Silver Ketenide

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Summary X-Ray and electron diffraction analyses, together with spectroscopic and chemical properties, show silver ketenide, Ag_2C_2O (I), to have an unusual covalent layer structure in which strong directed bonds exist between metal atoms and the terminal carbon atoms of linear ketenide groups: the distance between adjacent silver atoms in a layer is 2·84 Å, slightly less than in silver metal (2·88 Å), and the interlayer separation is 5·846 Å.

METAL ketenides have not been described hitherto although evidence for the existence of silver ketenide has recently been noted,[1] and Büchner[2] has suggested that compounds having a ketenide-type configuration M(MO)C=C=O are formed by reaction of carbon monoxide with alkali metals in liquid ammonia. Complexes containing keten[3] and diketen[4] as neutral ligands have been described.

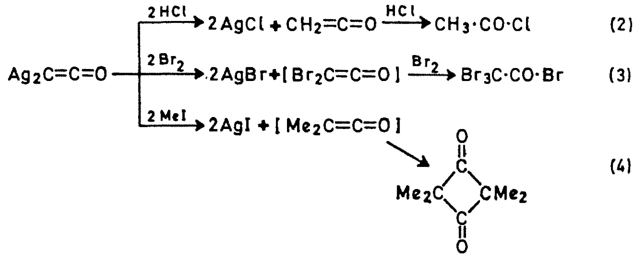
We now report the formation of silver ketenide (I) by reactions of many silver(I) salts with keten, or with Ac_2O, in pyridine. Typically, addition of Ac_2O to a solution of AgOAc in pyridine at 20° gives a bright yellow precipitate of silver ketenide pyridinate $Ag_2C_2O.(py)$ (II) within several seconds.

$$2AgOAc + Ac_2O \xrightleftharpoons{(py)} Ag_2C_2O\,(py) + 3AcOH \qquad (1)$$

In the presence of an excess of Ac_2O, removal of AcOH and pyridine by fractional distillation gives quantitative conversion of the silver acetate into silver ketenide Ag_2C_2O (I).

Silver ketenide (I) and its pyridinate (II) are yellow infusible compounds which are explosive, and insoluble in water, 0·880 ammonia and all common organic solvents.

Reaction of an excess of ketone (I) suspended on glass wool with HCl gas (diluted with N_2 to prevent detonation of the silver complex) gives keten and AcCl: with an excess of HCl, AcCl is the only volatile product.



Treatment of ketenide (I) with an excess of Br_2 in CCl_4 at 20° (Equation 3) gives tribromoacetyl bromide ($>90\%$). Tetramethylcyclobutane-1,3-dione is produced by the reaction with MeI in octane at 90°.[5] These reactions are consistent with the formulation of (I) as a disilver(I) ketenide in which both silver atoms are covalently linked to the terminal carbon of the ketenide group.

Rapid thermal decomposition ($>150°$) of ketenide (I) under argon proceeds almost quantitatively as in Equation 5 to give carbon suboxide of high purity.†

$$2Ag_2C_2O \rightarrow C_3O_2 + C + 4Ag \qquad (5)$$

The i.r. spectrum of ketenide (I) resembles those of other silver compounds, *e.g.* AgNCO[6] and Ag_2NCN,[7] which contain linear triatomic groups isoelectronic with the ketenide dianion. Observed absorption bands in the 400—4000 cm.$^{-1}$ region and their tentative assignments are: 435s (ν Ag–C); 642m (δ CCO), and 2060vs (νCO) cm.$^{-1}$: in the spectrum of the pyridinate (II) these bands occur at 425, 635, and 2020 cm^{-1}, respectively. The strong sharp absorption bands in the spectra of (I) and (II) at 435 and 425 cm^{-1} respectively imply that the Ag–C bonds are essentially covalent.[6,7]

The ketenide (I) and its pyridinate (II) have good crystallinity. Large thin crystalline wafers of (II) are obtained under certain preparative conditions, but both these and the derived, exceedingly thin (<50 Å) flakes of (I) have proved unsuitable for single-crystal *X*-ray structural analysis. However, it has been possible to index the *X*-ray powder diffraction pattern of (I) on the basis of a tetragonal unit cell. *Crystal data*: Ag_2C_2O, $M = 255{\cdot}8$, tetragonal, $a = b = 4{\cdot}028 \pm 0{\cdot}001$; $c = 5{\cdot}846 \pm 0{\cdot}004$ Å, $D_m = 4{\cdot}45 \pm 0{\cdot}03$ (by CCl_4 displacement), $Z = 1$, $D_c = 4{\cdot}477$ g cm^{-3}. The molecular unit has a four-fold symmetry axis.

In the powder photograph, $hk0$ lines are sharp, and hkl, $h0l$, and $00l$ lines are broad indicating that the crystals are platelike and are very thin in the direction of c. In accord with this, single-crystal electron diffraction patterns show only $hk0$ spots due to plates lying perpendicular to the electron beam. Line intensity data are consistent with a tentatively assigned space group $P4$, which requires the silver atoms to occupy special position (2*c*) with coordinates [$0\tfrac{1}{2}0$], [$\tfrac{1}{2}00$]‡ giving an Ag–Ag distance 2·84 Å. The silver positions refined to an R value of 0·21 for the 25 observed reflections with an acceptable temperature factor. Attempts to locate the light atoms were unsuccessful although considerable electron density was noted on the $\tfrac{1}{2},\tfrac{1}{2},c$ axis, consistent with a linear CCO group lying in special position (1*b*) with each terminal atom equidistant from its four neighbouring silver atoms. A suggested structure for ketenide (I) consistent with the above data is shown in the Figure: monatomic layers of silver atoms are separated by rod-like ketenide groups perpendicular to the layer planes. The unusually short distance between silver atoms in a layer (2·84 Å; Ag metal, 2·88 Å) suggests that metal–metal bonding is present, giving, in effect, massive sheet-like silver atom clusters: *cf.* ref. 1. This structure is obviously consistent with the tendency of the crystals to exist as extremely thin flakes, and superficially resembles that of the orthorhombic form of silver fulminate which contains silver atom layers based on a primitive rectangular net having translations of 3·864 and 2·926 Å.[8]

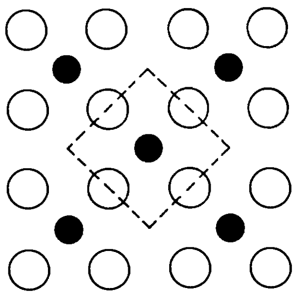


FIGURE. *Suggested structure of silver ketenide* (I) *projected on to* ab *plane. Light circles denote silver atoms in plane of page* (Ag–Ag = 2·84 Å, *interplanar spacing* 5·846 Å), *and dark circles denote* C-1 (*of linear* C_2O *groups*) *lying below this plane and eclipsing* C-2 *and* O.

Preliminary *X*-ray and electron-diffraction studies of the pyridinate $Ag_2C_2O.(py)$ (II) indicate that it has essentially the silver-atom layer structure of ketenide (I) but that the distance between layers is approximately double that in (I). Pyridine absorption bands in the i.r. spectrum of complex (II) indicate that the substance is intermediate between a clathrate and a normal pyridinate: the absorption band of the free base at 403 cm^{-1} is shifted to 413 cm^{-1}, but the band at 601 cm^{-1} is unchanged: in a normal pyridinate, *e.g.* $AgBF_4.2(py)$, these bands occur at 421 and 636 cm.$^{-1}$ respectively.[9] Loss of pyridine from finely-divided complex (II) occurs readily at 20° and leads to the collapse of its structure to thin platelets of ketenide (I). Presumably the flat pyridine molecules in complex (II) are accommodated between adjacent sheets of oxygen and silver atoms.

Silver acetate reacts with keten or acetic anhydride in the presence of triethylamine at 20° to give a yellow silver complex (III) which is similar to (I) in composition and most properties, but gives a different *X*-ray powder diffraction pattern. Silver acetate also reacts with keten to give complex (III) in the absence of an organic base, but reacts with Ac_2O under reflux (138°) to give a complex (IV)

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† *Caution.* This decomposition occurs violently, even explosively, especially if the ketenide is not mixed with inert material. All the present complexes can explode when heated strongly or struck.

‡ Note that z is arbitrarily fixed at zero, as is permissible in this space group.

of empirical formula $Ag_3C_3O_2$ which gives an *X*-ray diffraction pattern different from those of complexes (I) and (III).

Complexes (III) and (IV) resemble complex (I) in giving keten and acetyl chloride with hydrogen chloride, and carbon suboxide on rapid pyrolysis under argon (caution†), and all three complexes give complex (II) on prolonged treatment with pyridine, and react with 6M-$AgNO_3$–H_2O to give the same highly explosive crystalline adduct $AgNO_3.2Ag_2C_2O$. The i.r. spectra of complexes (III) and (IV) resemble that of (I) over the range 400—4000 cm^{-1}, so the ketenide structural element may be common to all three. But there are considerable differences in the 40—400 cm^{-1} region.

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