

Copper(I) Ketenide

By ERNEST T. BLUES, DEREK BRYCE-SMITH,* BERNARD KETTLEWELL, and MANIKA ROY

(Department of Chemistry, The University, Whiteknights Park, Reading RG6 2AD)

Summary The preparation and some properties of copper(I) ketenide are described.

THE potential acidity of the hydrogen atoms in keten was recently demonstrated by the formation of silver ketenide from keten and silver acetate.¹ We now describe the new compound copper(I) ketenide, $\text{Cu}_2\text{C}_2\text{O}$, obtained as an orange-red solid from the reaction of keten with a copper(I) salt, *e.g.* the trifluoroacetate or nitrate, in acetonitrile under argon at 25°. The keten may be generated separately, or, more conveniently, *in situ* from acetic anhydride and a mixture of pyridine and triethylamine. This latter procedure gives a pyridine complex having the stoichiometry $\text{Cu}_2\text{C}_2\text{O}(\text{py})$. This stoichiometry is unique among copper complexes of monodentate ligands, but has also been observed in analogous complexes of copper(I) ketenide with 2-, 3-, and 4-methylpyridine, quinoline, and isoquinoline. The bases are slowly lost *in vacuo* at 20°–40° or, more rapidly, on washing with 10% aqueous AcOH.

Copper(I) ketenide is mildly explosive when dry, giving carbon suboxide, C_3O_2 , as the major gaseous product (*cf.* $\text{Ag}_2\text{C}_2\text{O}$ ¹). Treatment with an excess of silver acetate in pyridine gives silver ketenide in high yield: reaction with aqueous silver nitrate gives the previously reported^{1b} red, explosive adduct $\text{AgNO}_3 \cdot 2\text{Ag}_2\text{C}_2\text{O}$ almost quantitatively

according to equation (1). Silver metal may be removed from the products by treatment with 10% aqueous AcO_2H .

Reaction of copper ketenide with bromine in CCl_4 gives tribromoacetyl bromide; reaction with EtOH-HCl gives ethyl acetate, presumably *via* keten. Acetylene and mono-substituted acetylenes react readily with copper ketenide to give the corresponding acetylides. Thus, treatment of copper ketenide suspended in acetone at 25° with phenylacetylene and aniline gives copper phenylacetylide (identified by X-ray diffraction) and acetanilide.

The i.r. spectrum of copper ketenide closely resembles that of silver ketenide.¹ Principal absorption bands in the 400–4000 cm^{-1} region occur at 475 s ($\nu\text{Cu-C}$), 680 m ($\delta\text{-CCO}$), and 2030 vs (νCO) cm^{-1} : in the pyridine complex these bands are displaced to 450, 650, and 1985 cm^{-1} respectively.

The reactions and spectroscopic properties of copper ketenide together with good elemental analyses indicate that it is correctly represented as $\text{Cu}_2\text{C=C=O}$. The poor crystallinity and total insolubility in all common solvents have so far prevented establishment of the structure by X-ray diffraction, but it may well be a polymer (*cf.* $\text{Ag}_2\text{C}_2\text{O}$ ¹).

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¹ (a) E. T. Blues, and D. Bryce-Smith, *Discuss. Faraday Soc.*, 1969, **47**, 195; (b) E. T. Blues, D. Bryce-Smith, H. Hirsch, and M. J. Simons, *Chem. Comm.*, 1970, 699.