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Decarboxylation and simultaneous reduction of silver(I) β-ketocarboxylates with three types of coordination


A series of silver(I) β-ketocarboxylates were prepared by reaction of β-ketocarboxylic acids with silver nitrate in the presence of diethanolamine. The silver(I) β-ketocarboxylates decomposed over a narrow temperature range to form metallic silver, CO₂, and the corresponding ketones. In addition, products derived from radical intermediates were detected by mass spectroscopic analysis for some silver(I) β-ketocarboxylates. Infrared and solid state ¹³C-NMR spectra of silver(I) β-ketocarboxylates suggested the presence of two types of structures involving a carbonyl group in addition to the dimeric eight-membered ring structure as in the structure of silver(I) stearate. The silver(I) β-ketocarboxylate model compound used was HCOCH₂CONH₂Ag and its structures were determined using density functional theory (DFT) and atoms-in-molecules (AIM) methods. Three types of coordination around the Ag ion differing significantly in Ag-O bond strengths were found. Based on the calculated structures and experimental results, the relationship between the structures and decomposition temperatures are discussed in terms of the thermal decomposition process.

Introduction

Much attention has been paid to silver(I) carboxylates as photographic and printed electronic materials because of their unique structures and their reduction to metallic silver by thermal decomposition. However, these silver(I) carboxylates need temperature more than 200 °C for the thermal reduction. Silver-containing materials forming metallic silver at lower temperature have been demanded in the industrial fields.

In 1949, Vand reported a preliminary structure of silver salts of long alkyl fatty acids. The complete structure of silver perfluorobutyrate, composed of an eight-membered central ring containing two silver atoms and two carboxyl groups, had been elucidated. Due to the difficulty of crystallizing these salts and their light sensitivity, only a few studies describing the structure of silver carboxylates have been reported. Acland found that the silver salt of glycyglycine adopted an eight-membered ring structure about the silver carboxylate moiety. A series of crystal structures of silver carboxylate complexes containing an eight-membered ring were reported by Mak. Tolochko examined the structure of silver stearate by extended X-ray absorption fine structure (EXAFS) and reported that the Ag-Ag distance in the eight-membered ring was 2.90 Å, similar to the bond distance in metallic silver. Other structures of silver carboxylates that adopt an eight-membered ring have been reported, leading to the wide acceptance that silver carboxylates tend to form a dimeric (RCO₂)₂Ag eight-membered ring structure.

Silver(I) carboxylates tend to decarboxylate and thermally decompose at ~300 °C to give metallic silver, CO₂, and organic products. The temperature and mechanism of thermal reductive decomposition depends on the structure of the carboxylate moiety. For example, silver(I) benzoate decomposed at 276 °C via a complicated radical pathway to yield metallic silver and products such as polyphenyls derived from the radical intermediate. Similarly, vacuum thermal decomposition of a series of silver dicarboxylates, Ag₂C(CH₂)₃CO₂Ag, n = 0-3, provided metallic silver, CO₂, and polymeric compounds derived from diradicals. In contrast, silver(I) acetate thermally decomposed to give metallic silver and CH₃COOH via formation of silver oxide and anhydride from the corresponding carboxylic acids. Silver perfluorocarboxylate, CF₃(CF₂)₇CO₂Ag, thermally decomposes in a similar manner. Under decomposition conditions at temperatures greater than 200 °C, even with Ag₂O generation, Ag₂O could be thermally reduced to metallic silver. Therefore, uncertainty remains about whether silver ion is reduced by electron transfer during decarboxylation, or by thermal reduction of the Ag₂O formed during decomposition at temperatures above 200 °C.

The structural basis for the electron transfer process in silver acetate was studied by Olson and colleagues. They concluded that the Ag(I)-Ag(I) bond in silver acetate may be an important precursor to metallic silver formation, as single-electron reduction of the Ag₄(carboxylate)₄ species could result in the formation of (Ag₂)₃ known from the chemistry of photographic processing to be a precursor of metallic silver clusters.

This body of fundamental research has promoted the development of advanced silver nanoparticles. Silver carboxylates have been used to generate silver nanoparticles, which require an organic dispersant, such as non-volatile long alkyl fatty acids.
However, the non-volatile dispersant can contaminate the metallic silver nanoparticles produced, which is undesirable.

The decarboxylation of carboxylic acids modified with certain functional groups at the α or β position smoothly proceeds via the formation of carbanions or radical intermediates. β-Ketocarboxylic acids, in particular, readily decarboxylate under ambient conditions via a six-membered transition state.

\[ \text{Scheme 1} \quad \text{Mechanism of decarboxylation of } \beta\text{-ketocarboxylic acids.} \]

The goal of this study was to produce metallic silver from silver carboxylates at temperatures below 200 °C without the production of undesirable organic compounds. Despite the promise of silver(I) β-ketocarboxylates for this purpose, their preparation has not been reported, since β-ketocarboxylic acids prepared from the corresponding ester are unstable under hydrolysis conditions. Preliminary results for the preparation of several silver(I) β-ketocarboxylates have been published previously in a patent. The present report describes the detailed preparation of these silver(I) β-ketocarboxylates, decarboxylation in the solid state, and their structures based on infrared spectroscopy (IR) and ¹³C solid state nuclear magnetic resonance (¹³C-NMR) spectra. The calculated structures of a simple model compound and the relationship between the calculated structures and thermal decomposition also are discussed.

**Experimental Section**

1) Preparation

All commercially available reagents and solvents were used without further purification. Starting esters were purchased from the following chemical companies: methyl-propionylacetate (1) and ethyl-2-benzylacetacetate (8) from Aldrich, ethyl-butyrylacetae (2) and ethyl-2-n-butylacetacetate (7) from Alfa Aesar, methyl-iso-butyrylacetae (3) and ethyl-2-ethylacetacetate (6) from Wako, methyl-pivaloylacetae (4) from Nippon Fine Chemical, and ethyl-2-methylacetacetate (5) from Tokyo Kasei.

**General Reaction Procedure for Silver(I) β-Ketocarboxylates (1a-8a)** Sodium hydroxide (0.12 mol) was added to water (30 mL). Ethyl or methyl β-ketocarboxylate (0.1 mol) was added drop-wise to the resulting solution at approximately 60 °C. The reaction mixture was stirred for 1–4 hours at room temperature, followed by TLC (silica, n-hexane:ethyl acetate = 3:1). When the starting ester was detected, the reaction mixture was washed with ether to remove it. After evaporation to remove the alcohol produced by hydrolysis, the solution was cooled in an ice bath. A solution of diethanolamine (0.105 mol) in water (10 mL) was added, the ether layer was removed by decantation, then an aqueous solution (10 mL) of silver(I) nitrate (0.095 mol) was added drop-wise. The resulting white precipitate was filtered, washed with chilled water and then with 2-propanol, and dried in vacuo.

For compound 5a, the precipitate was soluble in water and thus washed carefully with the minimal amount of chilled water. The silver β-ketocarboxylates obtained were stored in brown bottles at -20 °C. The compounds obtained were characterized by elemental analysis (C, H, N) (JMN10; J-Science), Fourier transform infrared spectroscopy (FT-IR) (FT/IR4100; Jasco), and solid state ¹³C-NMR (Avance III 600WB; Bruker). Thermal analyses were conducted using differential scanning calorimetry (DSC) (DSC-50; Shimadzu) and thermogravimetry (TG) (DTG-50H; Shimadzu). Direct analysis in real time mass spectrometry (DART-MS) was conducted using an AccuTOF DART (Jeol).

2) Thermolysis

Each silver(I) β-ketocarboxylate compound (50 mg) was placed in a 30-mL round bottom flask. For compounds 1a-3a, the flask was heated in an oil bath at 150 °C; the silver salt foamed and started to decompose within 10 seconds. Immediately after foaming stopped, the products were extracted with acetone. For compound 4a, the flask was heated at 180 °C, and for compounds 5a-8a, the flask was heated at 130 °C. The other procedures were the same for all products. Acetone extracts were analyzed by gas chromatography-mass spectrometry (GC-MS) (GCMS-QP2010; Shimadzu) and the inorganic residues 1b-8b were examined by X-ray diffraction (XRD) (RINT-RAPID II-S; Rigaku).

3) Computational Methods

The DFT calculations were conducted at the B3LYP level of theory. A 6-31+G(d) basis set was used for C, H, and O, and an LANL2DZ effective core potential (ECP) was used for Ag. The optimized geometries were verified by vibrational normal mode analysis. All calculations were performed using the Gaussian 03 and Gaussian 09 software packages. The AIM calculations were performed using the AIMAll program to evaluate the nature of the bonds in optimized structures.

**Results and Discussion**

1) Preparation

Silver(I) β-ketocarboxylates were prepared as shown in Scheme 2. Their preparation by treating sodium β-ketocarboxylates with silver nitrate in a one-pot reaction resulted in the formation of inseparable by-products such as silver oxide. β-Ketocarboxylic acids are unstable under hydrolysis conditions, and thus were carefully prepared according to a previously described procedure on hydrolysis of acetoacetic ester. The free acid products were immediately treated with silver nitrate in the presence of diethanolamine to give the corresponding silver(I) β-ketocarboxylate. When R₁ and R₂ were alkyl groups (R₁ = H), hydrolysis of the esters proceeded smoothly to provide high-purity silver β-ketocarboxylates, listed in Table 1. The crystal shapes, yields, and results of CHN analyses are described in the notes. Although the preparation of silver(I) acetoacetates also proceeded smoothly to give colorless precipitates, the resulting precipitates appeared to be unstable and turned grey. When R₁ and R₂ were electron-withdrawing groups {R₁, R₂ = (C₆H₅)₂C=O, (C₆H₅)₂C=O, (CH₂, C₆H₅, (CH₂, C₆H₅), and (CH₂, CH₃)} and R₂ = H, silver(I) β-ketocarboxylates were formed but not isolated due to by-product formation resulting from nucleophilic attack at the β-carbonyl group. When (R₁, R₂) = (CF₃, H, H) and (CH₃, C₆H₅, C₆H₅), silver(I) β-ketocarboxylates were not formed. The prepared
silver(I) β-ketocarboxylates adopted the keto form as determined from their IR and NMR spectra, notes which are listed in Table 1. The resulting silver(I) β-ketocarboxylates were not soluble in organic solvents or water; only compound 5a showed solubility in 1-methyl-2-pyrrolidone (NMP) and in water.

The thermolysis of representative silver(I) β-ketocarboxylates and silver(I) neodecanoate (used as a reference) was examined using DSC and TG; results are shown in Figure 1 and the decomposition temperatures determined by DSC are listed in Table 1. Silver(I) neodecanoate melted at approximately 100 °C and gradually decomposed to give silver(0); the weight decrease occurred over a wide temperature range. Thermal analyses of silver(I) long-chain-fatty acylates reported previously decomposed over 100–250 °C. Therefore, results indicate that the decomposition of silver(I) neodecanoate is a complicated and gradual process that occurs over a wide temperature range.

In contrast, all silver(I) β-ketocarboxylates (1a–8a) decomposed without melting over a narrow temperature range with a rapid decrease in weight. Following decomposition (with the exception of compound 4a), TG showed a gradual decrease until 280 °C. The gradual decrease in weight observed appeared to correspond to the ketone with a high boiling point or the dimeric ketone which is discussed in Mass spectroscopic analysis section. Exothermic peaks

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**Scheme 2** Preparation and thermolysis of silver(I) β-ketocarboxylates.

**Table 1** Decomposition temperatures and FT-IR and solid state 13C-NMR data for silver(I) β-ketocarboxylates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R1</th>
<th>R2</th>
<th>D.T. (°C)</th>
<th>FT-IR(^{a}) (cm(^{-1}))</th>
<th>Solid state(^b) 13C NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C=O</td>
<td>COO(^-)</td>
</tr>
<tr>
<td>1a</td>
<td>C(_2)H(_5)-</td>
<td>H-</td>
<td>130 - 138</td>
<td>1715</td>
<td>1505</td>
</tr>
<tr>
<td>2a</td>
<td>CH(_3)(CH(_2))(_2)-</td>
<td>H-</td>
<td>139 - 148</td>
<td>1712</td>
<td>1505</td>
</tr>
<tr>
<td>3a</td>
<td>(CH(_2))(_2)CH-</td>
<td>H-</td>
<td>139 - 150</td>
<td>1712</td>
<td>1507</td>
</tr>
<tr>
<td>4a</td>
<td>(CH(_3))(_3)C-</td>
<td>H-</td>
<td>167 - 176</td>
<td>1711</td>
<td>1703</td>
</tr>
<tr>
<td>5a</td>
<td>CH(_3)-</td>
<td>CH(_3)-</td>
<td>101 - 109</td>
<td>1715</td>
<td>1697</td>
</tr>
<tr>
<td>6a</td>
<td>CH(_3)-</td>
<td>C(_3)H(_7)-</td>
<td>102 - 121</td>
<td>1716</td>
<td>1698</td>
</tr>
<tr>
<td>7a</td>
<td>CH(_3)-</td>
<td>CH(_3)(CH(_2))(_2)-</td>
<td>110 - 119</td>
<td>1716</td>
<td>1699</td>
</tr>
<tr>
<td>8a</td>
<td>CH(_3)-</td>
<td>C(_3)H(_7)(CH(_2))(_3)-</td>
<td>109 - 114</td>
<td>1694</td>
<td>1555</td>
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<tr>
<td>Silver acetate</td>
<td></td>
<td></td>
<td>210 - 330</td>
<td>1709</td>
<td></td>
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<tr>
<td>Silver laurylate</td>
<td></td>
<td></td>
<td>170 - 290</td>
<td>1518</td>
<td></td>
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<tr>
<td>Silver neodecanoate</td>
<td></td>
<td></td>
<td>95 - 240</td>
<td>1512</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) measured by DSC (rate of temperature increase 10°C/min in air)

\(^{b}\) measured by TG (rate of temperature increase 10°C/min in air)

\(^{c}\) attenuated total reflection (ATR)
were evident near 300 °C in silver(I) β-ketocarboxylates (1a-7a). Because generated ketones and plausible dimeric products are volatile and do not show exothermic peaks, these peaks could be attributed to aggregated Ag particles, as suggested by Logvinenko.28

The TG pattern of compound 4a showed 43.2% of the weight ratio at 176 °C remained (exothermic peak in DSC Figure 1-i, ii, and notes), which corresponded to the theoretical weight ratio of Ag(0): 43.0%. No gradual decrease in weight was observed following decomposition. Little residue remained following decomposition, likely because ketone 4c that formed had a low boiling point (106 °C) and volatilized upon Ag(0) formation during decomposition. Silver(I) β-ketocarboxylates 4a clearly demonstrated simultaneous decomposition and reduction of Ag⁺.

The TG of compound 8a differed from the other silver(I) β-ketocarboxylates: only a 14.6% weight loss was measured during decomposition at 97–104 °C, and weight loss continued gradually following decomposition. The observed weight loss at 97–104 °C corresponded to the weight ratio of CO₂ in compound 8a: 14.7%, indicating that metallic silver and the corresponding ketone 8c (b.p. 235 °C) or the dimeric product remained at the decomposition temperature.

In compound 5a, 42.8% of the weight was lost at 109 °C (the decomposition temperature), corresponding to 83.0% of the weight of the organic moiety. Subsequently, the weight gradually decreased to 50.6% of the original mass of compound 5a (98.1% of the weight of the organic moiety) at 350 °C. As the theoretical weight ratio of Ag(0) is 48.4%, the plausible dimeric or trimeric ketone must have remained.

TG analysis of compounds 1a-3a, 6a, and 7a showed patterns similar to that of compound 5a. The theoretical weight ratio of Ag, and the residual weight ratios at 280 °C, 350 °C, and just after decomposition are described in the notes.

2-2) Mass spectroscopic analysis of products formed during thermolysis

The products formed during thermolysis were analyzed by mass spectroscopy; detailed results are presented in the notes.

The products formed by thermolysis from compounds 1a-8a at their decomposition temperatures (see Experimental Section) were extracted with acetone and examined by GC-MS. Thermolysis of compound 8a at 130 °C provided a peak corresponding to 8c: 4-phenyl-2-butanol with a boiling point of 235 °C. The gradual decrease between 200 and 250 °C in the TG curve of compound 8a in Figure 1-ii was attributed to thermal behavior of 8c. Similarly, thermolysis of compound 7a at 130 °C provided a peak corresponding to 7c, 2-heptanone (MW 114), with a boiling point of 150 °C, and a weak peak corresponding to the dimer (MW 226). For compounds 1a-6a, the corresponding ketones 1c-6c were not detected as their boiling point is lower than the temperature used for thermolysis.

Powdery silver(I) β-ketocarboxylates were analyzed by DART-MS using a 300 °C ion source. Compounds 1a-8a gave peaks corresponding to the molecular weights (MₑSc + 1) of their corresponding ketones, 1c-8c. In addition, intense peaks with a molecular weight of (2MₑSc - 1), due to dimerized radical intermediates, and peaks corresponding to the trimer (3MₑSc - 3) were observed. Although GC-MS data of peaks corresponding to dimers do not prove their formation during thermolysis, the results suggest the formation of keto-radicals during thermolysis.

Figure 1 i) DSC of silver(I) β-ketocarboxylates (4a, 5a, 8a) and silver(I) neodecanoate. ii) TG of silver(I) β-ketocarboxylates (4a, 5a, 8a) and silver(I) neodecanoate. Rate of temperature increase: 10 °C/min in air
Formation of the ketone and dimer may explain the gradual decrease in weight following decomposition and the exothermic peaks around 300 °C in the TG data. Volatilization of the resulting ketones and dimer provided endothermic peaks. Thus, in each case, the gradual decrease in weight following decarboxylation corresponded to volatilization of the dimer and resulting ketone with boiling points at temperatures greater than 200 °C, whereas the exothermic peak near 300 °C can be attributed to aggregation of the Ag particles.

2-3) Chemical composition analysis of the inorganic residue
Silver(I) β-ketocarboxylates 1a-8a thermally decomposed at temperatures below 190 °C. At these temperatures, if the mechanism of decomposition occurred via acid anhydride and Ag₂O, similar to those in silver carboxylates,AgAgO should be formed. The Ag₂O was not thermally reduced to afford metallic silver at temperatures below 190 °C. The inorganic residues were examined using XRD after conducting thermolysis at the decomposition temperatures. No silver oxides or silver salt (Ag₂O, AgO, or Ag₂CO₃) were observed after thermolysis: only Ag(0) was found.

Decomposition by decarboxylation was complete at temperatures below 190 °C. The resulting products included metallic silver and organic compounds derived from the corresponding ketoradical. These results clearly suggest that silver oxide was not involved in these reactions and that metallic silver, ketoradicals, and CO₂ were formed.

3) Structure
3-1) FT-IR and solid state ¹³C-NMR data for silver(I) β-ketocarboxylates
Characteristic spectroscopic data and decomposition temperatures of the isolated silver(I) β-ketocarboxylates 1a-8a are listed in Table I. Representative solid state ¹³C-NMR spectra are shown in Figure 2. The IR spectra of compounds 1a, 2a, and 3a showed a band corresponding to β-carbonyl groups at 1712–1715 cm⁻¹ and strong bands corresponding to carboxylate groups at 1505–1507 cm⁻¹. Solid state ¹³C-NMR spectra of these compounds showed single signals for the β-carbonyl and carboxylate groups.

In contrast, the IR spectra of compounds 4a-7a contained two bands corresponding to β-carbonyl groups, at 1711–1716 cm⁻¹ and at 1697–1703 cm⁻¹, and bands for their carboxylate groups at 1526–1542 cm⁻¹. The solid state ¹³C-NMR spectra of compounds 4a-7a showed two signal groups for the β-carbonyl and carboxylate groups.

The IR spectrum of compound 8a showed a band corresponding to the β-carbonyl group at 1694 cm⁻¹ and of the carboxylate group at 1555 cm⁻¹. In contrast with the solid state ¹³C-NMR spectra of compounds 1a-3a, there is a signal at lower magnetic field (210.6 ppm) for the β-carbonyl group and a signal for the carboxylate group at higher magnetic field (171.6 ppm). This signal pattern was simpler than those of compounds 5a-7a. The signals near 210.6 ppm seen in Figures 2-8a were attributed to side bands.

Absorption bands and ¹³C-NMR signals arising from the carbonyl group at the β-position and from the carboxylate group suggested the presence of a number of coordination modes involving the carbonyl group.

3-2) Proposed Structures
The carbonyl group in silver(I) β-ketocarboxylates may coordinate the silver ion. This suggests structures other than the eight-membered ring coordination of silver salts of fatty acids, as shown in Figure 3. Type I is the same type as silver salts of fatty acids. In Type II, one of the two carbonyl groups is involved in the coordination. Type III coordinates the silver ion between two COO-groups and two C=O groups. Spectroscopic features of these different types of coordination can be predicted empirically as follows. For the Type III structure, the IR absorption bands of the β-carbonyl group would shift to lower wavenumbers and those of the carboxylate groups would shift to higher wavenumbers compared with the corresponding absorption bands of Type I compounds. In Type II coordination, two IR absorption bands are seen. Solid state ¹³C-NMR of Type III compounds show the β-carbonyl group signal shifted to lower magnetic field and the carboxylate group signal shifted to higher magnetic field compared with the corresponding signals in Type I compounds. In Type II compounds, two signals for each C=O group and each COO- group can be seen.

3-3) Classification of silver(I) β-ketocarboxylates
Compounds 1a-8a were classified into Types I-III based on their spectra. Compounds 1a, 2a, and 3a showed spectra similar to silver(I) aliphatic carboxylates and were therefore classified into the Type I structure. The spectroscopic patterns obtained for compound 8a corresponded with the expected pattern for Type III compounds: the absorption bands of the β-carbonyl group shifted to lower wavenumbers and those of the carboxylate groups shifted to higher wavenumbers than the corresponding absorption bands of compounds 1a, 2a, and 3a. The solid state ¹³C-NMR signal of the β-carbonyl group shifted to lower magnetic field and the signal from the carboxylate group shifted to higher magnetic field compared with Type I compounds. When compound 8a adopted a Type III structure with the twelve-membered ring, steric repulsion by the benzyl groups may decrease compared to a Type I structure.
Figure 2 Typical solid state $^{13}$C-NMR spectra.

Figure 3 Plausible structures of silver(I) β-ketocarboxylates.
Steric repulsion by the substituents at the α positions of compounds 5a, 6a, and 7a should be less than that in compound 8a. The spectra suggest that compounds 5a, 6a, and 7a may adopt a Type II or mixture of Type I and III structures. A sharp exothermic peak was present at low temperatures. If these compounds were a mixture of Type I and III structures, the exothermic peak would be broad. But from this point, they are more likely to adopt Type II.

The spectrum of compound 4a showed patterns similar to those of compounds 5a-7a, with some differences. In the solid state $^{13}$C-NMR of compounds 5a-7a, two broad signals for C=O and COO-groups were present. In the IR spectra of compounds 5a-7a, the differences between the wavenumbers of the two absorption bands for carbonyl groups C=O were in the range of 17–18 cm$^{-1}$. In contrast, in the solid state $^{13}$C-NMR of compound 4a, two sharp signals and a small chemical shift difference between the carbonyl signals were observed. In the IR spectrum of compound 4a, two absorption bands for a carbonyl group C=O were observed at wavenumbers above 1700 cm$^{-1}$, with a difference between the wavenumbers of 8 cm$^{-1}$, which differed from the shifts: 17–18 cm$^{-1}$ as seen in Type II: compounds 5a-7a. These spectroscopic differences might be attributed to stereoisomers of compound 4a with a Type I rather than Type II structure in the crystals.

Based on the spectroscopic data, compounds 1a-4a, compounds 5a-7a, and compound 8a were categorized as Type I, Type II, and Type III, respectively. Definitive assignment required determining the structures of the proposed types by X-ray analysis and EXAFS, but this was not possible due to practical difficulties.

3-4) DFT calculations and AIM analysis of silver(I) β-ketocarboxylates

Possible structures of silver(I) β-ketocarboxylates were investigated using structural calculations of a model compound lacking substituents. The compound, HCOCH$_2$COOAg [R$^1 = R^2 = R^3 = H$], was chosen to investigate a wide range of skeletal structures due to flexibility (no rotational hindrance caused by substituents).

The structures optimized for symmetry and potential energy and the results of AIM calculations are illustrated in Figure 4. The bond critical points (BCP) are shown as green dots and the ring critical points (RCP) are shown as red dots. The bond paths with an electron density value ($\rho$) at a BCP below 0.025 a.u. are drawn as dashed lines instead of solid lines. Optimized energies of the five resulting categories of structures, their relative energies, and the calculated IR vibrational frequencies of the intense COO- and C=O stretching modes are listed in Table 2. Selected bond lengths and AIM properties at each BCP are listed in Table 3 (supporting information).

The resulting structures were divided into three main categories. Type I is an eight-membered ring structure, which is the same structure as the well-known silver carboxylate dimers. Several conformers of this type differing in rotational bond angle between the α-carbon and carboxylate carbon were found in this study. Figures 4(a) and (b) show examples of $C_1$ symmetry and $C_{2n}$ symmetry structures, respectively. Only small differences in the energy and ring structural parameters exist in Type I conformers; in addition, the Ag(1)-Ag(2) distances were all approximately 2.83 Å, and BCPs were found between Ag(1) and Ag(2). Two RCPs were found at each AgOCOAg five-membered ring. These results are in good agreement with the experimental and theoretical results of related complexes reported previously.

Type 2 structures have one side that forms the same five-membered ring as in Type I compounds, whereas the other side forms three-oxygen coordination. Carboxylic oxygen O(4) coordinated to Ag(1), and carboxylate oxygen O(5) and carboxyl oxygen O(6) coordinated to Ag(2), as shown in Figure 4(c). Two rotational conformers existed around the α-carbon and carboxylate carbon bond that differed only slightly in energy (< 0.1 kcal/mol). The Ag-Ag bond length was calculated to be 2.988 Å, indicating metalophilic interaction.

In Type 3, both carboxylates coordinate with two silver atoms through three-oxygen coordination. Two distinct structures were evident with significantly different Ag(1)-Ag(2) distances (3.297 Å and 3.669 Å). Type 3a has $C_2$ symmetry, whereas Type 3b has $C_1$ symmetry. AIM results indicated that Type 3a had a weak BCP, whereas Type 3b had no BCP between Ag(1) and Ag(2).

Of the types of structures obtained, Type 1 is the most stable, followed by structure Type 2, whose calculated energy is about 5 kcal/mol greater than that of Type 1a. The calculated energy of Type 3b is about 9 kcal/mol greater than that of Type 1a; that of Type 3a, the least stable structure is about 10 kcal/mol greater than that of Type 1a. These relative energies indicate that all four structure types can exist stably or isomerize easily due to the small energy differences between them.

The calculated vibrational frequencies of the COO- and C=O groups are listed in Table 2. Type 2 compounds showed two peaks arising from C=O stretching of the β-carbonyl groups. In contrast, for Type 3, the peak of the β-carbonyl group shifted to lower wavenumber compared to the corresponding β-carbonyl group of Type 1. From these results, it is possible that the Type 1 structure calculated here corresponds to Type I of the plausible structure shown in Figure 3, Type 2 corresponds to Type II, and Type 3 corresponds to Type III.

These computational results allowed the re-examination of the structures of the compounds synthesized in this study. The above discussion regarding two isomers, such as Type 1a and Type 1b, in the eight-membered ring structure is pertinent to compound 4a. DFT calculations clearly showed the presence of isomers with very similar energy levels; furthermore, the difference observed between the wavenumbers of the C=O groups, 8 cm$^{-1}$, was consistent with the calculated difference. Thus, the observed spectroscopic differences can be attributed to stereoisomers of compound 4a with a Type I structure. As predicated by the calculated isomers, each carbon showed two signals, as seen in Figures 2-4a.

The structure of compound 8a was assigned to Type III based on the spectroscopic patterns. DFT calculations showed two possible coordination types: Types 3a and 3b, depicted in Figure 4. The Ag-O=C bond length in Types 2 and 3a was 2.603 Å and 2.641 Å, respectively; however, a shorter bond length of 2.410 Å was calculated for Type 3b. Thus, the bond strength of Ag-O=C in Type 3b is stronger than in Types 2 and 3a. In accordance with the strong Ag-O=C bond strength, the FT-IR spectrum of compound 8a shows C=O shifted to lower wavenumber. In addition, the observed COO absorption bands are similar to the calculated bands. Therefore, the structure of compound 8a is more likely Type 3b rather than Type 3a.
Figure 4 Optimized structures of silver β-ketocarboxylates. The green dots show BCPs and small red dots show RCPs. The electron density threshold value for defining “weak” BCPs is 0.025 a.u.

Table 2 Calculated energies and vibrational frequencies of COO- and CO stretching modes with strong IR intensities.

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<thead>
<tr>
<th>Type</th>
<th>(E ) (hartree)</th>
<th>(\Delta E ) a) (kcal/mol)</th>
<th>(\Delta E_{ZPE} ) a,b) (kcal/mol)</th>
<th>(v) (COO') (cm(^{-1}))</th>
<th>(v) (CO) (cm(^{-1}))</th>
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a) Relative energies to Type 1a.

b) Including vibrational zero point energy correction.
4) Relationship between thermal decomposition and structure

The factors affecting the formation of metallic silver upon thermal decomposition of silver(I) dicarboxylates have been discussed in terms of bonding strength to the Ag⁺, the structure of the intermediate, and the length of the Ag-Ag bond. Similarly, the thermal decomposition of silver(I) β-ketocarboxylates 1a-8a were examined. As discussed above, the thermal decomposition temperature of compounds 1a-4a (130–176 °C), compounds 5a-7a (101–121 °C), and compound 8a (109–114 °C), coupled with spectroscopic data and the results of AIM calculations, suggest these compounds be categorized as Type 1a or 1b, Type 2, and Type 3a or Type 3b, respectively.

Burleva examined the relationship between decomposition temperature and structure of silver dicarboxylates Ag₂O₂C(CH₃)₂CO₂Ag and determined that decomposition temperature depended on the strength of the Ag-O bond. The bond strength between Ag and the oxygen atom of the carboxylate group in Type 3a [p value: 0.0477 for Ag(1)-O(4)], Type 3b [p value: 0.0217 for Ag(1)-O(2)], and Type 2 [p value: 0.0467 for Ag(2)-O(3)] are weaker than those of Types 1a and 1b [p value: ca. 0.068]. The decrease in p value of Type 3a, Type 3b, and Type 2 compounds was attributed to the coordination of Ag⁺ by the C=O group. According to the relationship suggested by Burleva, a decrease in the bond strength between the Ag ions and carboxylates decreases the decomposition temperature. Compounds categorized as Types 2, 3a, and 3b, which have lower p values, are expected to decompose at lower temperatures than Type 1a or 1b compounds. In fact, compounds 1a-4a, categorized as Type 1a or 1b, decomposed at 130–176 °C, and compounds 5a-8a, categorized as Types 2, 3a, and 3b, decomposed at 101–121 °C. Thus, the thermal decomposition temperature of silver(I) β-ketocarboxylates depended on the strength of the bond between Ag and the oxygen atom of the carboxylate group; a decrease in strength due to C=O group participation caused a decrease in the decomposition temperature.

Compounds 1a-4a were categorized as Types 1a and 1b; no coordination occurred between the Ag⁺ and the C=O groups, but C=O group participation might occur during the thermal decomposition. As shown in Table 1, the decomposition temperature increased with the bulkiness of R¹. The small differences in potential energy (< 10 kcal/mol) indicate that each type could be converted to another type. Thus, the calculations conducted on the model compound suggested that the C=O group may participate in coordination to Ag⁺ during thermal decomposition. It is likely that increased bulkiness may disrupt coordination by the C=O group. In the Type 1 compounds 1a-4a, an increase in the bulkiness of R¹ increased the decomposition temperature. Furthermore, simple silver aliphatic carboxylates lacking a C=O group decomposed at temperatures above 200 °C, indicating that the coordination of C=O to Ag ion lowers the decomposition temperature.

Silver(I) β-ketocarboxylates 1a-8a were characterized by both their lower decomposition temperature and abrupt decomposition observed by thermal analysis. The abrupt decomposition indicates the decomposition mechanism. Products derived from ketoradicals were observed by mass analysis. Observation of ketoradical-derived products coupled with the results of DFT and AIM calculations allowed the proposal of a mechanism of decomposition. The coordination of C=O to Ag ion may lead to formation of Ag(C=O)⁺ by electron transfer, as well as by the single electron-reduction proposed by Olson. In particular, the structure of Type 2 and Type 3a compounds are similar to that of the intermediate, making them conducive to electron transfer. After electron transfer, successive bond-cleavages yield products derived from the keto radical, CO₂, and metallic silver.

The short Ag-Ag bond suggested by Tolochko is likely to be advantageous for the formation of (Ag₂)⁺ by electron transfer. The Ag-Ag distance in the dimeric structure in Types 1a and 1b, Type 2, and Type 3a obtained by AIM calculations were 2.831–3.29 Å, similar to that of simple silver aliphatic carboxylates. However, Type 3b compounds showed a non-bonding Ag-Ag bond distance (3.669 Å). Compound 8a belongs to Type 3b and yet decomposed abruptly at 109–114 °C. Consequently, the effect of the bond distance between Ag-Ag needs to be reconciled with the calculations for structural changes of compound 8a and/or the model compound with the observed formation of silver radical cation.

Initially, silver(I) β-ketocarboxylates were expected to decompose inherently via the well-known six-membered ring transition state, similar to that shown in Scheme 1, or silver(I) dicarboxylates were expected to decompose via Olson’s intermediate. The calculated structures suggested that the decomposition of dimeric Type 2 and Type 3a, b compounds may proceed via a deformed six-membered ring transition state involving the C=O group, and that in Type 1a and b compounds, the structures may be deformed to a Type 2 or Type 3-like structure. Thus, the substituent of R² decides the Types of the structures and in Type 1: compound 1a-4a, increasing the bulkiness of R¹, transformation to the expected intermediate: Type 2- or Type 3a-like intermediate requires higher temperature. The characteristic sharp thermal decompositions of silver(I) β-ketocarboxylate at lower temperatures can be attributed to the coordination of the C=O group to the Ag⁺ ion. Viewed from another perspective, the decomposition temperature can be controlled by intramolecular or intermolecular coordination to the Ag⁺ ion. To understand the decomposition processes in detail, the structures of silver(I) β-ketocarboxylates with R¹ and R² substituents are currently being determined.

Conclusions

A series of silver(I) β-ketocarboxylates were prepared by reaction of β-ketocarboxylic acids from the corresponding esters with silver nitrate in the presence of diethanolamine. The obtained silver(I) β-ketocarboxylates thermally decomposed at lower temperature than silver(I) aliphatic carboxylates over a narrow temperature range and afforded metallic silver, volatile ketones, and CO₂. Product analysis by DART-MS and GC-MS indicated the involvement of radical intermediates during decomposition.

Differences in the decomposition temperatures of silver(I) β-ketocarboxylates, together with IR and solid ¹³C-NMR spectral data, allowed their classification into three structural categories: Type I, as well as silver(I) stearate with an eight-membered ring structure, Type II, and Type III. The β-carbonyl group is proposed to be involved in coordinating Ag⁺ in Type II and Type III compounds. The proposed structures were verified by calculating the structures of a simple model compound, HCOCH₂COOAg, using DFT and AIM methods. Three types of calculated structures, Types 1a-b, Type 2, and Type 3b, corresponded to the proposed structures Type I, Type II, and Type III, respectively. The three categories differed significantly in Ag-O bond strength. The decreased bond strength of the Ag-O bond caused by C=O group participation lowered the decomposition temperature. Coordination of C=O to Ag ion resulted in smooth electron transfer during decomposition to yield (Ag₂)⁺. The apparent similarity of the Type 2 and Type 3a structures to the intermediate made compounds 5a-8a favorable...
for electron transfer. After electron transfer, successive bond-cleavages yielded products derived from the keto radical, as well as CO₂ and metallic silver.

Silver(I) β-ketocarboxylates thermally decompose into volatile ketones and metallic silver without the need for a chemical reducing reagent. Consequently, silver(I) β-ketocarboxylates are potent compounds for the formation of metallic silver by thermal decomposition and are a useful source of metallic silver for industrial materials.

Acknowledgements
We wish to express our gratitude to Ms. Asano, Dr. Shu, Mr. Haneoka, and Mr. Matsuzaki of the Comprehensive Analysis Center at ISIR, Osaka University. This work was partially supported by NEDO JAPERA project in 2014.

Notes
Silver(I) n-propionylacetate (Silver(I) 3-oxopentanoate) (1a): colorless microcrystals; 80% yield; ¹³C NMR (600MHz, Solid); δ 6.8(CH₂), 34.9(CH₂CH₂CO₂), 51.2(CO₂CH₂CO₂), 174.7(CO₂), 203.8(CO); Elemental analysis (measured values; C 26.87, H 2.95, calculated values; C 26.93, H 3.16); TG(138°C 55.7%, 280°C 51.5%, 350°C 50.5%, theoretical silver content 48.4%); DART-MS (ESI+, 12V) m/z 73 (M⁺ + 1) 9, 143 (2M⁺ - 1)100, 213 (3M⁺ - 3)44, (M⁺ = M - (CO₂Ag) + 1: C₂H₅COCH₂);

Silver(I) n-butyrylacetate (Silver(I) 3-oxohexanoate) (2a): colorless microcrystals; 76% yield; ¹³C NMR (600MHz, Solid); δ 12.9(CH₃), 16.5(CH₂CH₂CO₂), 44.2(CH₂CH₂CO₂), 52.2(CO₂CH₂CO₂), 175.1(CO₂), 203.7(CO); Elemental analysis (measured values; C 30.39, H 3.69, calculated values; C 30.40, H 3.84); TG(148°C 55.7%, 280°C 48.9%, 350°C 47.8%, theoretical silver content 45.6%); DART-MS (ESI+, 12V) m/z 87 (M⁺ + 1) 6, 171 (2M⁺ - 1)100, 255 (3M⁺ - 3)31, (M⁺ = M - (CO₂Ag) + 1: CH₃(CH₂)₂COCH₂);

Silver(I) iso-butyrylacetate (Silver(I) 4-methyl 3-oxopentanoate) (3a): colorless microcrystals; 83% yield; ¹³C NMR (600MHz, Solid); δ 17.5(CH₃), 18.7(CH₃), 40.2(CH₂CO₂), 50.4(CO₂CH₂CO₂), 175.2(CO₂), 207.2(CO); Elemental analysis: (measured values C 30.33 H 3.65 calculated values C 30.41 H 3.84); TG(150°C 51.9%, 280°C 46.3%, 350°C 45.5% theoretical silver content 45.6%); DART-MS (ESI+, 12V) m/z 87 (M⁺ + 1)15, 171 (2M⁺ - 1)100, 255 (3M⁺ - 3)51, (M⁺ = M - (CO₂Ag) + 1: (CH₃)₂CH₂COCH₂);

Silver(I) t-pivaloylacetate (Silver(I) 4,4-dimethyl 3-oxopentanoate) (4a): colorless microcrystals; 84% yield; ¹³C NMR (600MHz, Solid); δ 27.0, 27.2(CH₃), 44.0, 44.3(CO₂), 48.0, 49.4(CO₂CH₂CO₂), 174.1, 175.2(CO₂), 209.1, 210.6(CO); Elemental analysis: (measured values C 33.42 H 4.47 calculated values C 33.49 H 4.42); TG(176°C 43.2%, 280°C 42.3%, 350°C 41.8% theoretical silver content 43.0%); DART-MS (ESI+, 12V) m/z 101 (M⁺ + 1)31, 199 (2M⁺ - 1)67, 279 (2M⁺ + 79, 3M⁺ - 3 – 18)100, 297(3M⁺ - 3)49, (M⁺ = M - (CO₂Ag) + 1: (CH₃)₂COCOCH₂);

Silver(I) β-methylacetooacetate (Silver(I) 2-methyl 3-oxobutyrate) (5a): colorless microcrystals; 65% yield; ¹³C NMR (600MHz, Solid); δ 14.6(CH₃CH₂), 28.7, 29.0(CH₂CO₂), 56.4, 57.7(CO₂HCO₂), 176.0, 177.4(CO₂), 202.9, 203.2, 210.7, 211.1(CO); Elemental analysis (measured values; C 26.64, H 2.88, calculated values; C 26.93, H 3.16); TG(109°C 57.2%, 280°C 51.1%, 350°C 50.6% theoretical silver content 48.4%); DART-MS (ESI+, 12V) m/z 73 (M⁺ + 1)61, 143 (2M⁺ - 1)100, 195(2M⁺ + 51)42, (M⁺ = M - (CO₂Ag) + 1: CH₃CO₂CH₂H₃);

Silver(I) β-ethylacetooacetate (Silver(I) 2-ethyl 3-oxobutyrate) (6a): colorless microcrystals; 71% yield; ¹³C NMR (600MHz, Solid); δ 13.0(CH₂CH₃), 22.2, 25.0(CH₂CH₂CH₃), 29.0, 30.9(CH₂CO₂), 60.6, 63.0, 63.9, 68.3(CO₂HCO₂), 172.8, 173.5, 175.7(CO₂), 200.9, 204.2, 210.2(CO); Elemental analysis: (measured values; C 30.11, H 3.68, calculated values; C 30.40, H 3.84); TG(121°C 53.2%, 280°C 47.3%, 350°C 46.4% theoretical silver content 45.6%); DART-MS (ESI+, 12V) m/z 87 (M⁺ + 1)38, 171 (2M⁺ - 1)100, 255 (3M⁺ - 3)7, (M⁺ = M - (CO₂Ag) + 1: CH₃CO₂(CH₂)₃CH₂);

Silver(I) β-butylylacetooacetate (Silver(I) 2-n-butylyl-3-oxobutyrate) (7a): colorless microcrystals; 84% yield; ¹³C NMR (600MHz, Solid); δ 13.8(CH₂CH₃), 22.2, 23.5, 25.5, 26.5(CH₃), 29.9, 31.5(CH₂CO₂), 60.4, 62.2, 62.5, 65.0(CO₂HCO₂), 172.5, 173.6, 176.0, 177.6(CO₂), 210.3, 202.9, 209.6, 210.6(CO); Elemental analysis: (measured values; C 36.14, H 4.86, calculated values; C 36.25, H 4.94); TG(119°C 53.2%, 280°C 41.7%, 350°C 40.0% theoretical silver content 40.8%) DART-MS (ESI+, 12V) m/z 115 (M⁺ + 1)99, 227 (2M⁺ - 1)100, 339 (3M⁺ - 3)9, (M⁺ = M - (CO₂Ag) + 1: CH₃CO₂(CH₂)₃CH₂);

Silver(I) β-benzylacetooacetate (Silver(I) 2-n-benzyl-3-oxobutyrate) (8a): colorless microcrystals; 83% yield; ¹³C NMR (600MHz, Solid); δ 33.8(CH₃), 35.3, 36.6(CH₂), 64.3(CO₂HCO₂), 126.0, 129.0, 139.9, 141.3(CH₂), 171.6(CO₂), 210.6(CO); Elemental analysis: (measured values; C 44.02, H 3.52, calculated values; C 44.18, H 3.71); TG(97°C 99.4%, 104°C 84.8% 114°C 81.0% 280°C 46.5%, 350°C 43.6% theoretical silver content 36.1%); DART-MS (ESI+, 12V) m/z 149 (M⁺ + 1)36, 295 (2M⁺ - 1)100, 441 (3M⁺ - 3)12, (M⁺ = M - (CO₂Ag) + 1: CH₃CO₂(CH₂)₂C₂H₄);

References
Supporting Information.

\(^\text{C}-\text{NMR data of Compounds 1a-8a}\)
\(^\text{FT-IR data of Compounds 1a-8a}\)
\(^\text{Dart Mass data of Compounds 1a-8a}\)
\(^\text{GC Mass data of Compounds 7a-8a}\)
\(^\text{TG data of Compound 1a-8a}\)
\(^\text{DSC data of Compounds 1a-8a}\)
\(^\text{XRD data of Inorganic residue: Compounds 1b-8b}\)

Cartesian coordinates of optimized structures