

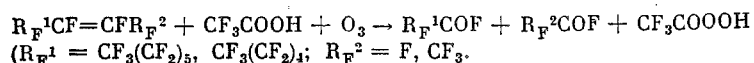
# OZONATION OF PERFLUOROOLEFINS IN TRIFLUOROACETIC ACID SOLUTION

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In contrast to the ozonation of unsaturated hydrocarbons [1-3], the reactions of halogenated and, in particular, higher perfluorinated olefins with  $O_3$  have not been studied extensively [3]. In the gas phase,  $O_3$  initiates the epoxidation of tetrafluoroethylene by molecular  $O_2$  [4] and also reacts with low-molecular-weight perfluoroolefins to form oxides and acid fluoride derivatives of perfluorocarboxylic acids [3].

We have found that the ozonation of perfluoro-1-octene (1-PFO) and perfluoro-2-octene (2-PFO) by 1-6%  $O_3$  in oxygen at from 0 to  $-18^\circ C$  in  $CF_3CO_2H$  leads to the formation of the acid fluoride derivatives of perfluoroheptanoic and perfluorohexanoic acids, respectively as indicated by  $^{19}F$  NMR spectroscopy. The quantitative analysis was carried out for the methyl esters by gas-liquid chromatography. The product yields were from 80 to 100%. The conversion of 1-PFO at  $0^\circ C$  was 81% after 20 min ( $[1-PFO]_0 = 0.2 M$ ).  $CF_3CO_2H$  was found by titration with permanganate to be present in the reaction solutions in amounts comparable to the acid fluorides, while no peracid was found upon the ozonation of pure  $CF_3CO_2H$ . These findings indicated the combined oxidation of  $CF_3CO_2H$  and the perfluoroolefin.



The addition of 0.8 M  $HClO_4$  or  $\sim 0.9 M$   $SbF_5$  does not affect the reaction rate. This finding casts doubt on the participation of species such as  $HO_3^+$  in the reaction. The combined ozonation of 1-PFO and 2-PFO showed that ozone in  $CF_3CO_2H$ , in contrast to other oxidizing agents such as  $MnO_4^-$ , hydrogen peroxide, and oxygen, reacts with 2-PFO more rapidly than with 1-PFO. It is also unusual that the cyclic analog of 2-PFO, namely, perfluorocyclohexene, is virtually not ozonized under the same conditions, while cyclic and acyclic alkenes react with  $O_3$  at comparable rates [1]. These data indicate differences in the mechanism of the ozonation of higher perfluoroolefins in  $CF_3CO_2H$  relative to the ozonation mechanisms for both unsaturated hydrocarbons and low-molecular-weight perfluoroolefins in the gas phase.

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