Production, in Electrical Discharges, of FCN, FCCH, and Related Substances as Monitored by Microwave Spectroscopy

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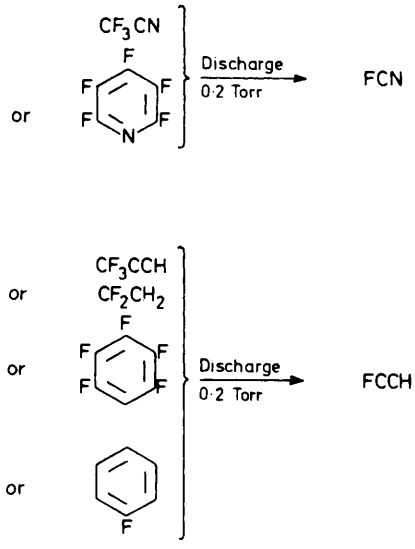
Summary Fluorine cyanide and fluoroacetylene have been detected by microwave spectroscopy in the products formed by the passage of electrical discharges through low pressures of some fluorine containing substances; the formation in discharges of other simple acetylenes and nitriles is reported.

THE direct fluorination of cyanogen,[1] the pyrolysis of cyanuric trifluoride,[2,3] and the reaction of $C(CN)_4$ with caesium fluoride[4] are known routes to fluorine cyanide, FCN. Fawcett and Lipscomb[2] have also reported 30% yields of FCN when CF_3CN was passed through the flame of a carbon arc. The usual preparation of fluoroacetylene, FCCH, involves the pyrolysis of monofluoromaleic anhydride on silica chips at 650 °C.[5] Both FCN[3,6] and FCCH[3] have been extensively studied by microwave spectroscopy and here we have used this technique to monitor their production by electrical discharges through various fluorine containing compounds (Scheme).



SCHEME

In a typical experiment *ca.* 0·2 Torr of the volatile precursor was admitted into the glass vacuum manifold of the microwave spectrometer and a discharge struck by applying a Tesla coil to the glass. The discharge extended throughout the vapour and was maintained for just a few seconds, after which time the products were admitted into the absorption cell for investigation. Alternatively, discharges were carried out directly in the Stark cell using the 100 kHz modulator as the excitation source. Generally, the former method was preferred as, after several experiments, considerable quantities of carbonaceous and polymeric materials were deposited in the discharge region.

Both trifluoroacetonitrile and pentafluoropyridine gave large amounts of FCN in these experiments and these substances provide convenient sources of FCN for spectroscopic purposes. Discharges through mixtures of BF_3 or WF_6 with ClCN, BrCN or even CH_3CN also gave detectable amounts of FCN.[7] Discharge periods were best kept short as FCN itself was destroyed by prolonged excitations.

3,3,3-Trifluoropropyne, fluorobenzene, pentafluorobenzene, and vinylidene difluoride[8] were found to be effective sources for FCCH. For the first three substances the best results were obtained by making the discharge directly in the Stark cell and of rather longer duration than that appropriate for FCN.

Substantial quantities of chloroacetylene have been found when vinylidene dichloride or trichloroethylene were subjected to discharges; compounds containing Cl, C, and N usually gave ClCN. Discharges in substances containing H, C, and N generally produced HCN as expected. However, with CH_3CN or, better, C_2H_5CN, cyanoacetylene, HCCCN, was also detected. 2-Chloroacrylonitrile was found to be a very efficient and convenient source for HCCCN. The synthesis of cyanoacetylene by passing R.F. discharges through acetylene–HCN mixtures has recently been described.[9] Hydrocyanic acid[10] and cyanoacetylene[11] are species found in the interstellar medium; both are easily formed in electrical discharges.

While the relative efficiencies of different routes to a particular product could easily be assessed, only rough estimates of absolute yields could be made from line intensities. Maximum yields probably exceeded 25% for all the routes reported, except for $CH_3CN \rightarrow HCCCN$ (yield *ca.* 10%).

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