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# OBTENTION OF PERFLUOROMETHYL PEROXOFLUOROFORMATE BY PHOTOLYSIS OF PERFLUOROCYCLOBUTANONE-FLUORINE-OXYGEN MIXTURES *

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## RESUMEN

La fotólisis de mezclas gaseosas de perfluorociclobutanona, fluor y oxígeno, llevada a cabo en recipientes de cuarzo y con luz de una lámpara de mercurio de alta presión filtrada con vidrio Pyrex, produce peroxofluoroformiato de perfluorometilo $FC(O)OOCF_3$, con un rendimiento del 35 %. Los otros productos principales de la reacción son fluoruro de carbonilo y trióxido de bis(perfluorometilo), siendo el rendimiento en este último también del orden del 35 %.

La fracción volátil entre $-130$ y $-40°$ del producto bruto, constituida por peroxofluoroformiato de perfluorometilo y trióxido de bis(perfluorometilo), pudo ser separada en sus componentes por codestilación fraccionada en corriente de hidrógeno.

En la reacción también se forman, aunque en cantidades menores, peróxido de bis (perfluorometilo), fluoroformiato de perfluorometilo y una fracción pesada de naturaleza peroxídica y carbonílica.

## SUMMARY

A new method for the obtention of perfluoromethyl peroxofluoroformate, $FC(O)OOCF_3$, is described. Photolysis of gaseous mixtures of perfluorocyclobutanone, fluorine and oxygen, performed in a quartz vessel under UV radiation from a high pressure mercury lamp filtered through Pyrex glass gives rise to perfluoromethyl peroxofluoroformate, the yield being *ca.* 35 %. Other main reaction products are carbonyl fluoride and bis (perfluoromethyl) trioxide, the yield for the latter is also *ca* 35 %. Bis (perfluoromethyl) peroxide, perfluoromethyl fluoroformate and a heavy, carbonylic and peroxidic fraction are also formed, though in lesser amounts.

Fractionation of the reaction mixture was achieved by low temperature vaporizations and fractional codistillation.


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Two independent synthetic routes to perfluoromethyl peroxofluoroformate (PFMPFFM), $FC(O)OOF_3$, have been described recently. Talbott[1] prepared this substance-which he called fluoroformyl perfluoromethyl peroxide- upon irradiation of bis(fluoroformyl) peroxide, $FC(O)O_2C(O)F$, and perfluorodiazirine, $CF_2N_2$, and Cauble and Cady[2] found it as a secondary product in the photochemical reaction of bis(fluoroformyl)peroxide with fluorine.

With a very low yield, PFMPFFM is also produced in the non-explosive thermal decomposition of bis(fluoroformyl)peroxide. This reaction gives also rise to small quantities of bis(perfluoromethyl) trioxide (BPFMT) [3,4], $CF_3OOOCF_3$.

Now we have found that PFMFFM and BPFMT are also formed upon irradiation of mixtures of perfluorocyclobutanone (PFCB), $c\text{-}C_4F_6O$, fluorine and oxygen, the yield being *ca.* 35 % for each one (this yield is calculated on the basis of consumed PFCB, and assuming an equimolecular relationship between this reactant and the products).

## EXPERIMENTAL

Irradiation was performed in a 250 ml cylindrical quartz vessel with flat windows, provided with a quartz spiral manometer (according to Bodestein). Handling of reactants and products was done in a conventional vacuum manifold made of Pyrex tubing and stopcocks, although in certain critical locations valves made in Monel, aluminum and Teflon were used. Glass stopcocks as well as standard tapered joints were lubricated with Halocarbon grease.

The radiation source was a high pressure mercury lamp (Osram HBO 500) the light of which vas adequately collimated and filtered through 2 mm of Pyrex plate glass. The reaction vessel was thermostatized to 35° C (For a more detailed description of the apparatus see reference [14]).

In a typical experiment, 50 mm Hg of PFCB, 150 mm Hg of oxygen (electrolytic) and 100 mm Hg of fluorine (Allied Chem. Corp.) were mixed in the reactor and photolyzed. The reaction was followed manometrically. Three stages were thus clearly appreciated: *a)* a short initial period during which the total pressure increased slightly; *b)* a comparatively fast reaction which took place until nearly all PFCB was consumed and the total pressure decreased in a value roughly equal to the initial pressure of ketone; *c)* a much slower reaction, with maximum rate smaller than 25 % of that of the former stage. This third step was never carried to completion as some trial experiments showed that the only reaction occurring was the photochemical fluorination of the carbonyl fluoride previously formed [5,6]. Therefore, it was deemed convenient to stop the irradiation as soon as the former stage was completed.

The treatment of the reaction mixture was as follows: residual fluorine and oxygen (which were always in excess) were pumped off at −196°. The non-volatile was then warmed to *ca.* −130° and fluorophosgene together with smaller amounts of carbon dioxide, bis(perfluoromethyl) peroxide, $CF_3O_2CF_3$, and perfluoromethyl fluoroformate, $FC(O)OCF_3$, were distilled off. This fraction was not analysed in much detail, as we were primarily interested in the next cut, namely the volatile at −40°, which proved to be a mixture of PFMPFFM and BPFMT. Small quantities of a non-volatile at −40° were also found, the IR spectrum of which indicated the presence of one or more carbonylic substances. This material released iodine from potassium iodide solutions, suggesting a peroxidic nature.

Separation of PFMPFFM from BPFMT was achieved by fractional codistillation [7] using hydrogen as carrier. With the precaution of submitting small fractions at a time and performing several succesive runs, it was possible to resolve cleanly the mixture into its components, which were collected in separate traps inmersed in liquid air. Identity and purity of the fractions were checked by infrared spectroscopy.

The stoichiometry of reaction was determined from partial pressures of reactants and main products in the various fractions, as measured from infrared and pressure data. Results indicate that the main reaction pathways could be represented by the equations:

$$c - C_4F_6O + 2\,O_2 + F_2 = 2\,COF_2 + FC(O)O_2CF_3$$

and

$$c - C_4F_6O + 2\,O_2 + 2\,F_2 = 2\,COF_2 + CF_3O_2CF_3$$

## DISCUSSION

The course of the reaction and the nature of the products suggest that it is a chain reaction involving perfluoromethyl and other radicals. The perfluoromethyl radicals must necessarily be formed with a relatively high yield from the perfluoromethylene groups of the ketone; by further reaction with oxygen they should give rise to the polyoxides. It is already well known that bis(perfluoromethyl) trioxide is formed when perfluoromethyl radicals are generated in the presence of oxygen by photolyzing either perfluoroazomethane [8] or fluorine-perfluoroacetone mixtures [9, 10].

The fluoroformyl group in PFMPFFM could originate in the final step of the degradation of the PFCB skeleton. A simultaneous or alternative source for this group could be the carbon monoxide arising from the photolysis of the ketone [11]. Nevertheless, if this latter way were operating, formation of bis(fluoroformyl) peroxide shoud be expected [12, 13] although this substance was never detected among the reaction products.

We can therefore conclude that the key step in the chain should be the attack to the carbonyl group by atomic fluorine rather than the photolysis of the ketone. This is similar to the case of perfluoroacetone [9, 10].

These results can also serve as a further proof that in the photochemical reaction between perfluoroacetone, fluorine and oxygen —which does not yield either perfluoromethyl peroxofluoroformate or bis(fluoroformyl)peroxide— no fluoroformyl radicals are involved.

We should mention that if no oxygen is added, PFCB is able to react explosively with fluorine, even at temperature, with formation of a carbonaceus deposit.

Indeed, oxygen inhibits such a thermal reaction, in agreement with previous examples of this effect (c.f. reference 13). The different behaviour of PFCB and perfluoroacetone towards fluorine free from oxygen could be attributed to the ring strain of the cyclic ketone and/or to the possible production of biradicals upon its breakage.

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