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°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°C was 81% after 20 min ($[1\text{-PFO}]_0 = 0.2$ M). CF_3CO_3H 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.

$$R_F{}^1CF{=}CFR_F{}^2 + CF_3COOH + O_3 \rightarrow R_F{}^1COF + R_F{}^2COF + CF_3COOOH$$
$$(R_F{}^1 = CF_3(CF_2)_5,\ CF_3(CF_2)_4;\ R_F{}^2 = F,\ CF_3.$$

The addition of 0.8 M $HClO_4$ or ~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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