Perfluorocyclopropene and Its Isomers

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Abstract: Perfluorocyclopropene has been identified as an oxidation product of 1,3-perfluorobutadiene. The infrared and mass spectra were obtained and were consistent with the c-C_3F_4 structure. The nuclear magnetic resonance spectrum confirmed the structure of this previously unreported compound. In addition, the two other C_3F_4 isomers were observed. Perfluoromethylacetylene has not been reported previously and its infrared and mass spectra are presented. Perfluoroallene was observed but could not be isolated. The observation of these compounds is presented as supporting evidence for the identification of c-C_3F_4.

There have been several studies in recent years on cyclopropene which is the smallest possible cyclic olefin.[2] There have been no reports of perfluorocyclopropene although the cyclic C_4, C_5, and C_6 perfluoroolefins are known. We wish to report the preparation of c-C_3F_4 and its infrared and mass spectra.

We have now observed perfluorocyclopropene as a minor product in the mercury sensitization of mixtures of 1,3-C_4F_6 and O_2 and as a major product (along with CF_2O) in the reaction of $O(^3P)$ with 1,3-C_4F_6. It is not observed[3] in the mercury-sensitized decomposition of pure 1,3-C_4F_6.

Perfluorocyclopropene was identified by its infrared, mass, and nuclear magnetic resonance spectra and from molecular weight determinations. In addition, the mercury-sensitized decomposition of c-C_3F_4 was carried out and resulted in the formation of the two other possible C_3F_4 compounds, perfluoroallene and perfluoromethylacetylene. The infrared and mass spectra of the perfluoromethylacetylene were obtained, but only fragmentary data were obtained on the perfluoroallene as attempts at isolation were not successful. However, the information obtained on these isomers supports our identification of perfluorocyclopropene.

Experimental Section

1,3-Perfluorobutadiene was obtained from Peninsular Chemresearch, Inc. Gas chromatographic analysis showed 99% purity after degassing at −196°. Nitrous oxide and oxygen were obtained from the Matheson Co. All reactants were used without further purification.

The technique used for mercury sensitization was the same as that described in a previous report.[4] In this arrangement the infrared spectrum can be monitored during photolysis and in this case was used to determine the extent of reaction. After photolysis, the mixture was separated by means of a column packed with Union Carbide Fluorolube FS-5 on firebrick or Teflon support at 0°. With the firebrick column, the retention time of perfluorocyclopropene was about 39 min and that of perfluoromethylacetylene was about 20 min. Under the same conditions, the perfluorobutadiene had a retention time of 105 min.

Spectra were obtained in a routine manner on a Beckman IR-4 spectrophotometer, a Varian A-56/60 nuclear magnetic resonance spectrometer, and a CEC21-110 mass spectrometer (c-C_3F_4) or an Electronic Associates, Inc., quadrupole mass filter ($CF_3C{\equiv}CF$). For the nmr spectrum (as well as the gas density determination of molecular weight), an accumulation of product was required. After repurification, the sample was frozen into a sample tube, sealed, and maintained at a low temperature. A concentric tube was used for the reference compound, CF_3COOH. The cavity of the nmr was maintained at −12°.

Perfluorocyclopropene

The oxidation of 1,3-perfluorobutadiene induced by either mercury sensitization or oxygen-atom attack was found to produce perfluorocyclopropene. The photolysis of 1,3-perfluorobutadiene–oxygen mixtures produces nearly equal amounts of CF_2O and $C_3F_4O_2$.[5] Perfluorocyclopropene is produced in this reaction with a yield of about one-sixth that of the CF_2O. The details of this reaction are currently under study and will be reported more fully. However, perfluorocyclopropene was produced in much larger yield by the reaction of oxygen atoms with 1,3-perfluorobutadiene.

The reaction of 1,3-perfluorobutadiene and oxygen atoms was carried out by photolysis of mixtures of 1,3-C_4F_6 and N_2O with the N_2O in excess by a factor of 5–20. This reaction proceeded with a quantum yield of approximately unity for both CF_2O and c-C_3F_4. Apparently the oxygen atom reacts with a terminal CF_2 group to form CF_2O leaving a C_3F_4 fragment. The difficult step of a fluorine-atom migration is not required to form the perfluorocyclopropene. That fluorine-atom migration is difficult has been demonstrated in other systems.[6]

Gas density measurements gave a molecular weight of 112 as expected for C_3F_4. The heat of vaporization in the pressure range of 16–620 torr was 6.0 kcal/mole. The extrapolated boiling point was −16° which gives a Trouton's constant of 23.3. The melting point was measured as −58 to −63°.

The infrared spectrum is shown in Figure 1. Bands occur at 5.19, 7.35, 7.56, 8.11, 8.96, 9.04, 9.10, 9.17, 10.71, 10.81, 11.3, and ~12.8 μ. The spectrum is remarkably similar to that of perfluorocyclobutene. The characteristic double-bond stretch is shown to be at 1927 cm^{-1} (5.19 μ) which continues the trend shown by perfluorocycloalkenes for the frequency of the double-bond stretch:[7] c-C_6F_{10}, 1745 cm^{-1}; c-C_5F_8, 1771 cm^{-1}; c-C_4F_6, 1799 cm^{-1}. In addition, the low intensity of the 5.19-μ band shows that this is a nearly symmetrical stretch. The assignment is also consistent

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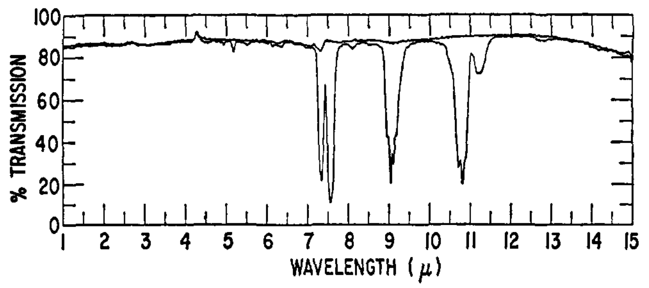

Figure 1. Infrared spectrum of perfluorocyclopropene recorded at 2 torr pressure in a 10-cm cell on a Beckman IR-4 spectrophotometer.

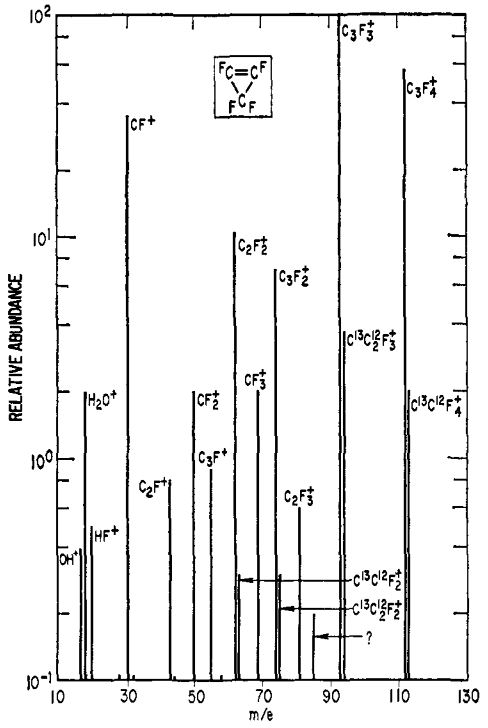

Figure 2. Mass spectrum of perfluorocyclopropene. Background peaks due to N_2^+, O_2^+, CO^+, and CO_2^+ are not shown. The most intense of these (*m/e* 28) would have an intensity of 7.0 on this scale. Spectrum was taken at 70 eV on CEC 21-110B mass spectrometer.

with the assignments for the other two isomers discussed in this paper. The bands in this region for tetrafluoroallene or for perfluoromethylacetylene would be expected to occur at higher energy.

The mass spectrum of perfluorocyclopropene is shown in Figure 2. The parent peak of $C_3F_4^+$ is observed even though in many fluorocarbon mass spectra this is not the case. However, the gas density measurements show that the $C_3F_4^+$ peak is not a fragment ion of some higher molecular weight compound. It is noted that perfluorocyclobutene, the next member of the perfluorocycloolefin series, also gives a prominent parent ion.[8] The observation of CF_3^+ is not surprising even though a CF_3 group does not exist in the molecule. Many fluorocarbons not containing CF_3 groups exhibit the CF_3^+ ion (*e.g.*, the CF_3^+ ion is observed in the mass spectrum of perfluorocyclobutene[8]). The other features of the mass spectrum are consistent with the perfluorocyclopropene structure.

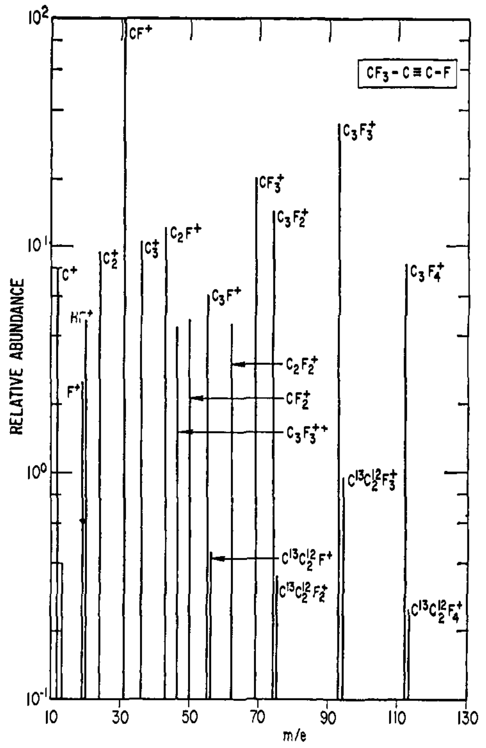

Figure 3. Mass spectrum of perfluoromethylacetylene at 70 eV.

The F^{19} nuclear magnetic resonance spectrum gives final confirmation of the perfluorocyclopropene structure. The observed spectrum shows two triplets of equal intensity which correspond to two sets of two equivalent F atoms. The triplets were observed at 66.68 and 18.28 ppm, both upfield and with respect to trifluoroacetic acid, with a splitting of 44 cps.

Perfluorocyclopropene was found to be stable at room temperature. No indications of decomposition were noted. In contrast, the hydrogen analog, cyclopropene, polymerizes on warming to room temperature. Preparation by the oxygen-atom reaction gave a high yield of product which was isolated easily by gas chromatography.

Perfluoromethylacetylene

The mercury-sensitized decomposition of perfluorocyclopropene led to both of the other isomers as well as to C_2F_4 as primary products. No other products were found. Tetrafluoroallene was clearly shown to be produced by the presence of the allenic stretch reported by Jacobs and Bauer.[9] Gas chromatographic analysis indicated two significant products. One was the perfluoromethylacetylene which was easily separated for subsequent identification by infrared and mass spectra. The other component was shown to be tetrafluoroethylene by the retention time and by its infrared spectrum.

The identification of $CF_3C{\equiv}CF$ is based on the following observations. (1) The peak of highest mass observed in the mass spectrum (Figure 3) is $C_3F_4^+$. Thus it would be expected to be one of the C_3F_4 isomers. Comparison with the *c*-C_3F_4 mass spectrum shows that the CF_3^+ peak is a factor of 10 larger for perfluoromethylacetylene than for perfluorocyclopropene. The

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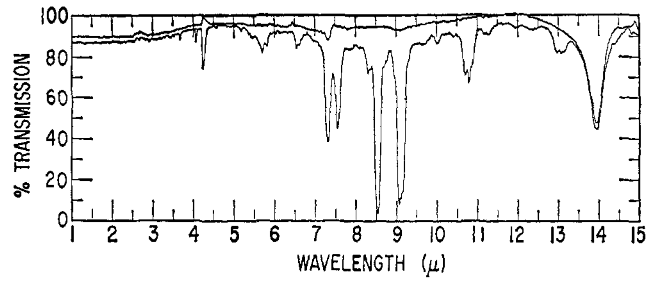

Figure 4. Infrared spectrum of perfluoromethylacetylene.

greater abundance of CF_3^+ is consistent with the presence of the CF_3 group in $CF_3C{\equiv}CF$. (2) The infrared spectrum (Figure 4) shows bands at 3.68, 4.07, 4.23, 5.7, 6.55, 7.31, 7.55, 8.51, 8.53, 9.07, 10.8, and 13.1 μ. The bands at 2457 and 2358 cm^{-1} (4.07 and 4.23 μ, respectively) correspond to the region associated with the triple-bond stretch. For comparison, similar bands were observed at 2342 and 2165 cm^{-1} in the infrared spectrum of $CF_3C{\equiv}CH$.[10] Typical values for the triple-bond stretch are from 2100 to 2250 cm^{-1}. One of the observed bands is presumably the triple-bond stretch and the other (probably the higher energy, lower intensity band) is an overtone or combination. No evidence of contribution from an allenic structure was seen from the perfluoromethylacetylene infrared spectrum.

Perfluoroallene

Perfluoroallene was observed from the mercury-sensitized decomposition of perfluorocyclopropene and perfluoromethylacetylene. The strong band observed at 2047 cm^{-1} closely corresponds to the band given by Jacobs and Bauer as 2065 cm^{-1} for perfluoroallene. Difficulties were encountered in attempts at purification so that a complete infrared or mass spectrum is not available. This product apparently underwent decomposition on the gas chromatographic column.

The mercury-sensitized decomposition of perfluoromethylacetylene, besides producing perfluoroallene, also gave other products which were not identified. After production of the allene from either reaction, the mixture was allowed to stand and the perfluoroallene decomposed slowly. The decomposition products were not identified but the products did show bands in the infrared region associated with the fluorinated double-bond stretch.

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Pentafluorosulfur Carbonyl Fluoride, Pentafluorosulfur Fluoroformate, and Pentafluorosulfur Peroxofluoroformate

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Abstract: The compounds pentafluorosulfur carbonyl fluoride, $SF_5C(O)F$, pentafluorosulfur fluoroformate, $SF_5OC(O)F$, and pentafluorosulfur peroxofluoroformate, $SF_5OOC(O)F$, are produced in low yields by ultraviolet irradiation of the following mixtures, respectively: (1) S_2F_{10} and $FC(O)C(O)F$; (2) SF_5OF and $FC(O)C(O)F$; (3) SF_5OOSF_5 with $FC(O)OOC(O)F$. Each of the new compounds reacts readily with a solution of sodium hydroxide and has infrared and ^{19}F nmr spectra in keeping with its structure.

While many compounds containing the FC(O) group are known, nearly all have been prepared by fluorination of compounds already containing the carbonyl function, such as carboxylic acids, acid chlorides, and chloroformates. It would be of interest to produce similar compounds by direct addition of FC(O) groups to substrates. In order to test this possibility, $SF_5\cdot$ and $SF_5O\cdot$ radicals were used as substrates for addition of $FC(O)\cdot$ and $FC(O)O\cdot$ groups.

The fluorocarbonyl radical has been inferred as a chemical intermediate from the kinetics[1] and the products[2,3] of a number of reactions. The existence of the radical was clearly shown in the recent matrix isolation and identification by Milligan, *et al.*[4] Now that oxalyl fluoride, FC(O)C(O)F, may be prepared easily,[5] this substance is a good material to use as a source for fluorocarbonyl radical.

Bis(fluorocarbonyl) peroxide,[6] FC(O)OOC(O)F, has been investigated as a potential source of $FC(O)O\cdot$ radicals and has been found to give $FC(O)OSO_2F$ upon reaction with SO_2,[7] or to give FC(O)OF by reaction with fluorine.[8]

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