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FLUOROCARBONYL TRIFLUOROMETHYL PEROXIDE

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Ronald L. Cauble and George H. Cady

A recent article[1] reporting the synthesis of FC(O)OF by the photochemical reaction of $(FCO)_2O_2$ with fluorine stated that the new compound $FC(O)OOCF_3$ was formed as a byproduct. The yield was about 5%, based upon the quantity of $(FCO)_2O_2$ consumed. This new compound is the same as one now described by Richard L. Talbott, who has used the name fluoroformyl perfluoromethyl peroxide and clearly established the formula[2].

1. R. L. Cauble and G. H. Cady, J. Am. Chem. Soc., 89, 5161 (1967)

2. Richard L. Talbott, J. Org. Chem.,

In our work, samples of the pure compound were obtained through separation either by gas chromatography using the

column described in reference 1 or by fractional co-distillation. The observed properties are given below.

Molecular Weight. The average molecular weight obtained from 4 vapor density measurements was 148 g./mole (theory for $FC(O)OOCF_3$, 148).

Volatility. Fractional codistillation indicated a boiling point within 10 degrees of -16°.

Infrared Spectrum. The infrared spectrum of the gas as observed with a Beckman Model IR10 spectrometer is shown in the figure. The substance was in a cell 10 cm long with silver chloride windows. Absorption bands, in cm^{-1}, were found at: 1918, vs, C=O str.; 1300, vs, C-F str.; 1247, vs, C-F str.; 1172, vs, C-F str.; 1007, m, C-O str.; 932, m, C-O str.; 753, m; 691, w, CF_3 sym. def.; and 615, m. All assignments should be considered tentative.

Nuclear Magnetic Resonance Spectrum. The F^{19} nmr spectrum was taken at 40 Mc with a Varian Model No. V4311 spectrometer using 76 mole percent CCl_3F as an internal standard. The resultant spectrum consisted of a sharply defined doublet with a chemical shift of 68.8 p.p.m. for the CF_3 group and a quadruplet with a chemical shift of 32.3 p.p.m. for the F-C=O group. The coupling constant, J, was 1.7 c.p.s.

For comparison, the chemical shift of the F-C=O group, with respect to external CCl_3F, of $(FCO)_2O_2$[3],

3. W. Fox and G. Franz, Inorg. Chem., 5, 946 (1966).

and of internal CCl_3F, of $FC(O)OOSF_5$[4], was +34.4 p.p.m.

4. R. Czerepinski and G. Cady, to be published.

The chemical shift of the OCF_3 group with respect to internal CCl_3F of CF_3OOCF_3 was +69.0 p.p.m.[5]

5. P. Thompson, J. Am. Chem. Soc., 89, 1811 (1967).

Reactions. Iodine was liberated when the peroxide was brought into contact with KI solution.

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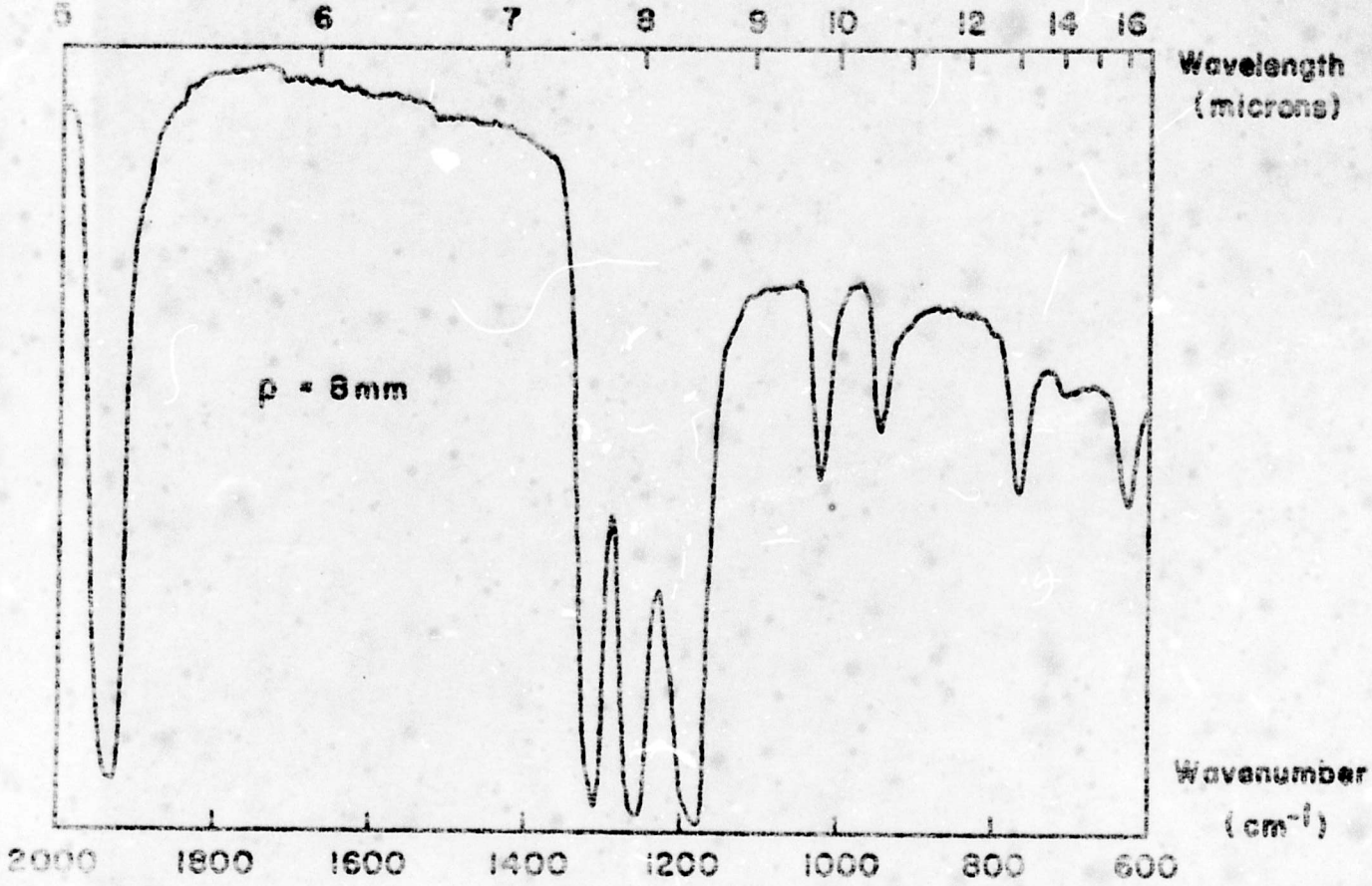

Infrared Spectrum of FC(O) $OOCF_3$

None

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13. ABSTRACT

The compound, $FOOOCF_3$, is produced in small yield by ultraviolet irradiation of a mixture of $FOOOCF$ with F_2.

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O FCOOCF$_3$						
Peroxide						
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