The Formation of Bis(difluorofluoroxymethyl) Peroxide

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RECENTLY, the preparations of compounds containing more than one fluoroxyl group have been reported.[1a,1b,1c,2] We now report the synthesis of a new bis(fluoroxy)-derivative which also contains a peroxide linkage, bis(difluorofluoroxymethyl) peroxide, $FO{\cdot}CF_2{\cdot}OO{\cdot}CF_2{\cdot}OF$. The compound is prepared by the catalytic fluorination of the corresponding acyl fluoride, bis(fluorocarbonyl) peroxide:[3]

$$\begin{matrix} FC{\cdot}OOCF \\ \| \quad \| \\ O \quad O \end{matrix} + 2F_2 \rightarrow FO{\cdot}CF_2{\cdot}OO{\cdot}CF_2{\cdot}OF$$

In a typical experiment, equimolar quantities of bis(fluorocarbonyl) peroxide and fluorine were allowed to react at $-95°$ for 5 hr. in the presence of an excess of KF in a prefluorinated stainless steel cylinder. The volatile contents of the cylinder were then fractionated through cold traps on a vacuum apparatus. A trap set at $-126°$ retained fairly high purity $FO{\cdot}CF_2{\cdot}OO{\cdot}CF_2{\cdot}OF$ (yield 95%). Further purification of the fluoroxyl compound was accomplished by passing it through a 15 ft. perfluorotri-t-butylamine on Chromosorb P column at $-30°$.

The $FO{\cdot}CF_2{\cdot}OO{\cdot}CF_2{\cdot}OF$ thus obtained is colourless (Found: C, 11·40, F, 56·0. Calc. for $C_2F_6O_4$: C, 11·88; F, 56·43%; *M* (vapour density), 202·9 Calc. 202·0). The infrared spectrum shows bands at 1258vs, 1193vs, and 1143vs cm.$^{-1}$ in the C–F stretching region and at 939m and 869w cm.$^{-1}$ which are both in the O–F[4] and C–O[5] stretching regions. The ^{19}F n.m.r. spectrum is diagnostic and consists of a triplet centred at ϕ −158·6 and a doublet at ϕ 80·9 relative to CCl_3F which was used as an internal standard. The splitting of each resonance is 36 c./sec. The area ratio of the lower field to the higher field resonance is 1·0 : 1·8. According to this data, the O–F fluorine nuclear absorptions are assigned to the low-field multiplet[4] while the doublet is assigned to the CF_2 group fluorines. Furthermore, the chemical shift and splitting values are very close to those reported for $CF_2(OF)_2$.[1] Consequently, both the chemical and physical data are in good accord with the suggested structure, $FO{\cdot}CF_2{\cdot}OO{\cdot}CF_2{\cdot}OF$.

CAUTION! Explosions have been encountered when working with bis(difluorofluoroxymethyl) peroxide. Workers should therefore be properly shielded.

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