NITRATION OF PERFLUOROISOBUTENE

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The nitration of fluoro olefins was first carried out in 1948 by Hass and Whitaker [1] and was later studied by Coffman and co-workers [2] and by Haszeldine [3]. By the action of nitrogen dioxide on tetrafluoroethylene and chlorofluoroethylenes these authors obtained the corresponding dinitro compounds, e.g.

\[
\text{CF}_2 = \text{CF}_2 + \text{O}_2 \text{N} \rightarrow \text{CF}_2 \text{CF}_2 \text{N} = \text{O} \text{CF}_2 \text{CF}_2 \text{N} = \text{O}.
\]

In 1956 Knunyants and Fokin [4] showed that the action of nitrogen dioxide on tetrafluoroethylene gives not only dinitro compounds, but also tetrafluoro-2-nitroethyl nitrite, the formation of which results from the fact that the radical-like particle of nitrogen dioxide monomer can react both in form A with an unpaired electron on the nitrogen atom and in form B with an unpaired electron on the oxygen atom.

SCHEME 1

\[
\begin{align*}
\text{N}_2\text{O}_4 & \rightarrow 2\text{NO}_2; \\
\text{A} \quad \text{O} & \quad \text{N} = \text{O} \\
\text{B} \\
\text{CF}_2 = \text{CF}_2 + \text{O} & \rightarrow \text{CF}_2 \text{CF}_2 \text{N} = \text{O} \rightarrow [\text{O}_2 \text{N}\text{CF}_2\text{CF}_2.] \\
& \xrightarrow{\text{O} = \text{N} = \text{O}} \text{CF}_2 \text{CF}_2 \text{N} = \text{O} \\
& \downarrow \text{O} \rightarrow \text{N} = \text{O} \\
& \text{CF}_2 \text{CF}_2 \text{N} = \text{O} \\
\end{align*}
\]

The same authors found that by the hydrolysis and alcoholysis of tetrafluoro-2-nitroethyl nitrite difluoronitroacetic acid and its esters are formed; other difluoronitroacetic derivatives were also obtained [5]:

\[
\begin{align*}
\text{CF}_2 \text{CF}_2 \text{N} = \text{O} \rightarrow \text{CF}_2 \text{CF}_2 \text{COOH} \\
\rightarrow \text{CF}_2 \text{CF}_2 \text{COOR}
\end{align*}
\]

Later, Bissel obtained a large number of difluoronitroacetic esters by the same method [6].

The conversion of difluoronitroacetic acid into chlorodifluoronitrosomethane by the action of hydrochloric acid was described in 1962 by Knunyants, Fokin, Blagoveshchenskii, and Kosyrev [7]:

\[
\text{O}_2 \text{NCF}_2\text{CF}_2\text{N} = \text{O} \rightarrow \text{H}_2\text{O} \rightarrow \text{O}_2 \text{NCF}_2\text{COOH}
\]

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\[
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\]

In one of these investigations [4] it was shown that the higher fluoro olefins—perfluoropropene CF₃CF = CF₂ and perfluoroisobutene (CF₃)₂C = CF₂—can also be nitrated with nitrogen dioxide. In view of the unsymmetrical structure of these fluoro olefins and the dual reactivity of nitrogen dioxide several courses of reaction would be expected. In the case of perfluoropropene it would be expected that hexafluoro-1,2-dinitropropane (I), hexafluoro-3-nitro-2-propanol nitrite (II), hexafluoro-2-nitro-1-propanol nitrite (III), and hexafluoro-1,2-propanediol dinitrite (IV) would be formed.
For perfluoroisobutene it may again be supposed that four nitration products will be formed: pentafluoro-1,2-dinitro-2-(trifluoromethyl)propane (V), pentafluoro-3-nitro-2-(trifluoromethyl)-2-propanol nitrite (VI), pentafluoro-2-nitro-2-(trifluoromethyl)-1-propanol nitrite (VII), and pentafluoro-2-(trifluoromethyl)-1,2-propanediol dinitrite (VIII).

In the first place we took the view that the nitration of perfluoropropene and perfluoroisobutene goes by the following general scheme (Scheme 2):

\[
\begin{align*}
\text{SCHEME 2} \\
\text{CF}_3\text{CF} = \text{CF}_2 \xrightarrow{\text{O} = \text{N} = \text{O}} \left[\text{CF}_3\text{CF} = \text{CF}_2\right] \xrightarrow{\text{O} = \text{N} = \text{O}} \text{CF}_3\text{CF} \text{CF}_2\text{NO}_2, \\
\text{NO}_2 \xrightarrow{\cdot \text{O} - \text{N} = \text{O}} \\
\text{X} = \text{F, CF}_3 \\
\text{CF}_3\text{CXCF}_2\text{ONO} \xrightarrow{\text{H}_\text{O}, \text{H}_2\text{SO}} \text{CF}_3\text{CXCOOH} \\
\text{NO}_2 \xrightarrow{\text{NO}_2} \\
\text{ONO} (\text{I}) \\
\text{ONO} (\text{II})
\end{align*}
\]

In the nitration of perfluoropropene the dinitro compound (I) was obtained together with a nitro nitrite to which the structure (III) was attributed. However, further more detailed investigations by the same authors [8] showed that the latter is actually (II); on hydrolysis it gave pentafluoronitroacetone hydrate, from which pentafluoronitroacetone itself was obtained by the action of concentrated sulfuric acid:

\[
\begin{align*}
\text{SCHEME 3} \\
\text{CF}_3\text{CF} = \text{CF}_2 \xrightarrow{\text{O} = \text{N} = \text{O}} \left[\text{CF}_3\text{CF} = \text{CF}_2\right] \xrightarrow{\text{O} = \text{N} = \text{O}} \text{CF}_3\text{CF} \text{CF}_2\text{NO}_2, \\
\cdot \text{O} - \text{N} = \text{O} \xrightarrow{\text{H}_\text{O}, \text{H}_2\text{SO}} \text{CF}_3\text{CF} \text{CF}_2\text{NO}_2 \\
\text{CF}_3\text{CXCF}_2\text{ONO} \xrightarrow{\text{H}_\text{O}, \text{H}_2\text{SO}} \text{CF}_3\text{CXCOOH} \\
\text{NO}_2 \xrightarrow{\text{NO}_2} \\
\text{ONO} (\text{I}) \\
\text{ONO} (\text{II})
\end{align*}
\]

We now report a study of the nitration of perfluoroisobutene [pentafluoro-2-(trifluoromethyl)propene]. The nitration was carried out by heating an equimolecular mixture of perfluoroisobutene and nitrogen dioxide in a steel autoclave at 170-180° for 6-8 h. In this way almost complete conversion of perfluoroisobutene was attained. To establish their structures the reaction products were treated with water. This resulted in a vigorous reaction accompanied by the liberation of a large amount of oxides of nitrogen. As a result of the hydrolysis we obtained two substances—pentafluoro-3-nitro-2-(trifluoromethyl)-2-propanol (IX) and trifluoro-2-(trifluoromethyl)lactic acid (bistri-fluoromethylglycolic acid) (X):

\[
\begin{align*}
Pentafluoro-3-nitro-2-(trifluoromethyl)-2-propanol is insoluble in water, but soluble in aqueous sodium hydroxide or carbonate: from its alkaline solutions it is recovered unchanged on acidification. This alcohol is in fact an acid; it is stronger than acetic acid and has \( p_K_a = 3.9 \). This property is explained by the strong inductive effect of the difluoronitromethyl and two trifluoromethyl groups. With water it forms an azeotrope, which corresponds in analysis and neutralization equivalent to the monohydrate. When the hydrate is distilled over concentrated sulfuric acid the