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PRELIMINARY NOTE

NAFION HYPOHALITES

DARRYL D. DESMARTEAU *

Kansas State University, Manhattan, Kansas 66506 (U.S.A.)

SUMMARY

The perfluorinated ionomers containing sulfonate groups can be converted to the hypochlorite by reaction of the acid with ClF at low temperature. The hypochlorite can be converted to the hypobromite by reaction with a mixture of Br_2 and Cl_2. In this work Nafion - 511 manufactured by the DuPont Company was utilized. These unique hypohalites allow functionalization of the polymer in a variety of new reactions. Conversions of the Nafion hypobromite to the methyl and trifluoromethyl derivatives are described.

Interest in perfluorinated ionomers in technology and chemical research is very high. Electrolytic cell membranes for the chlor-alkali industry are commanding much attention[1] and utilization of these materials as catalysts[2] and as polymer supported reagents[3] is growing rapidly.

We have previously shown that the perfluoroalkanesulfonic acids CF_3SO_2OH and n-$C_4F_9SO_2OH$ can be converted to the corresponding hypohalites R_fSO_2OX (X = Cl, Br) in excellent yield.[4,5] These hypohalites are remarkable sources of electrophilic halogen and are the basis of consider-

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* Present address :
Department of Chemistry, Clemson University, Clemson, SC 29631 (USA).

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able new and interesting chemistry.[5-9] It was therefore of interest to explore whether related polyperfluorosulfonic acids could be similarly converted to the hypohalites. We report here the facile conversion of Nafion-511* to the corresponding hypochlorite and hypobromite and the utilization of these compounds in the covalent functionalization of the polymer.

Granular Nafion-511 as the potassium salt was converted to the acid form by treatment with HCl and dried under vacuum at 90-100°C to constant weight. The equivalent weight was then determined by titration and this value was used in subsequent chemical conversions.

The hypochlorite was prepared in high yield by reaction of the Nafion-H with ClF at low temperature.

$$\text{Nafion-H} + \text{ClF} \xrightarrow[\text{ClF, 18h}]{-111\text{ to }-30^\circ\text{C}} \text{Nafion-Cl} + \text{HF}$$

The resulting pale yellow solid was then purified by pumping under dynamic vacuum for 3 h at -30°C. Iodometric analyses gave 99.4% of the expected oxidizing equivalents. Nafion-Cl begins to decompose at -15°C and the decomposition is rapid at 22°C. Direct gas inlet of the volatile decomposition products at 22°C into a mass spectrometer shows a burst of Cl_2, followed by SO_3 and minor fluorocarbon fragments. By analogy with CF_3SO_3Cl,[4] the decomposition probably proceeds in a related manner.

$$CF_3SO_3Cl \longrightarrow CF_3SO_3\cdot + Cl\cdot \longrightarrow CF_3Cl + SO_3$$

$$\text{Nafion-Cl} \longrightarrow \text{Nafion}\cdot + Cl\cdot \longrightarrow \text{Polymer} + Cl_2 + SO_3$$

However, the immobility of the resulting polymer radical leads to the formation of Cl_2 instead of a chlorofluorocarbon polymer analogous to CF_3Cl.

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*Nafion is a registered trademark of the DuPont Co. Nafion-511 is a perfluorosulfonic acid ion exchange resion, supplied as a granular potassium salt with an equivalent weight of ∿ 1100.

The reaction of Nafion-Cl with a 1:1 mixture of Br_2 and Cl_2 forms Nafion-Br in high yield.

$$\text{Nafion-Cl} + \text{BrCl} \xrightarrow[\text{BrCl}]{-50 \text{ to } 0^\circ\text{C}} \text{Nafion-Br} + Cl_2$$

Iodometric analyses gave 93.3% of the expected oxidizing equivalents. Nafion-Br is an orange solid, thermally stable at 0°C, but it decomposes in a manner analogous to Nafion-Cl at 22°C forming Br_2.

The utility of these new hypohalites in synthesis can be illustrated by the reaction of Nafion-Br with CH_3Br and CF_3Br. The resulting SED reaction[6] gives rise to the corresponding methyl esters in high yield.

$$\text{Nafion-Br} + CH_3Br \xrightarrow[\text{16hr, } CH_3Br]{-50 \text{ to } 22^\circ\text{C}} \text{Nafion-}CH_3 + Br_2$$

$$\text{Nafion-Br} + CF_3Br \xrightarrow[\text{16hr, } CF_3Br]{-50 \text{ to } 22^\circ\text{C}} \text{Nafion-}CF_3 + Br_2$$

The conversion from Nafion-H to Nafion-Br to Nafion-ester preceeded in 91% yield based on the equivalents of acid, the amount of recovered CH_3Br and CF_3Br, and the amount of Br_2 formed. The esters exhibit high thermal stability and do not readily decompose below 200°C, as indicated by mass spectrometry.

We believe Nafion-X (X = Cl, Br) offers exciting new possibilities for the functionalization of Nafion and that these new polymer derivatives will be useful in many ways, ranging from synthesis to fundamental studies of ionomers.

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