of the symmetry-forbiddenness or an increased effectiveness in intensity-stealing from the color band.[16,18] The compression of a crystal should show evidence of out-of-plane polarization, but this experiment has not been performed. It might be expected that a weak transition is more easily perturbed and that the local symmetry could be distorted by the closer proximity of the solvent electrons or the simultaneous excitation of antisymmetric vibrations.

It has been argued that the diffuse character of the n–π^* band arises from strong mixing with the color band.[15,16,18] Such mixing is enhanced by decreasing the separation of the two states, which is indeed the result of external pressure application since $\nu_{\pi\pi^*}(P) > \nu_{n\pi^*}(P)$. However, the pressure dependence of $1/\Delta E$ cannot be the largest factor determining intensity changes because ΔE is the smallest in PVA at 25 kbars, and yet its intensity rises less than in the other plastics. Hence, increases in the interaction matrix must make a sizable contribution at high pressures.

The precise source of the greater intensity in a strongly perturbed environment cannot be determined from the present information which nevertheless demonstrates the magnitude of the differences in the pressure behavior of localized π–π^* and n–π^* transitions in the same molecule.

Bis(fluoroxy)difluoromethane, $CF_2(OF)_2$

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Received September 28, 1966

Abstract: The static fluorination of carbon dioxide with excess fluorine in the presence of cesium fluoride results in the formation of a substance having the empirical formula CF_4O_2. Its infrared and nuclear magnetic resonance spectra suggest the structure $F_2C(OF)_2$. The compound, which is a colorless liquid at −184°, readily reacts with mercury and oxidizes acidic iodide solution to give elemental iodine.

Static fluorination of thionyl fluoride at room temperature in the presence of cesium fluoride provides a simple route to the hypofluorite, pentafluorosulfur(VI) hypofluorite (SF_5OF).[1] However, if fluorination is attempted in the absence of CsF, only thionyl tetrafluoride is obtained. We have examined the fluorination of carbon dioxide under similar conditions and report the formation of a bis(hypofluorite), bis(fluoroxy)difluoromethane, $F_2C(OF)_2$. Under the experimental conditions used, there was essentially no reaction of fluorine with carbon dioxide without cesium fluoride.

Experimental Section

A. **Materials.** Cesium fluoride (99%) was obtained from K and K Laboratories, Inc. Fluorine was obtained from Allied Chemical Co. and passed through a sodium fluoride scrubber and a −184° cold trap before use. Carbon dioxide was obtained from Northwest Oxygen Co. Analytical grade reagents were used in analyses.

B. **Reaction Vessel.** The reaction vessel was a 75-ml stainless steel cylinder (Hoke 6HS75) equipped with a reduction fitting, a Teflon-packed stainless steel needle valve (Hoke 323), and a brass ₸10/30 inner joint. Threads were sealed with Teflon TFE tape.

C. **Vacuum Systems.** A standard Pyrex glass high-vacuum line was used for most operations. The mercury manometer was protected with a thin layer of Kel-F No. 1 polymer oil. Molecular weight determinations were made on a metal high-vacuum line having a Wallace and Tiernan FA-145 precision dial manometer.

D. **Procedure.** In a typical run, 2.7 g (18 mmoles) of cesium fluoride was placed in the reaction vessel. Fluorine was admitted and the reaction vessel prefluorinated at 190°. The remaining fluorine was then removed and the vessel heated to 195° under dynamic vacuum for several hours.

The evacuated vessel was cooled to −184°, and 1.11 mmoles of carbon dioxide was condensed into it. Excess fluorine, approximately 9 mmoles, was then admitted and the vessel permitted to warm to room temperature. After 6 hr, the vessel was again cooled to −184° and all noncondensable materials were pumped off through a soda-lime trap. The remaining material, 0.132 g, had an experimental molecular weight of 118.9. The average yield, based on carbon dioxide, was 99.7%.

E. **Analyses.** Null-point potentiometric determination of fluoride[2,3] after sodium fusion of a weighed sample of product gave 62.3% fluorine. Volumetric determination of fluorine from lead chlorofluoride[4] after basic hydrolysis at 90° of a weighed sample gave 61.0% fluorine. The theoretical value for CF_4O_2 is 63.3%.

When the compound was allowed to react with cold potassium iodide solution, iodine was liberated readily. Titration of the latter with standard thiosulfate showed that the compound had an experimental equivalent weight of 30.6. Bis(fluoroxy)difluoromethane would have a theoretical equivalent weight of 30.0 when undergoing a four-electron change.

F. **Molecular Weight.** The molecular weight of the compound was calculated from the vapor density assuming ideal gas behavior. The vapor density was determined using a 208.4-ml Pyrex flask equipped with a 1.25-mm Teflon stopcock (Fischer and Porter Co., No. 795-50001-14). The average value obtained was 118.9. The theoretical value for CF_4O_2 is 120.0.

G. **Melting Point.** The compound condenses at −184° as a colorless liquid. Even after several days at this temperature, no crystallization was observed.

H. **Infrared Spectrum.** The infrared spectrum of the compound (Figure 1) was obtained using a Beckman IR5A and a 5.2-cm cell with sodium chloride windows. The following bands are observed: 658 (w), 690 (w), 900–940 (w, complex), 1200 (vs), 1245 (s), 1270 (s), and 1370 (vw) cm^{-1}. The compound is stable, for short times at least, in contact with sodium chloride windows.

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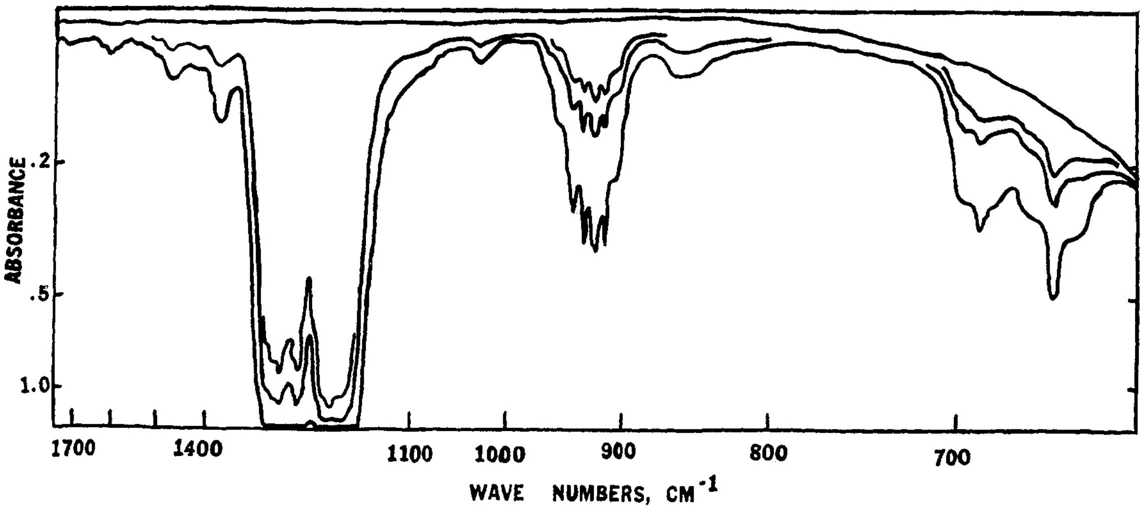

Figure 1. Infrared spectrum of bis(fluoroxy)difluoromethane, $CF_2(OF)_2$, at 4, 12, and 40 mm.

I. Nmr Spectrum. The nuclear magnetic resonance spectrum of the compound was determined on a Varian Model 4311B high-resolution nuclear magnetic resonance spectrometer at 40 Mc. A 10% solution of the compound in trichlorofluoromethane, which served as the internal reference, showed two triplets (1 : 2 : 1) of equal areas at −155.7 and +81.7 ppm. These have been assigned to the OF and CF fluorines, respectively. The coupling constant between the two chemically different kinds of fluorine is 38.6 cps.

J. Thermal Stability. The compound is stable at ambient temperature in both glass and prefluorinated metal vessels for several days. The compound appears to be stable for at least 2 hr at 150° in a prefluorinated stainless steel vessel.

Discussion

The data are consistent with the structure

$$\mathrm{FO\underset{F}{\overset{F}{C}}OF}$$

The infrared spectrum of bis(fluoroxy)difluoromethane is of added interest since it is not predicted from a cursory consideration of the compound. While the peaks at 650–700 cm^{-1} are probably attributable to CF bending, and the peaks at 1200–1300 cm^{-1} to CF stretch, the region near 900 cm^{-1}, where absorption is usually assigned to the OF group, is unusually complex. A more detailed examination of the infrared spectrum of this compound would therefore appear desirable.

Although we have encountered no evidence of lack of stability of the compound, Prager[5] has emphasized the dangers of explosions arising from 1,3-bis(fluoroxy)perfluoropropane, and this should be kept in mind when working with compounds of this nature.

Further study of the reactions of this new bis(hypofluorite) is under way.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation and thank Mr. B. J. Nist of the University of Washington for the nuclear magnetic resonance spectrum.

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