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"Preparation of Bis(fluoroxy)difluoromethane"

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Contribution from the Department of Chemistry
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Preparation of Bis(fluoroxy)difluoromethane

by Ronald L. Cauble & George H. Cady

The known existence of $CF_2(OF)_2$ as established by Thompson & Prager[1] of the 3M Company together with a knowledge

1. Private communication.

of the usefulness of cesium fluoride as an aid to the formation of hypofluorites, as established by Ruff & Lustig,[2] suggested the

2. J. Ruff & M. Lustig, Inorg. Chem., 3, 1422 (1964).

possibility of preparing $CF_2(OF)_2$ by the fluorination of carbon dioxide. The procedure was tried and found to be very effective.

In a typical run, 0.298g. (6.78 millimoles) of carbon dioxide and 1.03g. (27.1 millimoles) of fluorine were condensed together from a 2310 ml. glass vacuum line into a heavy walled, 9 ml. Monel metal bomb which contained 7.80g. of dry cesium fluoride at about -195°. The bomb was then closed and placed in a safety shield consisting of a piece of heavy walled pipe. It warmed slowly and remained at room temperature for three days. The gases were then transferred to the vacuum line and found to have a volume corresponding to 20.1 millimoles (theory, 20.3). When the gas was pumped slowly through a U trap cooled by liquid nitrogen (-196°), fluorine was removed and the material condensed in the trap, upon evaporation, had the volume of 6.72 millimoles (theory, 6.78) of gas. Fractional codistillation[3] gave one peak,

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

indicating that the compound was pure. Successive fractions taken by evaporation had vapor densities expressed as molecular weights of 120.0, 119.2 and 120.8 (theory for $CF_2(OF)_2$, 120.0)

The reaction described above showed each molecule of product to contain (like CO_2) one atom of carbon. When a similar run was made using an excess of carbon dioxide, the fluorine was completely consumed and substantially no material volatile at -196° remained in the bomb. This meant that oxygen was not produced and that a molecule of product (on the average) contained two atoms of oxygen. The product had the same volume as the carbon dioxide used in the process. Fractional codistillation separated the product into two fractions. Infrared spectra showed one to be carbon dioxide, and the other to be the same new compound that was produced by the reaction involving an excess of fluorine. Two moles of fluorine were consumed for every mole of product formed in the first reaction. This evidence clearly established the reaction to be:

$$CO_2 + 2F_2 \xrightarrow[25°]{CsF} CO_2F_4$$

The compound was not observed to freeze when chilled. It was a liquid at -183° and a glassy material, or very viscous liquid, at -196°. It reacted vigorously with an aqueous solution of potassium iodide liberating iodine. The infrared spectrum of the gas as observed through silver chloride windows using a

Beckman, IR 10 spectrometer had absorption bands in microns at 7.84 (vs), 8.01 (vs), 8.22 (vs), 8.30 (vs), 8.43 (vs), 10.6 (m), 10.7 (m), 10.8 (m), 10.9 (m), 11.0 (m), 14.5 (m), and 15.2 (m). Several weaker bands were also present.

The fluorine 19 nmr spectrum was obtained with a Varian Associates high resolution, 40 Mc, nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed frequency radio frequency transmitter using $CFCl_3$ as an external standard. Two triplets of equal area were observed, centering at chemical shifts (from $CFCl_3$) of -155 p.p.m. and 88.5 p.p.m. The coupling constant, J, had a value of 39 c.p.s. This spectrum is consistent with the structure, $CF_2(OF)_2$.

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13. ABSTRACT

Bis(fluoroxy)difluoromethane, $CF_2(OF)_2$, ~~is~~ produced by the reaction of fluorine with carbon dioxide in the presence of cesium fluoride at room temperature.

Bis(fluoroxy)difluoromethane

$CF_2(OF)_2$

Carbon dioxide

Cesium fluoride catalyst

Hypofluorite of carbon

Fluoroxy compound