

OZONOLYSIS OF UNSATURATED PERFLUOROCOMPOUNDS:
ANOMALOUS BEHAVIOR OF SUBSTRATES

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An unusual cooxidation reaction of CF_3COOH and perfluoroalkenes by ozone has been discovered. Ozonolysis of perfluorooctene-1 (1) and trans-perfluorooctene-2 (2) with O_2/O_3 mixture at -18°C gives rise to fluoroanhydrides of corresponding perfluorocarboxylic acids in yields of 80-100%. Peroxytrifluoroacetic acid (CF_3COOOH) was found to be formed in amounts commensurate with those of fluoroanhydrides. Thus the reaction could be described by equation:



No reaction between CF_3COOH and O_3 was observed in the absence of perfluoroalkenes.

Perfluorobenzene C_6F_6 also undergoes the ozonolysis in CF_3COOH solutions. The reactivity of the substrates under investigation diminishes in a sequence: $\underline{2} > \underline{1} > \text{C}_6\text{F}_6 \gg \text{cyclo-C}_6\text{F}_{10}$ revealing the inversion of activity of internal and terminal perfluoroalkenes usually observed in oxidation reactions.

The reaction (1) was not affected by the presence of HClO_4 or SbF_5 additives. Thus species of type HO_3^+ seemingly do not take part in the reaction (1). All the facts available could be explained in the framework of a mechanism including intermediate formation of tetroxide CF_3COOOOH (3) through action of CF_3COOH with O_3 . The transfer of O_2 (presumably in ${}^1\text{O}_2$ form) from 3 to the substrate is considered to be a step leading to the oxidation products. In this context the anomalous low reactivity of cyclo- C_6F_{10} could be explained in terms of the Woodward-Hoffmann rules.