

Isolation, Characterization and Some Properties of Free Difluoroethyne, $\text{FC}\equiv\text{CF}$

Hans Bürger and Silvia Sommer

Anorganische Chemie, FB 9, Universität-Gesamthochschule, D-5600 Wuppertal 1, Germany

Difluoroethyne, $\text{FC}\equiv\text{CF}$ **1**, has been prepared by vacuum pyrolysis of perfluoro-1,2,3-triazine, isolated in pure form and characterized by ^{19}F NMR and gas phase IR spectroscopy; its decomposition, with a half-life-time at 300 K and *ca.* 2.5 mbar of *ca.* 15 min, yields in the first step a polymer and $:\text{CF}_2$, the latter either oligomerizing or reacting with **1** to form three different C_3F_4 isomers.

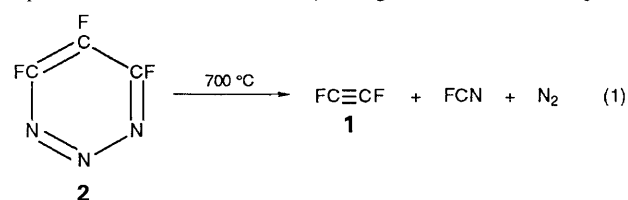
Difluoroethyne, $\text{FC}\equiv\text{CF}$ **1**, was claimed in a patent¹ to be formed, along with other compounds, when difluoromaleic anhydride was passed through a quartz tube heated to 650 °C. Although **1** was not isolated or characterized, except by a peak at m/z 62 (M^+) in the mass spectrum, it was reported to be very volatile, condensing at liquid nitrogen temperature, and extremely unstable. Rapid decomposition at room temperature in the gas phase was on some occasions accompanied by emission of light and some charring, unstable C_4F_4 being one of the decomposition products.¹ Later, products obtained in radiolysis,² thermolysis³ and photolysis experiments⁴ were more or less tentatively assigned to **1**, partly on the basis of the gas chromatographic retention time,² or by evidence of an IR absorption at 1341 cm^{-1} in an Ar matrix³ and at 1149 cm^{-1} in the gas phase⁴ respectively. The two latter observations are clearly incompatible with each other. Furthermore, He (1α) photoelectron spectra⁵ of material obtained with low yield in electrical discharges from C_6F_6 , $\text{C}_5\text{F}_5\text{N}$ and $\text{C}_6\text{F}_5\text{CN}$ ⁶ have been attributed to **1**.

In spite of the interest in this small molecule, which has been recently formed as a ligand in a bridging position between $\text{Co}(\text{CO})_4$ moieties⁷ or stabilized in a cluster,⁸ and has been the subject of numerous theoretical calculations,⁹ we attempted to

synthesize free **1**, to characterize it unambiguously by several independent methods and to study its chemical properties in the gas and condensed phases.

The reported appearance of the m/z 62 peak in the mass spectra of several aromatic fluorocarbons, in particular perfluoro-1,2,3-triazine,¹⁰ and the successful synthesis of $(\text{CF}_3)_2\text{CF}-\text{C}\equiv\text{C}-\text{F}$ by vacuum pyrolysis of perfluoro-4,6-diisopropyl-1,2,3-triazine¹¹ prompted us to investigate the vacuum pyrolysis of **2** as a possible route to **1**. The conditions of pyrolysis and compound separation were optimized by product analyses employing a quadrupole mass spectrometer.

We found that **2** decomposes cleanly at *ca.* 700 °C and a pressure of 0.02–0.1 mbar in a quartz tube according to reaction (1). While unreacted **2** can be recovered in a -78 °C trap, C_2F_4 , the C_3F_4 fraction (arising from some decomposi-



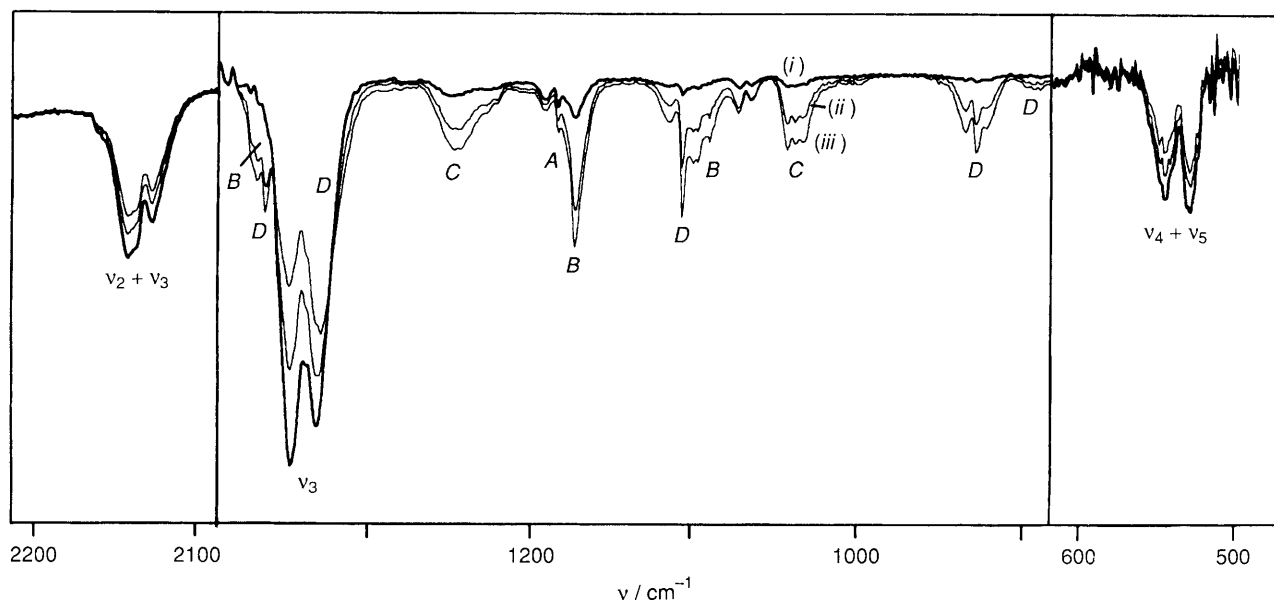


Fig. 1 Time-dependent IR spectrum of **1** recorded (i) 2, (ii) 30 and (iii) 80 min after admitting **1** to the cell.

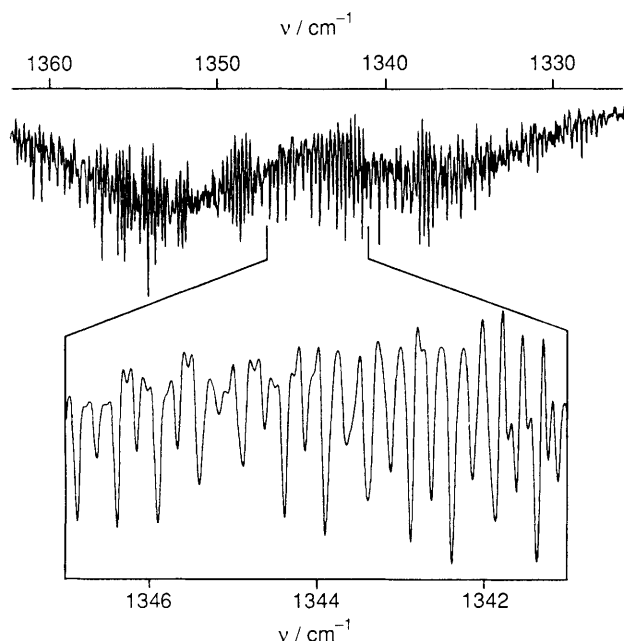


Fig. 2 Detail of the IR spectrum recorded with a resolution of 0.12 cm^{-1}

tion of **1**), FCN and SiF₄ are condensed in a -182°C (liquid O₂) trap. Thereafter, **1** is trapped at -196°C , and according to the spectroscopic investigations reported in the following it is free of contaminants.

For a linear FC≡CF molecule, symmetry $D_{\infty h}$, five IR vibrations ν_1 (Σ_g^+ , $\nu_{\text{C}\equiv\text{C}}$), ν_2 (Σ_g^+ , $\nu_{\text{s}} \text{ CF}$), ν_3 (Σ_u^+ , $\nu_{\text{as}} \text{ CF}$), ν_4 (Π_g , δ' *trans*) and ν_5 (Π_u , δ' *cis*) are expected, the IR active Σ_u^+ vibrations revealing P,R structure, while the Π_u vibrations are associated with P,Q,R-type IR bands. The Σ_g^+ and Π_g vibrations are only Raman active. Rotational J lines observed under high resolution should be separated by $2B$ ($B = \text{ca. } 0.12 \text{ cm}^{-1}$) with 3 : 1 intensity alternation for consecutive lines with odd and even J'' values due to statistics associated with the $I = 1/2$ nuclear spin of the F atoms.

We have recorded gas-phase IR spectra, resolution 2 cm^{-1} , in the $4000\text{--}400 \text{ cm}^{-1}$ region of **1** using a 15 cm cell and

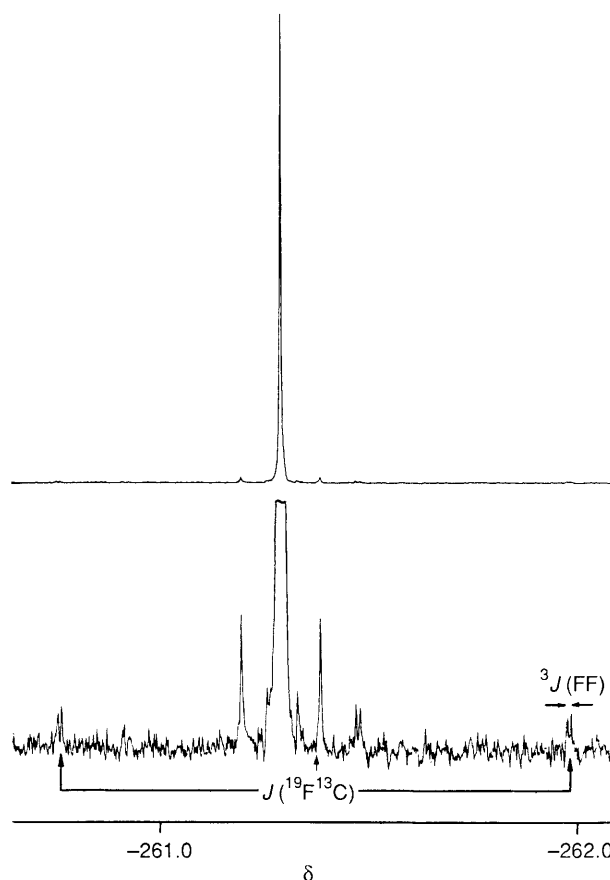


Fig. 3 ^{19}F NMR spectrum of **1** in isopentane- $[\text{2H}_8]$ toluene (3 : 1) at -100°C . Note the spinning sidebands.

measured changes of absorptions due to decay and subsequent product formation. With a pressure of **1** corresponding to the saturation pressure at -182°C ($<1 \text{ mbar}$) one single strong IR absorption with P,R structure at 1349 cm^{-1} was observed, Fig. 1. In agreement with the matrix data³ and an *ab initio* prediction⁹ this is assigned to ν_3 (Σ_g^+). Two additional weaker bands with P,R-type structure at 2136 and 539 cm^{-1} observed with the saturation pressure at -160°C revealed the same

depletion with time as the 1349 cm^{-1} band and are assigned to $\nu_2 + \nu_3$ (Σ_u^+) and $\nu_4 + \nu_5$ (Σ_u^+) respectively, the absence of a Q branch ruling out Π_u symmetry, Fig. 1. Neglecting anharmonicity ν_2 is therefrom located at $(2136 - 1349) = 787\text{ cm}^{-1}$ [cf. the *ab initio* predictions,⁹ $\nu_2 = 787$, $\nu_3 = 1377$ and $(\nu_4 + \nu_5) = 537\text{ cm}^{-1}$]. The IR band reported by Hecklen and Knight⁴ to lie at 1149 cm^{-1} was not found.

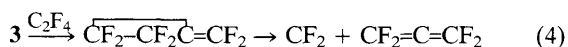
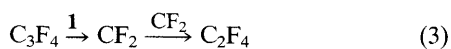
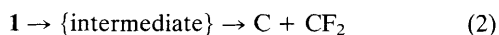
Further unequivocal evidence for a linear $\text{FC}\equiv\text{CF}$ molecule comes from rotational details appearing in IR spectra recorded with a resolution of 0.12 cm^{-1} , Fig. 2, the observed 3 : 1 intensity alternation of J lines separated by *ca.* 0.25 cm^{-1} ruling out any structural isomer like vinylidene $\text{F}_2\text{C}\equiv\text{C}$: **3**. At the given resolution the centre of the ν_3 rovibrational band is obscured by strong absorptions due to hot bands; for example, the intensities at room temperature of $(\nu_3 + \nu_4) - \nu_4$ and $(\nu_3 + \nu_5) - \nu_5$ are 50 to 60% of that of ν_3 .

The decay of absorptions attributed to **1** is accompanied by the appearance of new bands, Fig. 1, which can be convincingly assigned to C_2F_4 (*A*), $\text{CF}_3\text{C}\equiv\text{CF}$ (*B*), $\text{CF}_2=\text{C}=\text{CF}_2$ (*C*) and $\text{CF}=\text{CF}-\text{CF}_2$ (*D*) by comparison with authentic spectra.¹²

The depletion of the 1349 cm^{-1} band follows approximately second-order kinetics; at a pressure of 2.5 mbar the half-life time $\tau_{1/2}$ at *ca.* 25°C was 13, 15 and 6 minutes in glass, Teflon and stainless steel absorption cells, respectively. A similar lifetime was determined by mass spectrometry.

Compound **1** was studied in an isopentane- $[\text{H}_8]$ toluene (3 : 1) solution at -100°C by ^{19}F NMR spectroscopy employing a Bruker AC 250 instrument operating at 235.36 MHz. Initially only the signal reproduced in Fig. 3 appeared, with $\delta -261.3\text{ ppm}$ (*vs.* ext. std. CFCl_3), $1J(^{19}\text{F}^{13}\text{C})$ 287.3 Hz, $^3J(\text{FF})$ 2.1 Hz, $\delta^{19}\text{F}(^{12}\text{C}) - \delta^{19}\text{F}(^{13}\text{C}) = 0.08\text{ ppm}$. Within 2 hours the solution had darkened and the signal attributed to **1** considerably weakened while new signals had emerged, that of C_2F_4 ($\delta -131.1$, s) being by far the strongest. Of the C_3F_4 isomers, small quantities of *D* were identified ($\delta -90.4$, t; -137.4 , t).

The mass spectrum of **1** was recorded with a Balzers QMG 311 quadrupole mass spectrometer, emission current 1 mA, acceleration voltage 70 V. The following fragments (relative intensities in % in parentheses) were observed: m/z 63(2), $[\text{C}^{13}\text{CF}_2]^+$; 62(100), $[\text{C}_2\text{F}_2]^+$; 43(45), $[\text{C}_2\text{F}]^+$; 31(76), $[\text{CF}]^+$; 24(12), $[\text{C}_2]^+$; 19(2), $[\text{F}]^+$; 12(55), $[\text{C}]^+$.



$\text{FC}\equiv\text{CF}$ slowly decomposes even at -196°C with formation of an initially purple material, which after evaporation of **1** forms a brown deposit with metallic lustre on the walls of the ampoule. We are presently investigating this deposit which according to its formation [reaction (2)] we assume to be carbon. This may contain some fluorine, *e.g.* as the perfluoroethyne component in $(\text{CF})_n\text{C}_m$. In a following step CF_2 can react with **1** or the equivalent intermediate, preferentially in the gas phase and at room temperature, to yield in comparable amounts the three isomeric C_3F_4 species *B*, *C* and *D* [reaction (3)], or alternatively, *e.g.* at low temperature and in the condensed phase, dimerize to form C_2F_4 owing to insufficient reactivity or availability of **1**. Whether the propyne *B* and the allene *C* are directly formed or arise from the cyclopropene *D* is an open question at present. The vinylidene **3** which was calculated to lie $25.4\text{ kcal mol}^{-1}$ above **1** ($1\text{ cal} = 4.184\text{ J}$)⁹ may well be the as yet unidentified intermediate. The kinetics, conditions and products of the homogeneous decomposition, however, hardly support a mechanism involving C_2F_4 as previously suggested for **3** [reaction (4)].¹³

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