

Silver(I) Carboxylates. I. Mass Spectra and Low Frequency Infrared Spectra

S. K. ADAMS, D. A. EDWARDS and R. RICHARDS

School of Chemistry and Chemical Engineering, University of Bath, Bath BA2 7AY, U.K.

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The mass spectra of six silver(I) carboxylates, AgO_2CR , ($R = Me, Et, Pr^n, Ph, CF_3$ and $(CF_2)_2CF_3$) show these compounds to be dimeric in the vapour phase, the base peak being the ion $Ag_2(O_2CR)^+$ in each case. Two fragmentation pathways are observed. The alkyl carboxylates initially lose mainly $RCO_2\cdot$ from the radical ion $Ag_2(O_2CR)_2^+$, whereas the benzoate and the perfluorocarboxylates also easily lose carbon dioxide from the radical ion leading to the formation of abundant organosilver ions. The low frequency ($500\text{--}40\text{ cm}^{-1}$) infrared spectra of these silver(I) carboxylates are compared with the spectra of the copper(I) analogues and bands selected which may be assigned to predominantly skeletal modes.

Introduction

Mass spectral studies of thallium(III)¹, molybdenum(II)^{2,3}, and rhodium(II)⁴ carboxylates have recently been reported. Some attention has also been focussed on the hitherto poorly characterised copper(I) carboxylates, including their mass spectral fragmentation patterns. Westmore and co-workers⁵ examined the thermal decomposition of copper(II) acetate and benzoate in a mass spectrometer and found amongst the products the copper(I) analogues. This work has recently been extended⁶ to a study of 25 copper(II) carboxylates and in 11 cases fragment ions derived from the corresponding copper(I) carboxylates were detected. We have previously reported the mass spectra of eight copper(I) carboxylates^{7,8} and Ogura and Fernando⁹ have carried out a similar study. The three independent studies are in general agreement that the major ions observed result from fragmentation of binuclear species. This interpretation is aided by the knowledge that such binuclear units are present in the solid state structure of copper(I) acetate^{10,11}, albeit linked together into a plane polymer by further weak copper–oxygen interactions. We alone however, have also observed ions in very low abundance containing three and four copper atoms, being an indication that the polymer is not solely broken down into binuclear

units on volatilisation, but that low concentrations of more highly associated species are also present.

X-ray single crystal structure studies of silver(I) perfluorobutyrate¹² and 3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanoate hydrate¹³ have revealed the presence of centrosymmetric binuclear units containing bridging carboxylate groups, the units being linked into polymeric structures by further weak silver–oxygen interactions. During a study of silver(I) carboxylates we have found several of these compounds to be sufficiently volatile to allow examination of their mass spectra. It was felt that a comparison with the fragmentation patterns of copper(I) carboxylates would be valuable and should provide evidence that a binuclear unit may be a common structural feature of silver(I) carboxylates.

The low frequency infrared spectra of the silver(I) carboxylates have also been recorded. Although metal carboxylates have been extensively studied in the sodium chloride infrared region, only a little effort has been devoted to a study of such compounds in the low frequency region. For carboxylate complexes the assignment of metal–oxygen stretching frequencies may be difficult in the presence of other metal–ligand modes, so that even for hydrates, metal–carboxylate oxygen, metal–water oxygen stretches as well as co-ordinated water librational modes and skeletal bending modes will all appear in the low frequency region and the modes may be significantly coupled with carboxylate internal vibrations. Recently however, the metal isotope shift method has been used to advantage¹⁴ in assigning copper–oxygen stretching frequencies of copper(II) carboxylate complexes. Anhydrous carboxylates should be suitable compounds for a study of skeletal modes and some results of this type have been presented for a variety of formates and acetates¹⁵, trifluoroacetates¹⁶, lanthanide carboxylates¹⁷, mercury(I) and (II) acetates¹⁸, several molybdenum(II) and rhodium(II) carboxylates^{19,20} and indium(III) formate and acetate²¹. We report here the low frequency infrared spectra of some silver(I) carboxylates, together with related results for copper(I) carboxylates obtained for comparative purposes.

Experimental

Silver(I) carboxylates were prepared by a published method²² or by adding a slight excess of silver(I) oxide to a stirred aqueous carboxylic acid solution at 50°C followed by filtration and crystallisation. Copper(I) carboxylates were prepared as before⁸. Unsuccessful attempts were made to prepare silver(I) formate, some reduction to the metal always being evident.

Mass spectra were recorded using A.E.I. MS 12 and MS 902 mass spectrometers, some spectra being obtained at the Physicochemical Measurements Unit, Harwell. Samples were introduced into the ionisation chamber on direct insertion probes, the source temperature being increased until the spectrum was of sufficient intensity to be precisely measured, this generally being in the range 170–250°C. An ionisation energy of 70 eV and a trap current of 100 μA was employed. Ion abundances were obtained by summation of the isotope contributions observed for a particular ion, such abundances being expressed relative to a silver-containing base peak of 100 units.

Infrared spectra were recorded using a Perkin-Elmer 621 spectrophotometer, with samples prepared as paraffin mulls held between caesium iodide plates, and using a R.I.I.C. FS 720 interferometer with samples dispersed in polyethylene.

Results and Discussion

Mass Spectra

The mass spectra of six silver(I) carboxylates have

been examined, Table I listing the observed metal-containing ions, their intensities being given relative to a metal-containing base peak of 100 units. These ions are readily identified by a consideration of the isotopic abundances ¹⁰⁷Ag 51.8% and ¹⁰⁹Ag 48.2%. Considering metal isotopes only, ions containing two silver atoms display a pattern of three peaks, each two mass units apart, with relative intensities in good agreement with the calculated ratio 1:1.866:0.865. Only silver-containing ions have been considered, the origin of the many organic ions not being clear since unfortunately no significant metastable peaks have been detected.

It is apparent from the data of Table I that the Ag(O₂CR)⁺ ion has not been found for any of the carboxylates and generally few mono-silver ions have been detected apart from the highly abundant Ag⁺ which must be expected as the final product in any fragmentation sequence. Since the relative intensities of the few mono-silver ions remain essentially constant on varying the source temperature it is reasonable to suggest that they arise by fragmentation of di-silver ions and that no significant concentrations of monomer are present in the vapour. Apart from the n-butyrate, where Ag₃[O₂C(CH₂)₂CH₃]₂⁺ (relative intensity 0.2; m/e 495, 497, 499, 501 in the ratio 1:2.79:2.59:0.80) has been detected, there is no evidence that species of higher association than the dimer are present in the vapour in detectable amounts. This situation is different from that of the analogous copper(I) carboxylates where very low abundances of fragment ions derived from trimers and tetramers were detected^{7,8}. All the

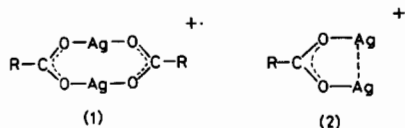
TABLE I. Monoisotopic Mass Spectra of AgO₂CR (based on ¹⁰⁷Ag).

Ion	R = CH ₃		R = CF ₃		R = CH ₂ CH ₃		R = (CH ₂) ₂ CH ₃		R = (CF ₂) ₂ CF ₃		R = C ₆ H ₅	
	m/e	R.I.	m/e	R.I.	m/e	R.I.	m/e	R.I.	m/e	R.I.	m/e	R.I.
Ag ⁺	107	8.1	107	23.6	107	17.6	107	11.3	107	36.1	107	72.0
Ag(OC) ⁺					135	2.9						
AgR ⁺							150	4.0				
Ag(O ₂ C) ⁺	151	3.7			151	5.6	151	6.3				
Ag ₂ ⁺	214	16.9	214	18.0	214	34.7	214	22.7	214	15.6	214	48.0
Ag ₂ H ⁺					215	4.5	215	9.4				
Ag ₂ CH ₃ ⁺	229	5.5					229	0.8				
Ag ₂ O ⁺	230	3.7	230	4.0	230	3.1	230	1.4	230	2.6		
Ag ₂ OH ⁺					231	0.7	231	0.8				
Ag ₂ F ⁺			233	12.2					233	8.3		
Ag ₂ R ⁺	229	5.5	283	36.4	243	0.5	257	0.7	383	26.0	291	64.2
Ag(O ₂ CR)R ⁺							237	0.5				
Ag ₂ (O ₂ C) ⁺					258	0.6	258	0.2				
Ag ₂ (CH ₃)R ⁺							272	0.4				
Ag ₂ (O ₂ CR) ⁺	273	100	327	100	287	100	301	100	427	100	335	100
Ag ₂ (O ₂ CR)R ⁺			396	6.7	316	0.5	344	0.8	596	4.5	412	42.1
Ag ₂ (O ₂ CR)(O ₂ C) ⁺	317	11.0			331	1.3	345	0.6				
Ag ₂ (O ₂ CR) ₂ ⁺	332	7.0			360	0.4	388	0.2				
Ag ₂ R ₂ ⁺											368	6.0

major fragment ions therefore contain two silver atoms, the base peak in each case being the even-electron ion $\text{Ag}_2(\text{O}_2\text{CR})^+$. The parent dinuclear molecular ion, $\text{Ag}_2(\text{O}_2\text{CR})_2^{+ \cdot}$, have only been detected where $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n$, and not for the perfluorocarboxylates where the electron withdrawing nature of the $-\text{CF}_3$ and $-(\text{CF}_2)_2\text{CF}_3$ groups will destabilise the molecular ions. Further, the molecular ions are radical ions, a feature which may mitigate against stability. Since the perfluorobutyrate¹² and the 3-hydroxy-4-phenyl-2,2,3-trimethyl-cyclohexanoate¹³ are known to contain centrosymmetric carboxylate bridged dimers in the solid state, it is logical to suggest that the molecular ions will be of the type 1, a structure in accord with the known preference for silver(I) to exhibit essentially linear co-ordination.

This cyclic radical ion can be described with the odd electron residing on either a carbon atom or a silver atom of the ring. The latter suggestion involving oxidation to silver(II) is reasonable since, for example, several silver(II) pyridinecarboxylates are well established²³. However, the most satisfactory bonding description of the radical ion would involve delocalisation of the positive charge and unpaired electron over the π -orbitals of both carboxylate groups and both silver atoms. Such delocalisation provides an explanation of the stability of the radical ion, unless R is an electron withdrawing group.

The base peak, $\text{Ag}_2(\text{O}_2\text{CR})^+$, is formed from the molecular ion by loss of $\text{RCO}_2 \cdot$. This may occur by sequential loss of $\text{R} \cdot$ and CO_2 , as evidenced by the detection of $\text{Ag}_2(\text{O}_2\text{CR})(\text{O}_2\text{C})^+$ where $\text{R} = \text{Me}, \text{Et}$, and Pr^n , but since this ion is not observed for the other carboxylates, a simultaneous loss of $\text{R} \cdot$ and CO_2 is also likely. $\text{Ag}_2(\text{O}_2\text{CR})^+$ is evidently very stable in each case, and a reasonable structure derived from the fragmentation of 1 is the cyclic structure 2. Although it is not necessary to postulate direct silver-silver bonds



in the solid carboxylates, nor in the molecular radical ion, the silver-silver distances in the two carboxylates whose solid state structures are known^{12,13}, are in the range 2.78–2.90 Å, similar to the separation in silver metal (2.89 Å). Other fragment ions containing two silver atoms in which direct silver-silver interactions must be considered include Ag_2R^+ , Ag_2F^+ , Ag_2H^+ and obviously $\text{Ag}_2^{+ \cdot}$.

The major fragmentation for all six carboxylates is the loss of $\text{RCO}_2 \cdot$ from the binuclear radical ion. However, particularly where $\text{R} = \text{Ph}$ or a perfluoroalkyl group, fragment ions produced by decarboxylation and migration of R to a silver atom to give organosilver ions are prominent. For these examples the radical

ions $\text{Ag}_2(\text{O}_2\text{CR})\text{R}^+$ and $\text{Ag}_2\text{Ph}_2^{+ \cdot}$ are observed in high relative abundance and the even-electron Ag_2R^+ ions are much more abundant than in the examples where $\text{R} = \text{alkyl}$. This situation can be related to the known²⁴ greater stability of σ -bonded aryl- and perfluoroalkyl-silver compounds compared with alkylsilver species. A similar picture has emerged⁸ from the mass spectra of the copper(I) analogues.

A further fragmentation route has been observed for the n-butyrate, since as well as loss of $\text{RCO}_2 \cdot$ and CO_2 from the binuclear radical ion, the elimination of ethylene and carbon dioxide with migration of the remaining methyl group to the metal leads to the observation of $\text{Ag}_2(\text{CH}_3)\text{R}^+$ and Ag_2CH_3^+ ions.

Other significant ions in the spectra are the even-electron Ag_2H^+ and Ag_2F^+ and the odd-electron $\text{Ag}_2\text{O}^{+ \cdot}$, the latter being observed in all cases except the benzoate. Their precursor is likely to be $\text{Ag}_2(\text{O}_2\text{CR})^+$. In the perfluorocarboxylates, Ag_2F^+ is formed to the exclusion of Ag_2H^+ and in greater abundance than $\text{Ag}_2\text{O}^{+ \cdot}$, a feature probably related to the greater Ag-F bond strength compared with either Ag-O or Ag-H. Ag_2H^+ is not observed for the acetate, presumably because the formation of CH_2 and CO_2 from CH_3COO would require much energy.

Infrared Spectra

Table II lists the low frequency (500–40 cm^{-1}) spectra of five of the silver(I) carboxylates studied by mass spectrometry together with their copper(I) analogues. The two monochloroacetates are also included, but data on the perfluorobutyrate have not been listed, the spectra being complex in this region due to the presence of many bands associated with perfluorobutyrate bending modes. Modes localized mainly within the carboxylate groups have been assigned by comparison with the spectra of the corresponding sodium salts. The spectra of some of the copper(I) carboxylates were only recorded to 200 cm^{-1} , as indicated in Table II.

The spectra are quite complex in this region, a feature probably associated with the low overall symmetry of the polymeric carboxylates. They presumably possess, as suggested by the mass spectral results, similar structural features to those established for silver(I) perfluorobutyrate¹² and copper(I) acetate^{10,11}, namely binuclear centrosymmetric eight-membered ring systems, linked by further weak metal-oxygen interactions into polymers. For example, copper(I) acetate has three types of Cu-O bonds with lengths of 1.89, 1.90 and 2.31 Å, so it is to be expected that the skeletal bands will be found over a wide frequency range, and, further, some coupling between the various modes including the internal carboxylate modes is likely.

The few infrared spectra recorded in the low frequency region for centrosymmetric binuclear acetates, namely chromium(II)²⁶, copper(II)^{15,25,26}, molybde-

TABLE II. Low Frequency Infrared Spectra (cm^{-1}).

Carboxylate	Carboxylate Modes	ν (M–O)	Other Skeletal and Lattice Modes
CuO_2CCH_3		381m, 374sh	242m, 190mw, 178mw, 122m
AgO_2CCH_3		284m	210m, 164w, br, 100mw, 56mw
$\text{CuO}_2\text{CCH}_2\text{CH}_3^a$	449m	377m, 314s	300m, 269m
$\text{AgO}_2\text{CCH}_2\text{CH}_3$	350m	252m	146m, br, 83m, 46w
$\text{CuO}_2\text{C}(\text{CH}_2)_2\text{CH}_3^a$	478m, 435m	311m	287m, 255s, 202m
$\text{AgO}_2\text{C}(\text{CH}_2)_2\text{CH}_3$	400s	273m	232s, 173m, 115m
$\text{CuO}_2\text{CCF}_3^a$	498m, 323w, 284s	343m	269s, 246s
AgO_2CCF_3	457s, 315s, 283s	193m	159m, 125m, 61m
$\text{CuO}_2\text{CC}_6\text{H}_5$	443vw	345m	287sh, 277w, 249m, 222m, 205m, 144m, br
$\text{AgO}_2\text{CC}_6\text{H}_5$	445m	276s	218m, 198m, 107w, 95w, 81w, 45w
$\text{CuO}_2\text{CCH}_2\text{Cl}^a$	454m, 414w	385sh, 374m	263s, 254sh, 237sh, 224s
$\text{AgO}_2\text{CCH}_2\text{Cl}$	473m	315s, 305sh	212m, br, 183s, 122sh, 110m, 64w, 48w

^a Recorded to 200 cm^{-1} only.

num(II)^{19,20,25}, and rhodium(II)^{20,25}, all include bands assigned to predominantly metal–oxygen stretching frequencies in the 400–300 cm^{-1} region. The bands so assigned in Table II for the present examples refer to the strong metal–oxygen interactions within the eight-membered ring systems. The stretching frequencies of the weaker metal–oxygen bonds linking these units into a polymer will undoubtedly be found at lower frequencies and are listed amongst those designated as other skeletal modes in the Table. The metal–oxygen stretches of the silver(I) carboxylates are markedly lower in frequency than those of the copper(I) analogues, a feature related not only to the heavier mass of silver but also to the greater ionicity of the silver–oxygen compared with the copper–oxygen bonds, particularly evident in the case of silver(I) trifluoroacetate. The spectrum of this carboxylate only has previously been reported¹⁶. Although there is reasonable agreement in band positions for the two sets of results, the bands at 445 and 320 cm^{-1} previously assigned to metal–oxygen modes are more reasonably assigned to rocking and wagging motions of the trifluoroacetate group.

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