for the preparation of $S_4N_4O_2$.

Registry No. **1**, 81260-53-9; [PPN][**1**], 81260-54-0; **2**, 86176-89-8; [PPN][**2**], 86176-90-1; **3**, 37370-07-3; [Bu_4N][**3**], 92526-10-8; **4**, 57932-64-6; **5**, 54460-74-1; **6**, 92526-11-9; **7**, 77133-46-1; S_3N^-, 53596-70-6; S_4N^-, 51330-98-4; $Ph_2CNSSNCPh_2$, 54884-22-9; NSO^-, 73439-98-2; S_4N_4, 28950-34-7; $SNSO^-$, 72704-72-4; $LiClO_4$, 7791-03-9; $NaClO_4$, 7601-89-0; Me_4NClO_4, 2537-36-2; Et_4NClO_4, 2567-83-1; Bu_4NClO_4, 1923-70-2; $PPNClO_4$, 65300-04-1; Pt, 7440-06-4; Hg, 7439-97-6; S, 7704-34-9.

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Mass Spectrometric Investigation of Silver Ion Promoted C–C Bond Scission

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Both the secondary ion mass spectra (SIMS) and the electron ionization mass spectra of silver salts of acetic acid, propionic acid, and benzoic acid exhibit positive ions associated with C–C bond scission. A formal relationship exists with the classical Hünsdiecker reaction in which the essential step is thermal decarboxylation. In both types of mass spectrometric experiments the observation of cationized forms of the hydrocarbon products of the Hünsdiecker reaction strengthens the analogy and suggests that ion beam impact as well as thermal heating can initiate cleavage reactions of silver salts in the solid state. There is also a gas-phase contribution to the C–C scissions observed in the mass spectrometer. This was demonstrated explicitly by mass selection of silver-containing ions and characterization of the fragments formed by collisional activation. Cluster ions C_2A^+, where C is the cation and A the anion, for example $(Ag_2\text{propionate})^+$, fragment to give C–C cleavage products $AgCO_2^+$ and $AgCO^+$, as well as Ag_2OH^+, Ag_2H^+, and Ag_2^+. Metal clusters are particularly prominent in SIMS spectra, which contain abundant Ag_3^+ ions not seen at all in the electron ionization mass spectra. Studies of ions such as Ag_2X^+ (X = H, O, OH, CH_3, CH_3CO_2, and $CH_3CH_2CO_2$) by tandem mass spectrometry reveal that most dissociate to the silver dimer ion Ag_2^+. However, Ag_2H^+ and Ag_2OH^+ do not do so and therefore appear not to contain metal–metal bonds. Parent and daughter spectra were used to obtain information that allows structures for these unusual ions to be formulated.

Introduction

Parellels between reactions occurring in solution and in the mass spectrometer provide insights into chemistry in both milieus. This comparison has been made for unimolecular reactions encountered in electron ionization mass spectrometery[1,2] and for bimolecular ion/molecule reactions carried out under chemical ionization conditions[3-5] in ion cyclotron resonance,[6-8] and in drift tube instruments.[9,10] Striking similarities as well as sharp contrasts have been reported. With the advent of desorption ionization procedures such as secondary ion mass spectrometry (SIMS),[11-13] new types of mass spectrometric reactions are being encountered and comparisons with solution chemistry should continue to be fruitful. This is a new area of activity typified by observations such as the apparent nucleophilic substitution (eq 1) seen in secondary ion

$$[\text{arylN}^+R_3]X^- \xrightarrow[\text{5 keV}]{\text{argon ion}} \text{arylX}^+ + NR_3 \qquad (1)$$
$$X = \text{Cl, Br, I}$$

$$M \xrightarrow[h\nu]{NaNO_3} (M - H + O)^- \qquad (2)$$
$$M = \text{polynuclear hydrocarbon}$$

mass spectrometry[14] and the oxygen displacement reaction (eq 2) observed in laser desorption of polynuclear aromatic hydrocarbons.[15] In some cases reactions accompanying desorption complicate the analysis, as in the examination of thiamine hydrochloride from glycerol matrix, where hydrogenolysis apparently occurs.[16]

The Hünsdiecker reaction[17] is a thermal decarboxylation; the prototype (eq 3) involves the silver salt of the acid in the presence of halogen and mercuric oxide.

$$RCO_2Ag + Br_2 \xrightarrow[HgO]{\Delta} RBr + CO_2 + AgBr \qquad (3)$$

A free-radical mechanism is usually invoked, and the formation of the alkane, RR, as a secondary product supports this postulate. Our interests in the nature of the fragmentation reactions occurring in secondary ion mass spectrometry (SIMS),[18] in organic reactions at silver,[19] and in the fragmentation of silver-containing compounds[20] led us to examine the SIMS spectra of silver salts of organic acids. Ions corresponding to C–C bond cleavage were observed, and this suggested that possible parallels with the Hünsdiecker reaction should be explored. This was done by generating some of the

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[‡] Department of Chemistry.

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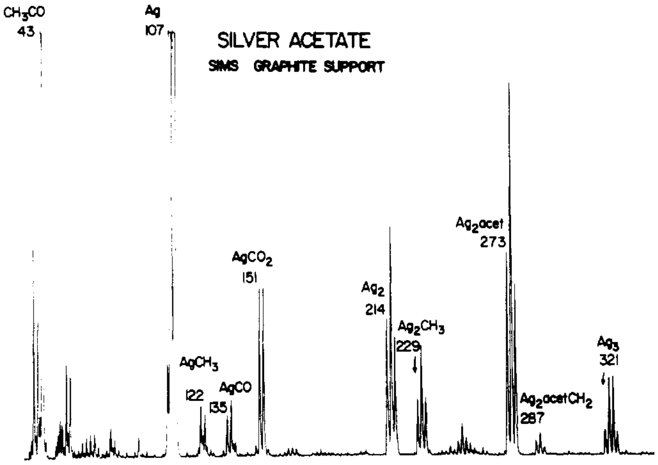

Figure 1. Positive ion SIMS spectrum of silver acetate, including cluster ions such as CAC$^+$ and Ag_3^+, and ions that correspond to cleavage of a C–C bond such as AgCO$^+$, $AgCO_2^+$, and $AgCH_3^+$.

ions observed in SIMS independently by a direct thermal process and characterizing individual mass-selected ions via the gas-phase fragmentations. This mass spectrometry/mass spectrometry (MS/MS) procedure[21] has previously formed the basis for ion structural characterizations that underpin mechanistic studies. The methodology is particularly valuable when rearrangements are suspected and has been applied, for example, to characterize the complex binuclear ions generated from metal methylacetonates[22] on laser irradiation.

Previous investigations of silver carboxylates using electron ionization[23,24] highlight a complex chemistry in the ion source. The tendency of organometallic compounds and inorganic complexes to exhibit cluster ions is manifest by these silver complexes. Metastable ions are valuable in elucidating their fragmentation pathways.[24] In addition to electron ionization, the field desorption spectra of several silver salts of organic acids have been reported;[24] they also exhibit simple cluster ions of the type $Ag_2O_2CR^+$, but no fragment ions occur.

Experimental Section

SIMS. The SIMS instrument has been described previously.[25] The substrate in all instances was roughened graphite foil onto which the solid silver carboxylate was burnished. The sample was bombarded with argon ions of 5-keV energy at an angle of incidence of 45°. The flux of primary ions was monitored at the sample by a picoammeter; currents of 10^{-8}–10^{-7} A/cm^2 were measured with a spot size of 10 mm^2. No sample charging was noted, and the spectra of 0.1-mg samples were stable for several hours. A scan speed of 3 s/amu was used. Output from the pulse-counting detection system was channeled directly to an XY recorder. The SIMS spectra are neither averaged nor corrected for background.

MS/MS. A Finnigan triple-quadrupole mass spectrometer equipped with an INCOS data system was used to obtain MS/MS spectra.[26,27] This instrument consists of three sequential quadrupoles of which the first and third function as mass analyzers, while the second acts as a field-constrained collision region. Various MS/MS experiments have been described in recently published review articles.[21,28,29] In daughter ion scans, the first quadrupole selects by mass the ion of interest, termed the parent ion, and transmits it to the collision region, where it fragments upon collision with a target gas molecule. These fragment ions are mass analyzed by the third quadrupole. Parent ion scans are generated when the third quadrupole is set to pass only a daughter ion of specified mass (e.g. $^{107}Ag^+$), and the first quadrupole is scanned over a large mass range. Any parent ion that fragments to the approproiate daughter ion then produces a signal at the detector.

Table I. Comparison of the Electron Ionization (EI) and Secondary Ionization Mass Spectra (SIMS) of Three Silver Carboxylates[a]

	EI			SIMS		
	acetate	propionate	benzoate	acetate	propionate	benzoate
Ag^+	M	M		S	S	S
RCO^+			S	S		S
RCO_2H^+			S			
$AgCO^+$		W		M	S	
$AgCO_2^+$	W	W	W	S	M	
AgR^+	W	W		M	M	W
AgR_2^+						W
$R_2CO_2^+$			S			
$(R_2CO_2 - H_2)^+$			S			
$(R_2CO - H_2)^+$			S			
Ag_2^+	M	M	W	S	S	M
Ag_2H^+		W			M	W
Ag_2O^+	W	W		W	W	
Ag_2CO^+		W[b]				
$Ag_2CO_2^+$	W[b]	W[b]				
Ag_2R^+	W	W[b]	W	M	W	M
$Ag_2O_2CR^+$	S	S	W	S	S	W
$(Ag_2(O_2CR)CO_2)^+$	M	M				
$(Ag_2(O_2CR)R)^+$		M	W			
$(Ag_2(O_2CR)CH_2)^+$		W		W	W	
$Ag_2(O_2CR)_2^+$	W	W	W[b]			
Ag_3^+				M	M	M

[a] R represents the hydrocarbon portion of the carboxylate; R = CH_3 for acetate, R = C_2H_5 for propionate, and R = C_6H_5 for benzoate. The letters W, M, S represent the relative ion abundance in a given spectrum; W = weak, M = moderate, and S = strong.

[b] Very weak in the mass spectrum although MS/MS spectra could be obtained.

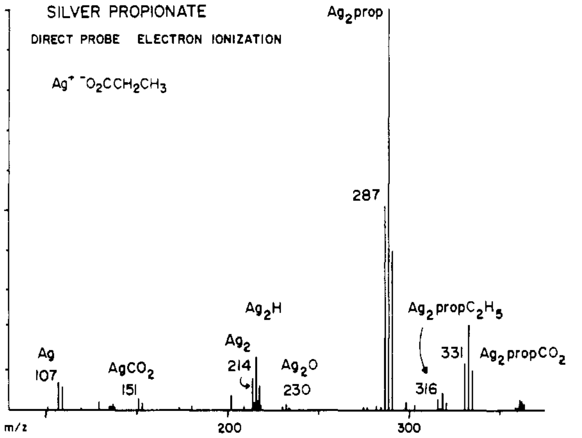

Figure 2. Electron ionization mass spectrum of silver propionate, containing some cluster ions common to those seen in the SIMS spectrum. The dominance of the CAC$^+$ ion is common.

Samples were introduced to the mass spectrometer via a direct-insertion solids probe, which was heated to 300 °C. A standard electron ionization (EI) source was used with an electron energy of 70 eV. Argon was used as the collision gas in the second quadrupole, and the axial kinetic energy of the ions entering the collision quadrupole was set at 20 eV.

Samples. Silver carboxylates used in this study either were available commercially or were synthesized with use of standard methods.[30] We thank Dr. Janelle L. Pierce-Menzie for providing some of these samples. The study focused on the behavior of silver acetate, silver propionate, and silver benzoate. The samples were found to be

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analytically and spectroscopically pure.

Results and Discussion

The ions that occur in the secondary ion mass spectra and EI mass spectra of some silver carboxylates are given in Table I. Figures 1 and 2 show a representative example of each type of spectrum. Of particular interest is the remarkable extent to which C–C bond scission occurs, as evidenced by such ions as $AgCO_2^+$ and $AgCH_3^+$. This can be seen in Figure 1, the SIMS spectrum of silver acetate. In addition to the ions indicative of C–C bond scission, viz. $AgCO_2^+$, $AgCH_3^+$, $AgCO^+$, and $Ag_2CH_3^+$, other major ions present include the cluster ion $Ag_2O_2CCH_3^+$, silver monomer, dimer, and trimer ions, and the acetyl ion. A similar but not identical set of ions has been reported[23,24] to be formed via electron ionization, an observation confirmed by the EI spectrum obtained in the present study. Three prominent features of both the SIMS and the EI spectra of silver acetate are as follows: (i) the occurrence of an abundant cluster ion of the type C_2A^+, where C is the intact cation and A the anion, viz. $Ag_2O_2CCH_3^+$; (ii) the extent to which C–C bond scission occurs, as evidenced by ions such as $AgCO_2^+$ and $AgCH_3^+$; (iii) the formation of ions containing metal–metal bonds, including the simple metal clusters Ag_n^+, where $n = 1, 2, 3$. A significant difference between the EI and the SIMS spectra is the absence in the latter of the low-abundance *radical* cations observed in EI, including the ionized silver acetate dimer.

The SIMS spectrum of silver propionate (Table I) parallels that of silver acetate. The C_2A^+ cluster ion is comparable in relative abundance to Ag^+, and ions corresponding to Ag_2^+, Ag_3^+, $AgCO^+$, $AgCO_2^+$, and $AgC_2H_5^+$ are observed. Carbon–carbon bond scission is again evident from the presence of the ions $AgC_2H_5^+$, $AgCO^+$, and $AgCO_2^+$ and from an ion of low relative abundance, $Ag_2C_2H_5^+$. In its general features, the SIMS spectrum resembles the EI spectrum. However, the EI mass spectrum of silver propionate (Figure 2) differs from the SIMS spectrum in the following particulars: (i) ions containing one and three silver atoms either are greatly reduced in relative abundance ($AgCO_2^+$, $AgC_2H_5^+$, and $AgCO^+$) or are absent (Ag_3^+) in the EI spectrum while (ii) ions apparently derived from the dimer, including $Ag(O_2CC_2H_5)CO_2^+$, $Ag_2(O_2CC_2H_5)C_2H_5^+$, and $[Ag_2(O_2CC_2H_5)_2 - H]^+$, are increased in relative abundance. The EI spectrum obtained in this study is similar but not identical with that reported by other workers.[23,24]

The SIMS spectrum of silver benzoate (Table I) parallels those of the aliphatic salts in some detail. The stability of the aryl group probably accounts for the observation of relatively abundant ions that correspond to $Ag_2C_6H_5^+$, and $AgC_6H_5^+$, while the relative abundances of $AgCO_2^+$ and $AgCO^+$ are negligible. The EI mass spectrum of silver benzoate (Table I) differs from the SIMS spectrum in ways that parallel behavior of the aliphatic silver carboxylates. The dimer ion $(AgO_2CC_6H_5)_2^{+\cdot}$ and ions derived from it are present in the EI spectrum but not the SIMS spectrum. Furthermore, the EI spectrum contains intense ions that do not represent cationized species, including $C_6H_5COOCOC_6H_5^+$, $(C_6H_5)_2^+$, $(C_6H_4)_2^+$, and $(C_6H_5)_2CO^+$. These ions are absent from the SIMS spectrum. The Ag_3^+ ion present in the SIMS spectrum is again absent in the EI spectrum.

The ion structural assignments implicit in the above discussion and summarized in Table I were confirmed by obtaining MS/MS data. The MS/MS daughter spectrum of the ^{107}Ag isotopic version of the cluster ion C_2A^+, $Ag_2O_2CC_2H_5^+$, of silver propionate (Figure 3) shows this ion to be the precursor to most of the lower mass ions observed in the mass spectrum, including $AgCO_2^+$, $AgCO^+$, Ag_2^+, and Ag_2H^+. These compositional assignments were easily confirmed by recording the MS/MS spectra of isotopic variants of the parent cluster ion.[31,32] Clearly the C_2A^+ ion either has or can dissociatively rearrange to give a metal–metal-bonded structure. The MS/MS spectra of the C_2A^+ cluster ions of silver acetate and silver butyrate were also obtained. The fragmentation observed is comparable to that found for silver propionate. The C_2A^+ cluster ion of silver benzoate was also examined by taking its daughter ion spectrum. The major fragmentation process was decarboxylation to give $Ag_2C_6H_5^+$.

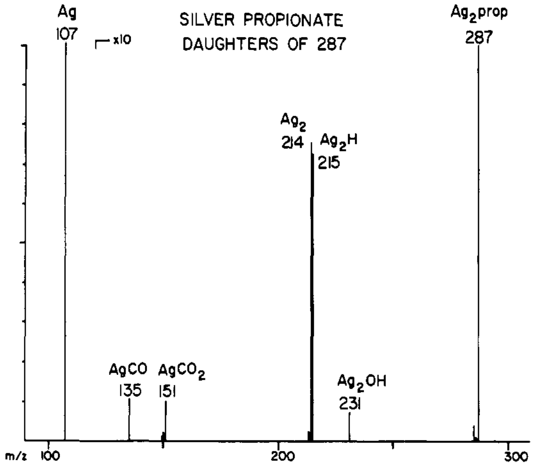

Figure 3. Daughter ion MS/MS spectrum of the CAC^+ ion for silver propionate, $(Ag_2O_2CC_2H_5)^+$ (all ^{107}Ag), showing that gas-phase C–C bond scission can take place but that the primary dissociation forms Ag^+. Ion assignments are confirmed by examining the daughter ion spectra of isotopic variants of the CAC^+ parent ion.

The MS/MS daughter spectra of ions that are suspected of resulting from C–C bond scission, for example $Ag_2O_2CC_2H_5(C_2H_5)^+$, $Ag_2O_2CC_2H_5(CO_2)^+$, $AgC_2H_5^+$, and $AgCO_2^+$ from silver propionate, were obtained. The MS/MS spectrum of $AgO_2CC_2H_5(CO_2)^+$ reveals the loss of CO_2 to form the $Ag_2O_2CC_2H_5^+$ ion (C_2A^+). In similar fashion the MS/MS spectrum of $Ag_2O_2CC_2H_5(C_2H_5)^+$ demonstrates the loss of C_2H_5 to form the C_2A^+ ion. Both spectra support the suspected assignments. In both cases collision-induced dissociation also produces a relatively abundant Ag^+ ion, which is the only fragment ion observed in the MS/MS spectra of $AgC_2H_5^+$ and $AgCO_2^+$. Another example of an ion associated with C–C bond scission is $Ag_2O_2CC_6H_5(C_6H_5)^+$, that is, the product of decarboxylation of the dimer ion of silver benzoate. Its spectrum shows phenyl loss to yield C_2A^+, benzoyl loss to give $Ag_2C_6H_5^+$, and the Ag^+ ion. The facile loss of CO_2 and of phenyl is suggestive of a loosely bound structure for the C–C bond scission product. Analogous conclusions arise from the daughter ion spectra of ions generated from the other silver carboxylates.

Parent spectra, which pinpoint all precursors of a chosen daughter ion, can also be utilized to obtain information concerning reaction pathways. Parent ion spectra of the $^{107}Ag^{107}Ag$ and $^{107}Ag^{109}Ag$ versions of Ag_2^+ and Ag_2H^+ are given in Figures 4 and 5, respectively. The use of two isotopic versions confirms the identity of the parent ions via the appropriate mass shifts.[32] More important than the ions that appear as precursors to Ag_2^+ and the ions that do not, namely Ag_2H^+ and Ag_2OH^+. This result indicates that these two ions do *not* contain metal–metal bonds. The precursors to Ag_2H^+ include the interesting ions $Ag_2H_2^+$, Ag_2HOH^+, and $Ag_2HC_2H_2^+$.

EI spectra, as opposed to SIMS spectra, allow the dimer C_2A_2 to be ionized and observed. The MS/MS spectrum of the ionized dimer was found to yield exclusively $Ag_2O_2CC_2H_5^+$

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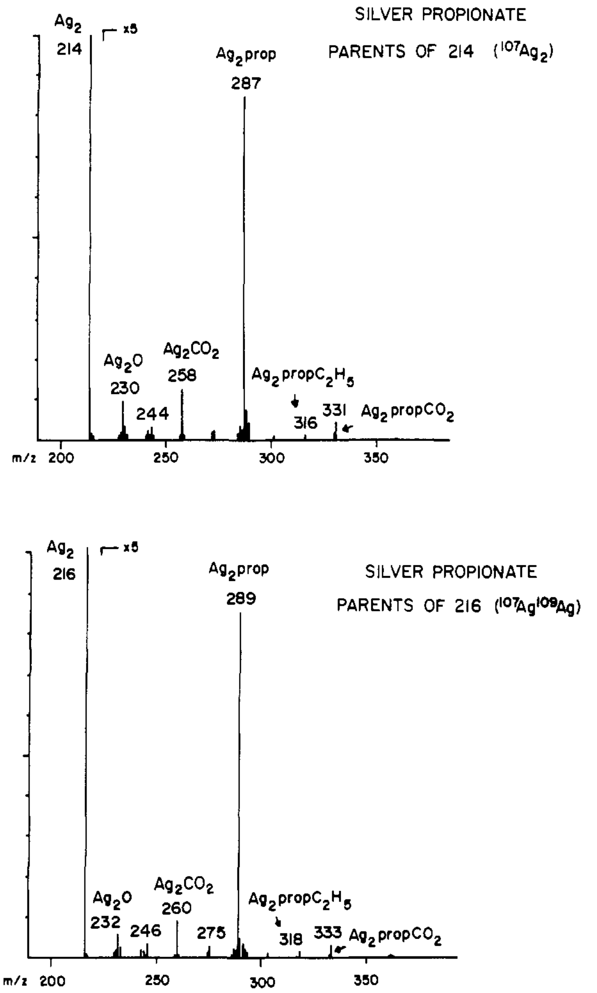


Figure 4. Parent ion MS/MS spectra for the $^{107}Ag^{107}Ag$ and $^{107}Ag^{109}Ag$ versions of Ag_2^+.

and Ag^+, that is the $C_2A_2^+$ parent ion dissociates to C_2A^+ or to C^+. Thus, fragmentation of the cluster ion itself, C_2A^+, appears to be responsible for the *common* features of EI and SIMS spectra. This situation follows well-established precedent in SIMS[21] but is less well-known in conventional electron ionization experiments.[22] The formation of metal–metal bonds occurs with apparent felicity in the fragmentation reactions of the C_2A^+ ion. Analogously, the occurrence of Ag_3^+ (confined to the SIMS spectra) may result from fragmentation of $C_3A_2^+$ or related species, themselves present at extremely low relative abundance (about 0.01%). It would seem reasonable that the SIMS experiment could more readily product these large cluster ions than could electron ionization using the solids probe. Nonetheless, since Ag_3^+ occurs in abundance similar to that of Ag_2^+, high intrinsic stability for this ion is indicated. The structure of the Ag_3^+ ion has indeed been studied; computational methods indicate that it has a triangular configuration and is relatively stable.[33] It has also been noted that the Ag_3 ionization potential is lower than that of other silver clusters Ag_n for $n < 9$.[34,35]

The focal point of this study, comparison of the gas-phase SIMS and EI results with the solution-phase Hünsdiecker reaction, concerns those ions whose formation involves scission of the C–C bond. This bond cleavage may be rationalized by considering the interaction occurring in the silver clusters after sputtering. It is proposed that the Ag^+–carboxylate interactions so weaken the C–C bond in AgO_2CR that cleavage occurs easily upon ionization and transfer to the gas phase, resulting in a set of fragments such as Ag^+, R, CO_2, and RCO_2^-. The ions Ag^+, AgR^+, $AgCO_2^+$, $Ag_2O_2CR^+$, $Ag_2(O_2CR)CO_2^+$, and $Ag_2(O_2CR)R^+$ can be derived from reactions of these initial species. The only major ions not accounted for by this model are the Ag_2X^+ species where X is H, O, OH, or CH_3. Two of these ions are unusual in not containing metal–metal bonds (vide supra).

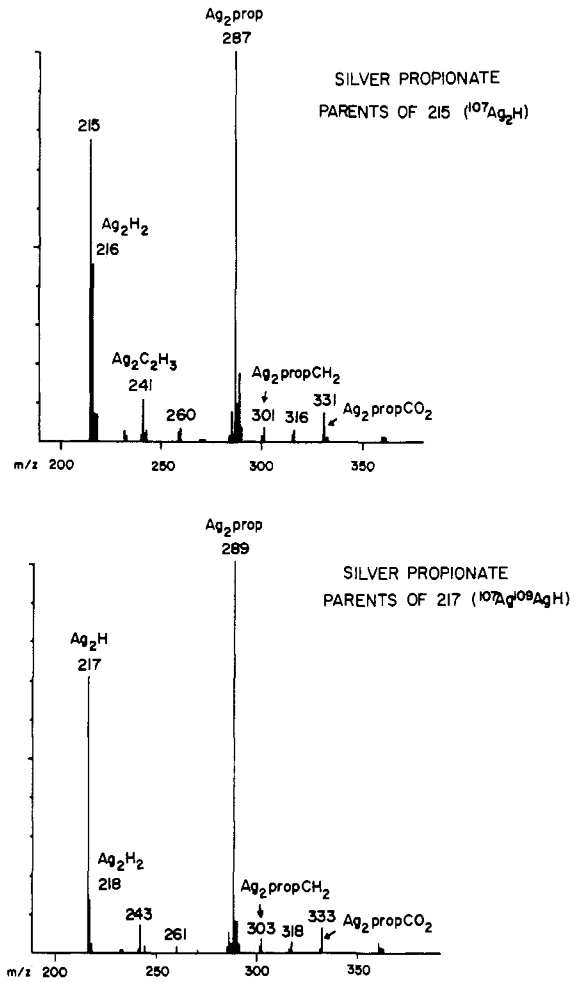
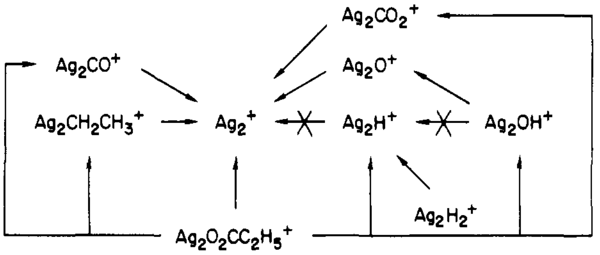


Figure 5. Parent ion MS/MS spectra for the $^{107}Ag^{107}Ag$ and $^{107}Ag^{109}Ag$ versions of Ag_2H^+.

Scheme I



The gas-phase reactions (4)–(7) (as seen in MS/MS) are examples of carbon–carbon cleavage in silver-containing species and are formally analogous to processes that occur in the Hünsdiecker reaction. Analogous reactions have previ-

$$Ag_2O_2CR^+ \rightarrow RAg + AgCO_2^+ \tag{4}$$

$$Ag_2O_2CR^+ \rightarrow ROAg + AgCO^+ \tag{5}$$

$$Ag_2O_2CR^+ \rightarrow AgCO_2 + AgR^+ \tag{6}$$

$$Ag_2O_2CAr^+ \rightarrow CO_2 + Ag_2Ar^+ \tag{7}$$

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ously been observed in the SIMS spectra of amides.[36] It should not be forgotten, however, that the predominant fragmentations of the C_2A^+ ion yield Ag^+, Ag_2^+, and Ag_2H^+, which are *not* C-C bond scissions. It may be possible to account for Ag_2^+ ion formation via Scheme I, which is illustrated for silver propionate and which is based on MS/MS data.

The Ag_2H^+ ion does not arise in a sequential manner as indicated by the absence of the fragmentation routes marked with an "X". This suggests a direct route from $(Ag_2O_2CC_2H_5)^+$ to Ag_2H^+ via loss of $CH_2{=}CHCOOH$. This is consistent with the results of the overall study, which show little or no Ag_2H^+ in the spectra of silver acetate (necessitating loss of an epoxidate) and silver benzoate (loss of a destabilized aromatic ring) but relatively abundant Ag_2H^+ ions for silver butyrate (loss of $CH_3CH{=}CHCOOH$ or an isomer).[24]

An unexpected result in this study were the implications for small silver cluster ion structures. The species encountered here are simple prototypes of metal cluster complexes and as such are of particular importance. Reference has been made to the inability of Ag_2H^+ to yield Ag_2^+ as evidence for lack of a metal-metal bond in the former. Also, since $Ag_2H_2^+$ does not form Ag_2^+, the lack of a metal-metal bond would seem to be indicated here, too. Two linear structures may be imagined ($AgHAgH^+$ or $AgHHAg^+$) as well as a four-membered cyclic structure. Since this ion dissociates readily to form Ag_2H^+, the second linear structure is less likely than the former. The structure and energetics of the Ag_2H^+ ion have been studied with use of computational methods,[37] which show it to be hydrogen bonded. Other Ag_2X^+ ions that appear to contain Ag-Ag bonds are $Ag_2CH_3^+$ and $Ag_2C_6H_5^+$; daughter spectra of these ions show both Ag^+ and Ag_2^+. In the case of $Ag_2CH_3^+$, the daughter spectra are very simple, with Ag^+ and Ag_2^+ being present in 100% and 30% relative abundance, together with a trace of $AgCH_3^+$.

Conclusions

Both secondary ion and electron ionization mass spectra of the silver salts of organic acids contain ions that result from cleavage of a C-C bond, in analogy with the Hünsdiecker reaction in solution. In contrast to the proposed involvement of halogen in the condensed-phase reaction, studies of the MS/MS spectra of cluster ions containing several silver atoms confirm the unimolecular cleavage of these bonds. Formation of side products corresponding to free-radical dissociations is observed, and this is particularly evident in the case of silver benzoate. EI produces ions similar to those observed in SIMS, since both yield the cation/salt complex C_2A^+, although apparently from different precursors. In addition to fragmentation processes involving the C-C bond scission, metal-metal bond formation, as in Ag_2O^+, $Ag_2CH_3^+$, and $Ag_2C_6H_5^+$, is a noteworthy feature of the ion chemistry of silver carboxylic acid salts.

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Registry No. Silver acetate, 563-63-3; silver propionate, 5489-14-5; silver benzoate, 532-31-0.

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The Molybdenum-Molybdenum Triple Bond. 15.[1] Compounds with Chains of Metal Atoms Having M-M Single and Triple Bonds: $M_2(M'(M'Me_3)_3)_2(NMe_2)_4$ ($M{\equiv}M$) Where M = Mo and W and M′ = Si and Sn

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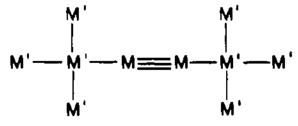
Metathetic reactions involving $M_2Cl_2(NMe_2)_4$ and $(THF)_3LiM'(M'Me_3)_3$, where M = Mo and W and M′ = Si and Sn, carried out at room temperature in hydrocarbon solvents yield yellow-orange crystalline compounds $M_2(M'(M'Me_3)_3)_2(NMe_2)_4$. These compounds have a branched 10 metal atom chain with M′—M′ and M—M′ single bonds and a central $M{\equiv}M$ bond. The compounds have been characterized by infrared, NMR, and mass spectroscopy and, for M = Mo and M′ = Si and Sn, by single-crystal X-ray crystallography. They are members of a series of compounds of formula $1,2\text{-}M_2X_2(NMe_2)_4$, which adopt the anti-ethane-like geometry in both the solid state and solution. There are unprecedentedly high barriers to rotation about the M-N bond estimated at ca. 16 kcal mol^{-1} (M′ = Sn) and >19 kcal mol^{-1} (M′ = Si), reflecting the severe steric crowding at the metal centers M (Mo and W). Pertinent averaged bond distances (Å) and angles (deg): for I (M = Mo, M′ = Si), Mo-Mo = 2.216 (1), Mo-Si = 2.670 (2), Mo-N = 1.95 (1), Si-Si = 2.38 (1), Mo-Mo-Si = 106.9 (1), Mo-Mo-N = 105 (1); for II (M = Mo, M′ = Sn), Mo-Mo = 2.201 (2), Mo-Sn = 2.77 (1), Sn-Sn = 2.77 (1), Mo-N = 1.95 (2), Mo-Mo-Sn = 100.7 (2), Mo-Mo-N = 105 (2). Crystal data for I at -165 °C: $a = 9.400$ (3) Å, $b = 9.949$ (4) Å, $c = 13.304$ (6) Å, $\alpha = 83.24$ (3)°, $\beta = 97.81$ (2)°, $\gamma = 69.80$ (2)°, $Z = 1$, $d_{calcd} = 1.259$ g cm^{-3}, space group $P\bar{1}$. Crystal data for II at -162 °C: $a = 14.600$ (4) Å, $b = 31.737$ (13) Å, $c = 13.545$ (4) Å, $Z = 4$, $d_{calcd} = 1.876$ g cm^{-3}, space group $Pbn2_1$.

Introduction

As part of our continuing studies of the chemistry associated with compounds containing a central $(M{\equiv}M)^{6+}$ unit (M = Mo, W), we describe here the preparation and characterization of compounds containing the metal atom connectivity shown below. These are the first examples of compounds containing chains of metal atoms incorporating a multiple metal-metal bond.[2]



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