New Photochemical Routes to Perfluoromethyl Carbonate

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RECENTLY, Anderson and Morlock[1] described the preparation of perfluoromethyl carbonate (PFMC) and perfluoromethyl fluoroformate (PFMF) by dimerization and trimerization of carbonyl fluoride. These reactions were carried out either thermally, in the presence of a basic catalyst, or photochemically, with light from a mercury resonance lamp.

As a part of a general study on new synthetic methods to produce perfluorinated carbonylic compounds, we have tried to synthesize PFMC by the addition of perfluoromethoxy-radicals (CF_3O) to carbon monoxide. We have irradiated, at room temperature, equimolecular mixtures of perfluoromethyl peroxide (PFMP) and carbon monoxide (total pressure: 300 mm Hg) in a quartz vessel, with a high-pressure mercury lamp (Osram HBO 500) and quartz optics. Though some PFMC was formed, as shown by the i.r. absorption spectrum of the crude product, the yield was surprisingly low. Instead, the main reaction product was a heavy substance, nonvolatile at $-30°$, which had already been observed in the reaction between fluoroxyperfluoromethane (CF_3OF) and carbon monoxide.[2] At present we are working on the elucidation of its structure and the study of its properties.

In the belief that the formation of this heavy substance could be due to some kind of condensation reaction favoured by an excess of carbon monoxide present from the beginning of the reaction, we tried as a controllable source of carbon monoxide perfluoroacetone, which releases carbon monoxide photochemically at room temperature in a very clean way.[3]

We have irradiated, for instance, mixtures of 100 mm. Hg of each of the reactants in the above apparatus and in this case the main reaction product was PFMC. Intensities of carbonyl bands in the i.r. absorption spectrum of the reaction mixture after *ca.* 20 hr. irradiation indicated a nearly quantitative conversion of 60% of the original perfluoroacetone into PFMC. Other reaction products were perfluoromethyl ether, perfluoroethane, carbonyl fluoride, and PFMF, which could be separated from PFMC by gas chromatography at 0° using a 5 m. column of 4 mm. nominal diameter aluminium tubing filled with Chromosorb P (30/60 mesh) containing 30% Halocarbon 13—21 oil. With dry nitrogen as carrier flowing at 60 ml./min., the retention time of PFMC was 7 min. By collecting the peaks from several runs, a sample of PFMC could be obtained whose molecular weight (measured by the gas density method) is 197 (calc.: 198) and shows no traces of known impurities by i.r. absorption spectrophotometry.

PFMC freezes giving a crystalline solid which melts at $-69°$ (in a Pyrex capillary under its own vapour pressure) into a liquid whose vapour pressure, measured between $-70°$ and $+10°$ with a quartz Bodenstein manometer, obeys the following equation: $\log p$ (mm. Hg) $= 8{\cdot}83 - 1676/T$ (°K) which by extrapolation gives a normal boiling point of $+12°$.

The i.r. absorption spectrum of a gaseous sample of PFMC (14 mm. Hg pressure in a 10 cm. Pyrex cell with KBr windows) is identical with Anderson and Morlock's and shows its most intense bands at the following wavenumbers (tentative assignments in parentheses): 1864 (C=O str), 1293, 1263, 1208, 1141, 1115, 1056 (C–F stretchings), 910, 888, 872, 845 (C–O str), 794 (?), 769 (C=O out-of-plane deformation), 617 (CF_3 deformation).

PFMC was also detected in small quantities in the i.r. absorption spectra of the reaction products of the photochemical reactions of fluoroxyperfluoromethane either with carbon monoxide[2] or perfluoroacetone.[4] In the first case, PFMF was the main product and in the second, perfluoroacetyl fluoride, carbonyl fluoride, and perfluoromethane.

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[1] B. C. Anderson and G. R. Morlock, U.S. Patent 3,226,418/1965 (*Chem. Abs.*, 1966, **64**, 9598).

[2] P. J. Aymonino, *Chem. Comm.*, 1965, 241.

[3] P. B. Ayscough and E. W. R. Steacie, *Proc. Roy. Soc.*, 1956, *A*, **234**, 476.

[4] P. J. Aymonino, unpublished results.