mercury lamp at 313 nm for 30 min, a gaseous mixture of Fe(CO)\textsubscript{5} (1.7 Torr), ATMeSi (15.9 Torr), and CS\textsubscript{2} (8.9 Torr) produced spherical sedimentary particles of yellowish brown color with a mean diameter of 0.56 \(\mu\)m over the whole glass plate placed at the bottom of the irradiation cell. A SEM image of the particles and the particle size distribution are shown in Figure 17.

Chemical processes in the gas phase were investigated by measuring FT-IR spectrum of the ternary gaseous mixture. Upon UV light exposure, the FT-IR bands ascribed to Fe(CO)\textsubscript{5} significantly decreased their intensities. After allowing for complete sedimentation of the formed aerosol particles, the band intensity (absorbance, \(A\)) of \(\nu(C\equiv O)\) band at 2039 cm\(^{-1}\) of Fe(CO)\textsubscript{5} [52, 53], of \(\delta(CH_3)\) band at 1259 cm\(^{-1}\) [67, 68] of ATMeSi, and of \(\nu(C=S)\) band at 1538 cm\(^{-1}\) of CS\textsubscript{2} [26, 30, 39] was measured, and the depletion (\(A/A_0\)) was evaluated.

Assuming the pseudo first order decay, the depletion rate of Fe(CO)\textsubscript{5} molecules was estimated to be \(2.3 \times 10^{-3}\) s\(^{-1}\) for the gaseous mixture and \(7.5 \times 10^{-3}\) s\(^{-1}\) for pure vapor. Depletion of Fe(CO)\textsubscript{5} molecules was decelerated by \(\approx\)3 times due to the presence of both the ATMeSi and CS\textsubscript{2} molecules.

For a binary gaseous mixture of Fe(CO)\textsubscript{5} (1.1 Torr) and CS\textsubscript{2} (2.0 Torr), the depletion rate of Fe(CO)\textsubscript{5} molecules was \(3.5 \times 10^{-3}\) s\(^{-1}\) [13]. Deceleration of the depletion rate of Fe(CO)\textsubscript{5} molecules due to the presence of CS\textsubscript{2} was more efficient than that due to the presence of ATMeSi, indicating that chemical interaction of CS\textsubscript{2} toward Fe(CO)\textsubscript{5} was more efficient than
that of ATMeSi, and both the CS₂ and ATMeSi molecules prevented Fe(CO)₅ molecules from forming Fe₂(CO)₉ species.

The number of molecules depleted from the gaseous phase was estimated. In the ternary gaseous mixture of Fe(CO)₅ (1.7 Torr), ATMeSi (15.9 Torr), and CS₂ (8.9 Torr), these molecules were depleted by 1.2, 0.7, and 0.6 Torr, respectively, over 10 min under UV light irradiation. The number of depleted Fe(CO)₅ molecules was almost equal to the sum of the numbers of depleted CS₂ and ATMeSi molecules.

Figure 17. (a) SEM image of sedimentary particles produced from a gaseous mixture of Fe(CO)₅ (1.7 Torr), ATMeSi (15.9 Torr), and CS₂ (8.9 Torr) under light irradiation with a medium pressure mercury lamp for 30 min and (b) particle size distribution therefrom. Original magnification of SEM, 10,000×.

To investigate the chemical structure of the sedimentary particles, FT-IR and Raman spectra were measured. FT-IR spectrum of the particles deposited from a gaseous mixture of Fe(CO)₅ (1.7 Torr), ATMeSi (15.9 Torr), and CS₂ (8.9 Torr) is shown in Figure 18, compared with those deposited from binary gaseous mixtures. The spectrum showed strong bands in the 2000 cm⁻¹ region assigned to ν(C≡O) of the terminal CO group, but did not exhibit any bands ascribed to bridging >C=O group in the 1800 cm⁻¹ region. Weak bands were observed at 1251 and 855 cm⁻¹ ascribed to trimethylsilyl group of ATMeSi and at 1612 cm⁻¹ originating from CS₂.

SEM-EDS analysis also confirmed the incorporation of ATMeSi and CS₂ molecules into the sedimentary particles. Atomic ratio of Fe atom to S and Si atoms was 1 : 0.40 : 0.06, showing that CS₂ and ATMeSi molecules were actually incorporated into the formation process of the sedimentary particles. Raman spectrum of the sedimentary aerosol particles produced from the ternary gaseous mixture is shown in Figure 19. The spectrum showed a medium band at 155 cm⁻¹ assignable to ν(Fe-Fe) and a strong band at 192 cm⁻¹ assignable to δ(Fe-S) or δ(C-Fe-C).
Figure 18. FT-IR spectra of sedimentary particles produced from a gaseous mixture of (a) Fe(CO)$_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS$_2$ (8.9 Torr), (b) Fe(CO)$_5$ (4.7 Torr) and ATMeSi (18 Torr), and (c) Fe(CO)$_5$ (1.1 Torr) and CS$_2$ (2.0 Torr) under light irradiation for (a) 12, (b) 3, and (c) 30 min.

During the nucleation process, CS$_2$ molecules reacted with Fe(CO)$_5$ to decelerate the formation of Fe$_2$(CO)$_9$. Considering that the bridging $>$C=O band observed in Fe$_2$(CO)$_9$ almost completely disappeared in the sedimentary particles and $\delta$(Fe-S) band was observed in Raman spectrum, CS$_2$ molecules reacted with Fe(CO)$_5$ to connect two Fe atoms. For iron carbonyls, $\pi$-coordination of CS$_2$ molecules and $\sigma$-coordination through a sulfur atom were reported in the liquid phase [65, 69]. Although the present experiment was done in the gaseous phase, Fe(CO)$_4$ species produced from excited Fe(CO)$_5$ may react with CS$_2$ through either $\pi$- or $\sigma$-coordination.

$$\text{Fe(CO)}_5 + h\nu \rightarrow \text{Fe(CO)}_4 + \text{CO} \quad (7)$$

$$\text{Fe(CO)}_4 + \text{CS}_2 \rightarrow (\text{Fe(CO)}_4 \cdot \text{CS}_2) \quad (15)$$

$\sigma$-Coordinated CS$_2$ can ligate another Fe atom to connect two Fe atoms as was observed for Co$_2$(CN)$_{10}$CS$_2$ [65, 69].

$$(\text{Fe(CO)}_4 \cdot \text{CS}_2) + \text{Fe(CO)}_5 \rightarrow \text{Fe(CO)}_4\cdot\text{S-C(=S)-Fe(CO)}_4 + \text{CO} \quad (16)$$
For the above complex, \( \nu(C=S) \) and \( \nu(C-S) \) bands were expected to appear at 840 - 980 cm\(^{-1} \) region [69].

Thiocarbonyl group can coordinate to Fe atom and combine two transition metal atoms via bridging carbon atom [70-72]. Considering that CS\(_2\) molecules were polymerized in the gas phase mainly as \((C-S)_n\) under UV light irradiation [35], Fe(CO)\(_4\) may react with CS to bridge two Fe atoms through a thiocarbonyl group.

\[
\text{CS}_2 + \text{hv} \rightarrow \text{CS}_2^* \\
\text{CS}_2^* + \text{CS}_2 \rightarrow (\text{CS}_2)_2^* \rightarrow 2\text{CS} \text{ (or (CS))}_2 + \text{S}_2
\]

\[
\text{Fe(CO)}_4 + \text{CS} + \text{Fe(CO)}_5 \rightarrow \text{Fe(CO)}_4\text{-C(=S)-Fe(CO)}_4 + \text{CO}
\]

Figure 19. Raman spectrum of sedimentary particles produced from a gaseous mixture of Fe(CO)\(_5\) (1.7 Torr), ATMeSi (15.9 Torr), and CS\(_2\) (8.9 Torr) under light irradiation for 12 min.

Fe-Fe bond may be formed between two Fe atoms connected via carbon-bridging thiocarbonyls as in the case of \([(\text{cyclopentadienyl})\text{Mn(CS)(NO)}]_2\) [72]. The observation of \( \nu(\text{Fe-Fe}) \) band in Raman spectrum strongly suggested that chemical structures originating from the species involving \( \sigma \)-coordinated CS\(_2\) (reaction (16)) and from the species involving a carbon-bridging thiocarbonyl (reaction (17)) were both formed during aerosol particle formation. As to ATMeSi, FT-IR spectrum of the sedimentary particles showed the bands characteristic of the trimethylsilyl group at 1251 and 855 cm\(^{-1} \). This strongly suggested that ATMeSi ligated to Fe atom via \( \pi \)-coordination of allyl group [73].

\[
\text{Fe(CO)}_4 + \text{CH}_2=\text{CH-CH}_2\text{-Si(CH}_3)_3 \rightarrow (\text{Fe(CO)}_3 \cdot \text{CH}_2=\text{CH-CH}_2\text{-Si(CH}_3)_3) + \text{CO}
\]
The \(\pi\)-coordinated C=C stretching vibrational band was expected to appear at 1470 - 1534 cm\(^{-1}\) [66, 74, 75]. In FT-IR spectrum (Figure 18(a)), several weak bands were observed in this region. One of them may be ascribed to the \(\pi\)-coordinated C=C stretching band.

### 2.2.2. Magnetic Field Effect on Particle Size

Spherical aerosol particles were produced from a gaseous mixture of Fe\((\text{CO})_5\) (1.3 Torr), ATMeSi (17.9 Torr), and CS\(_2\) (2.9 Torr) under a magnetic field of up to 5 T. Due to a smaller inner diameter (20 mm) of the cylindrical irradiation cell used in a superconducting magnet, the mean diameter of the sedimentary particles decreased to 0.30 \(\mu\)m from 0.56 \(\mu\)m (produced in a cylindrical cell with an inner diameter of 35 mm) in the absence of a magnetic field. Under a magnetic field of 1, 3, and 5 T, the mean diameter increased from 0.30 to 0.31, 0.33, and 0.35 \(\mu\)m, respectively, showing that chemical reactions during aerosol particle formation were accelerated by application of a magnetic field. SEM-EDS analysis of the sedimentary particles (which were produced under pulsed Nd:YAG laser light at 355 nm) showed that atomic ratio of Si to Fe atom increased by application of a magnetic field, suggesting that \(\pi\)-coordination of ATMeSi (such as in reaction (18)) was accelerated by application of a magnetic field. Furthermore, in a binary gaseous mixture of Fe\((\text{CO})_5\) and CS\(_2\), \(\sigma\)-coordinated \((\text{Fe(CO)}_4 \cdot \text{CS}_2)\) species favored the chemical reaction with Fe\((\text{CO})_5\) under a magnetic field [13]. These results strongly suggested that chemical reactions (16) and (18) in the ternary gaseous mixture were accelerated by application of a magnetic field.

### 2.2.3. Formation of Linearly Aggregated Fine Particles

UV light at 313 nm was irradiated on a gaseous mixture of Fe\((\text{CO})_5\) (1.7 Torr), ATMeSi (15.9 Torr), and CS\(_2\) (8.9 Torr) only for a short time (1-2 min) repeatedly (14 times) with an interval of 7 min. This intermittent light irradiation induced a modulated convective flow of the entire gaseous sample to result in a deposition of linearly aggregated particles (Figure 20). In Figure 20(a), linearly aggregated particles grew into the space from the front edge of a substrate placed at the bottom of the irradiation cell. Because deposited particles maintain the photochemical reactivity even after deposition, adjacent particles can stick to each other through chemical bonds to form chemically bonded linearly aggregated particles (i.e., particle wires) as shown in Figure 20(b).

From pure Fe\((\text{CO})_5\) vapor at a low pressure (0.2 Torr), a limited number of linearly aggregated particles as long as 50 \(\mu\)m were produced on the substrate under repeated UV light irradiation for a short time (1-2 min). On the other hand, a gaseous mixture of Fe\((\text{CO})_5\) (1.1 Torr) and CS\(_2\) (2.0 Torr) deposited randomly aggregated particles together with only a few particle wires as long as \(~15\) \(\mu\)m under repeated UV light irradiation for a short time (1-3 s). By adding ATMeSi to a gaseous mixture, particle wires were more easily formed. From the ternary gaseous mixture of Fe\((\text{CO})_5\), ATMeSi, and CS\(_2\), particle wires as long as 80 \(\mu\)m (with a mean diameter of 0.4 \(\mu\)m) were produced efficiently.
CS$_2$ is a typical molecule which can produce aerosol particles [4-8]. Addition of CS$_2$ molecules to a gaseous mixture is expected to produce sedimentary particles more easily and hence to form particle wires more efficiently. To study the effect of chemical tendency of CS$_2$ to form particle wires, both the sedimentary particles and particle wires were produced under light irradiation for 12 min from gaseous mixtures of Fe(CO)$_5$, ATMeSi, and CS$_2$ in which the partial pressure of CS$_2$ was varied significantly while those of Fe(CO)$_5$ and ATMeSi remained almost constant. The results are shown in Figure 21.
Figure 21. SEM images of particle wires produced from gaseous mixtures of Fe(CO)$_5$, ATMeSi, and CS$_2$ with respective partial pressures of (a) 0.8, 13.7, and 1.1 Torr, (b) 1.3, 14.7, and 2.6 Torr, and (c) 1.7, 15.9, and 8.9 Torr under light irradiation for 12 min. Original magnification of SEM, (a) 800×, (b) 1000×, (c) 2000×.
Figure 22. A panoramic view of the distribution of particle wires deposited from a gaseous mixture of Fe(CO)$_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS$_2$ (8.9 Torr) on a glass plate in the region of 0 - 7 mm in depth. Original magnification of SEM, 33×. Original magnification of SEM at spot (a), 500×, spots (b) and (c), 1,000×.

With increasing partial pressure of CS$_2$ from 1.1 to 2.6 and further to 8.9 Torr, the length of particle wires increased from 7 to 17 and further to 500 (the longest, 850) μm. The mean diameter of the particles was 0.43 μm in the last case, and the number of particles constituting a single particle wire exceeded to one thousand. In order to produce long particle wires, the partial pressure of CS$_2$ was needed to be several (~5) times higher than that of Fe(CO)$_5$. A panoramic view of the distribution of particle wires deposited from a gaseous mixture of Fe(CO)$_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS$_2$ (8.9 Torr) on a glass plate was shown in Figure 22. Particle wires as long as several hundreds of μm grew vertically to the surface of a glass plate (placed at the bottom of the irradiation cell) until to 1 mm in depth from the front edge of the glass plate (Figure 22, spot a). In the deeper region than 1 mm in depth from the front edge, the length of the particle wires became shorter until the region of 5 mm in depth (Figure 22, spot b). In the region of more than 5 mm in depth, particle wires were hardly formed. Aggregated particles were formed predominantly (Figure 22, spot c). During the sedimentation process, the long particle wires were produced efficiently in the vicinity of the front edge of the substrate.

The formation of particle wires is characteristic of the sedimentary particles produced by the photochemical method in the gas phase [16]. As was exemplified in the formation of sedimentary particles deposited from a gaseous Fe(CO)$_5$/CS$_2$ mixture [14], particle size was reduced to several tens of nm by shortening light irradiation time. By optimizing the experimental conditions, thinner particle wires can be produced. The particle wire is flexible, and can be connected to another particle wire so as to form a longer wire in any shape.

**CONCLUSIONS**

Ultrafine and fine particles involving organosilicon and/or organometal compounds were synthesized using the photochemical method applicable to gaseous molecules.
Spherical particles produced from a gaseous mixture of TMPSi and CS₂ involved chemical species originating from TMPSi efficiently with molar ratio of 1:1 to those originating from CS₂, and their chemical compositions were influenced by a magnetic field. Analysis of FT-IR and XPS spectra revealed that incorporation of TMPSi molecules into the aerosol particles decreased under a magnetic field, resulting in a greater abundance of sulfur atoms in C-S bonding than in >C=S bonding. From these results it was strongly suggested that the nucleation reactions (3) and (4) were accelerated by application of a magnetic field.

From a gaseous mixture of Fe(CO)₅ and Co(CO)₃NO, both the crystalline deposits and the spherical particles were produced. Chemical composition of the particles was rich in Co species, whereas that of the crystalline deposits being rich in Fe species. Chemical composition of the particles was influenced by a magnetic field differently from that of the crystalline deposits, showing that the formation processes were different in each other.

From a ternary gaseous mixture of Fe(CO)₅, ATMeSi, and CS₂, linearly aggregated particles (i.e., particle wires) were produced efficiently. Particle wires as long as 500 µm with a mean diameter of 0.4 µm were formed when the partial pressure of CS₂ was several times higher than that of Fe(CO)₅. As to the chemical structure of the particles, it was strongly suggested that two Fe atoms were connected by σ-coordinated CS₂ (reaction (16)) and/or by a carbon-bridging thiocarbonyl (reaction (17)).

REFERENCES