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ACTIVATION OF HEXAFLUOROETHANE BY CALCIUM ATOMS

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SUMMARY

Cocondensation of calcium atoms and hexafluoroethane yields a black powder that evolves hydrogen, methane, ethyne, and other unsaturated hydrocarbons upon hydrolysis.

Although Klabunde and his co-workers [1] have found that certain metal atoms oxidatively add to the carbon-fluorine bond of alkenyl fluorides, no reports describing the activation of fluoroalkanes with metal atoms and/or clusters have appeared in the literature. Our interest in finding systems which are inert to the action of metal atoms and/or clusters in their ground state but which might be induced to react photochemically prompted us to investigate the reactions of calcium atoms with hexafluoroethane.

We have found that the cocondensation at -196°C of calcium atoms and hexafluoroethane (Matheson Freon 116) in a static metal atom reactor [2] using a 40/1 molar excess of hexafluoroethane/calcium results in the formation of a black powder after the reaction is warmed to room temperature. The material is extremely water and air sensitive and must be kept under a rigorously pure inert atmosphere. Although infrared spectra of the cocondensate produced no useful information, X-ray powder diffraction patterns of the solid showed the presence of calcium fluoride.

Hydrolysis of the cocondensate yields the mixture of compounds shown in Table 1. The major products are hydrogen, methane, and ethyne. Ethane, ethene, and other higher unsaturated hydrocarbons are produced in lower yield. Pentafluoroethane is the only fluorocarbon observed in the volatile products. A trace of the hexafluoroethane was probably adsorbed on the product.

TABLE 1

Products from the hydrolysis of the cocondensate of hexafluoroethane and calcium

Product	Yield ^{a,b}
Hydrogen	6.8×10^{-3}
Methane	41×10^{-5}
Ethyne	32×10^{-5}
Ethene	1.4×10^{-5}
Ethane	6.0×10^{-5}
Pentafluoroethane	0.3×10^{-5}
Hexafluoroethane	0.1×10^{-5}
Propyne	7.7×10^{-5}
Allene	0.4×10^{-5}
Propane and propene	1.2×10^{-5}
1,3-Butadiene	0.8×10^{-5}
3-Penten-1-yne	0.1×10^{-5}

^a Yields are expressed in moles of gas per gram of solid.

^b Noncondensable gases were measured with a Gow-Mac gas balance using a 3 ft by 1/8 in. Ni column packed with 80/100 mesh Sphero carb. Condensibles were measured on a Finnigan 3000 GC/MS using a 6 ft x 1/8 in. S. S column packed with 80/100 Poropack N (peak areas are uncorrected).

These results indicate that the cocondensate is a mixture of calcium, calcium fluoride, calcium carbide, and probably other carbides. The absence of fluoroalkenes or fluoroalkynes in the cocondensate suggests that the hexafluoroethane is either completely defluorinated, perhaps in a diffusion controlled process on sub-micron particles of calcium, or that the partially defluorinated species are pumped from the reactor. Calculation of the mass balance in the powder (assuming the hydrogen was evolved from residual calcium, the methane from a 'Ca₂C' species, the ethyne from calcium carbide and the higher unsaturates from other CaC_n species with the concurrent formation of calcium fluoride) shows that the material contains an excess of about 0.38 g of calcium fluoride per gram of material. This 'excess' calcium fluoride is probably formed in a process leading to partially defluorinated products which would be pumped away either during the reaction or as the matrix is warmed to room temperature.

The isolation of products resulting from carbon-carbon bond formation is puzzling, but has been observed previously in the reaction of other organic substrates with calcium atoms [3].

In contrast to previous studies where π -bonds were available to assist in the activation process, the activation of carbon-fluorine bonds observed in this study probably occurs as the matrix is warmed to room temperature. Under these conditions, clusters would be the predominate species responsible for the activation process. Confirmation of these mechanisms are under investigation using matrix spectroscopy.

ACKNOWLEDGEMENT

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