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A NOVEL SYNTHESIS OF BIS(FLUOROCARBONYL) PEROXIDE

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University of Washington

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A NOVEL SYNTHESIS OF BIS(FLUOROCARBONYL) PEROXIDE[1]

by Ralph Czerepinski and George H. Cady

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(1) Presented, in part, at the Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June, 1967.

Bis(Fluorocarbonyl) peroxide was first reported by Schumacher and co-workers.[2] Their elegant synthesis uniting

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(2) A. Arvia, P. Aymonino, C. Waldow, and H. J. Schumacher, Angew. Chem. 72, 169 (1960).

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fluorine, carbon monoxide and oxygen at room temperature to give nearly quantitative yields of bis(fluorocarbonyl) peroxide has yet to be matched for convenience and simplicity. However, their preparation still requires handling elementary fluorine in the same system with carbon monoxide, introducing some potential hazard.

In the course of investigations of the chemistry of oxalyl fluoride, it was discovered that photolysis of oxalyl fluoride in the presence of oxygen led to the formation of bis(fluorocarbonyl) peroxide in yields approaching 50%. This

discovery is consistent with Schumacher's proposed mechanism for the formation of the peroxide,[3] involving fluorocarbonyl groups which combine with oxygen.

(3) J. Heras, A. Arvia, P. Aymonino, and H. Schumacher, Z. Physik. Chem. (Frankfurt) 28, 250 (1961).

EXPERIMENTAL

Oxalyl fluoride was prepared by treating oxalyl chloride with sodium fluoride in acetonitrile at reflux, essentially employing the method of Tullock and Coffman.[4] The crude product,

(4) G. W. Tullock and D. D. Coffman, J. Org. Chem. 25, 2016 (1960

contaminated with carbonyl fluoride, carbon dioxide, and acetonitrile was purified by several trap-to-trap distillations, discarding first and last fractions until the product was found to be free from impurities on the basis of its infrared spectrum,[5]

(5) D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford, and D. E. Mann, J. Chem. Phys., 42, 3187 (1965).

and fractional codistillation[6] of a sample.

(6) G. H. Cady and D. P. Siegwarth, Anal. Chem., 31, 618 (1959).

Irradiations were carried out in a two liter Pyrex glass glask equipped with a quartz finger containing a water-cooled Hanau 350 watt mercury arc lamp.

In a typical run 13.2 millimoles of oxalyl fluoride was condensed into the irradiation flask, 59.3 mmol oxygen was added, the flask was allowed to warm to room temperature and irradiation begun. After about 12 hours, irradiation was terminated. The products were bled through a trap held at -183° and substances volatile at that temperature were pumped away. The remaining materials were separated by fractional codistillation and identified by infrared spectroscopy. Found were: 5.0 mmol COF_2 and SiF_4 (combined); 9.9 mmole CO_2; 0.4 mmol $C_2O_4F_2$ impure with $C_2O_2F_2$; and 6.1 mmol pure $C_2O_4F_2$ (46% yield).

Bis(fluorocarbonyl) peroxide was identified by comparison of its infrared spectrum[7] with that of a sample prepared

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(7) A. T. Arvia and P. J. Aymonino, Spect. Acta., 18, 1299 (1962).

using Schumacher's synthesis, by its vapor density molecular weight (Theor. 126, Found 129), and by liberation of iodine from aqueous potassium iodide.

It is probable that higher yields of the peroxide could be obtained by irradiating for shorter times, and recycling the unreacted oxalyl fluoride after separation from $C_2O_4F_2$. Quantitative conversion is unlikely however, since both oxalyl fluoride and bis(fluorocarbonyl) peroxide decompose irreversibly under prolonged ultraviolet irradiation.

$$(FCO)_2 \xrightarrow{h\nu} COF_2 + CO$$

$$(FCO_2)_2 \xrightarrow{h\nu} COF_2 + CO_2 + 1/2\ O_2$$

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13. ABSTRACT

Bis(fluorocarbonyl) peroxide, $FC(O)OOC(O)F$, is produced by ultraviolet irradiation of a mixture of oxalyl fluoride, $FC(O)C(O)F$, with oxygen.

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