Perfluorourea, $(NF_2)_2CO$

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A STRAIGHTFORWARD, albeit hazardous, synthesis for small amounts of this previously unreported gaseous compound has been developed such that the product is easily isolated in high purity. The preparation must be done under strictly anhydrous conditions and whenever possible under high vacuum. In a typical experiment, anhydrous KF (0·5 mmol.) in a small Pyrex bulb which could be fitted with a stopcock was allowed to react with difluoraminocarbonyl fluoride,[1] NF_2CFO (0·6 mmol.), in acetonitrile solution at −40° for at least 24 hr. The residual gas was then removed at this temperature and the solvent was pumped off as completely as possible at 0°. Most of the remaining solvent was removed by pumping at 40°, although slight decomposition of the solid resulted. The decomposition products included NF_2CFO and COF_2, but not $(NF_2)_2CO$. The bulb was then immersed in a water bath at 95° while volatile materials liberated were removed by pumping through a trap at −184°. The solid decomposed rapidly yielding at least *cis*-N_2F_2, COF_2, NF_2CFO, $(NF_2)_2CO$ (about 0·04 mmol.), and small amounts of HNF_2 and CH_3CN. The gases were distilled out of the trap at −79° and separated by fractional codistillation using an unpacked 10-ft., ⅛-in. o.d. copper column.

Pure perfluorourea is stable in Pyrex at 25° at least for short periods. It is instantly and completely hydrolyzed when it contacts water. The only volatile infrared-active hydrolysis products are CO_2 and HNF_2. Since the reaction of HNF_2 with I^- is quantitative,[2] a weighed sample of $(NF_2)_2CO$ was hydrolyzed in 0·2 M-HI solution for analysis.* It condenses to a colourless glass at −184° and its normal boiling point, estimated from the fractional codistillation,[3] is near −20°.

The infrared spectrum of perfluorourea was obtained at 20 mm. pressure in a 50 mm. cell with NaCl windows using a Beckman IR5A instrument. The fundamental bands are (cm.$^{-1}$): 1860 (s), carbonyl stretch; 1150 (m); 978 (s); 926 (vs); 885 (m) (trace HNF_2?); 848 (m), doublet; and 720 (m), broad. The ^{19}F high-resolution nuclear magnetic resonance spectrum was obtained at 56·4 Mc./sec. using a modified Varian DP-60 instrument. The spectrum was scanned from −210 to +135 p.p.m. relative to an external CCl_3F reference. The only resonance detected for $(NF_2)_2CO$ was a broad, unresolved peak at −30·8 p.p.m. Under these conditions NF_2CFO gives a similar resonance at −28·7 p.p.m.

Nitrogen–fluorine compounds in contact with acetonitrile are potentially explosive. The solution described in this Communication must not be kept at room temperature due to the formation of N_2F_2. The apparatus must be particularly well-shielded during pyrolysis of the solid, as explosions have frequently occurred.

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* Satisfactory analysis obtained for nitrogen, satisfactory value obtained for molecular weight.

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[3] G. H. Cady and D. P. Siegwarth, *Analyt. Chem.*, 1959, **31**, 618.