THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

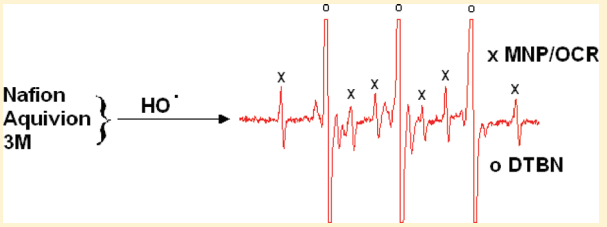
pubs.acs.org/JPCB

Fragmentation of Perfluorinated Membranes Used in Fuel Cells: Detecting Very Early Events by Selective Encapsulation of Short-Lived Fragments in β-Cyclodextrin

Mariana Spulber and Shulamith Schlick*

Department of Chemistry and Biochemistry, University of Detroit Mercy, 4001 West McNichols, Detroit, Michigan 48221, United States

ABSTRACT: The fragmentation of perfluorinated ionomeric membranes during fuel cell (FC) operation is studied in our laboratory by direct electron spin resonance (ESR) and by spin trapping ESR, and interpretation of the results is facilitated by the study of model compounds (MCs). The advantage of this approach is the ability to detect and identify "early events" in the fragmentation process, before the appearance of stable species that can be detected by NMR and other methods. We report a spin trapping ESR study of the fragmentation of Nafion, Aquivion, and 3M membranes in their water dispersions and of the corresponding model compounds in the presence of $HO^{\bullet}$, using 2-methyl-2-nitrosopropane (MNP) as a spin trap. Hydroxyl radicals were generated by UV irradiation of hydrogen peroxide. In the MCs the presence of both oxygen-centered radicals (OCRs) and carbon-centered radicals (CCRs) adducts as well as di-*tert*-butyl nitroxide radicals (DTBN, from spin trap decomposition) were detected. The presence of both OCR and CCR adducts is rationalized by the initial generation of OCRs with low stability and their transformation into the more stable CCRs. Addition of β-cyclodextrin (β-CD) led to a significant increase of the intensity of the MNP/OCR adducts and in one system also to the complete disappearance of the MNP/CCR adduct, results that we assign to the fast selective encapsulation of OCR adducts in the hydrophobic β-CD host. In the membrane dispersions the presence of oxygen-centered radical (OCR) adducts and DTBN radicals have been detected; this result is rationalized by the slower rate of transformation of OCR adducts to CCR adducts in the membrane systems.



INTRODUCTION

Perfluorinated ionomer membranes are performing well during fuel cell (FC) operation because of their superior chemical, mechanical, and thermal stability. With time, however, their performance is weakened because of the strong oxidizing conditions in a FC, especially at low humidity and under open circuit conditions.[1−4] Elucidation of the degradation mechanisms of these membranes is critical for a better understanding of their behavior in a FC and for encouraging synthetic efforts of structure modification. Recent work that ranked the stability of perfluorinated membranes has shown that modification of the side chain can lead to increased stability: 3M and Aquivion membranes, Chart 1, are more stable compared to Nafion and even compared to stabilized Nafion in which the number of COOH end groups was considerably reduced; ranking of the membrane stability was performed by the competitive kinetics approach, which leads to the determination of the reaction rate constants of the membranes with hydroxyl radicals.[5]

The fragmentation of perfluorinated model compounds (MCs) exposed to hydroxyl radicals has been studied by various methods. Fluoride emission rate, FTIR, ^{19}F NMR, Fenton degradation, and liquid chromatography−mass spectrometry (LC-MS) have allowed the identification of stable degradation products.[4] Recent solid state NMR (ssNMR) studies have confirmed the idea that the side chain of the perfluorinated membranes is vulnerable to hydroxyl radical attack.[6,7] Current studies have suggested that in Nafion the C−O−C bond in the middle of the side chain is preferentially cleaved at low humidity conditions.[8]

A study of MCs by spin trapping electron spin resonance (ESR) has concluded that both sulfonic acid and acetic acid groups can be attacked by hydroxyl radicals, and confirmed two possible degradation mechanisms in the membranes: initiated at the backbone end chains and at the side chains.[9] Our methods of study, based on direct electron spin resonance (ESR) and spin trapping ESR in an in situ FC inserted in the ESR spectrometer,[10] have demonstrated the centrality of the hydroxyl radical, $HO^{\bullet}$, as the most aggressive oxygen radical that can attack both the main and side chains in proton-exchange membranes (PEMs). Taken together, these studies have formulated three main degradation paths for the PEMs: main chain unzipping and side chain attack (both by attack of hydroxyl radicals) and main chain and side chain scission by hydrogen atoms at the tertiary carbon atoms. The emphasis on hydroxyl radicals as an aggressor received additional support in our study of membrane stabilization by Ce(III): In situ results indicated that the stabilization mechanism is based on the scavenging of hydroxyl radicals by Ce(III) and on the Ce(III)/Ce(IV) couple redox chemistry, thus allowing significant stabilization with a low stabilizer concentration.[11]

Received: August 24, 2011
Published: September 16, 2011

Chart 1. Structures of Perfluorinated Membranes (Nafion, Aquivion, and Classic 3M) and Corresponding Model Compounds (PFMHSA, PFEESA, and PFEBSA)[a]

Membranes	Corresponding Model Compounds
—$(CF_2CF_2)_mCF_2CF$— with $OCF_2CFOCF_2CF_2SO_3H$ and CF_3 Nafion, EW 1100, m=6.6	$F_3C\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF(CF_3)\text{-}O\text{-}CF_2\text{-}CF_2\text{-}SO_3H$ Perfluoro(3-methyl-2,4-dioxahexane)sulfonic acid (PFMHSA)
—$(CF_2CF_2)_nCF_2CF$— with $OCF_2CF_2SO_3H$ Aquivion, EW 830, n=5.5	$F_3C\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2\text{-}SO_3H$ Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)
—$(CF_2CF_2)_pCF_2CF$— with $OCF_2CF_2CF_2CF_2SO_3H$ Classic 3M, EW 825, p=4.5	$F_3C\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3H$ Perfluoro(2-ethoxybutane)sulfonic acid (PFEBSA)

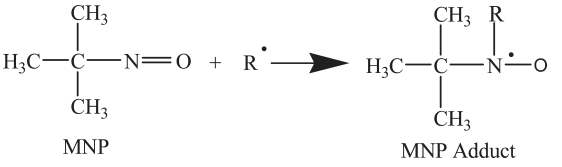
[a]EW is the membrane equivalent weight, g/sulfonic group.

We present an ex situ study of fragmentation of the membranes and corresponding MCs shown in Chart 1 using spin trapping ESR with 2-methyl-2-nitrosopropane (MNP) as a spin trap. In these systems MNP is preferable to other spin traps that have been used in our previous work because the radical trapped is close to the ^{14}N atom that carries the highest spin density, as seen in Scheme 1.[12] The main goals of this study were to identify the radicals generated by attack of $HO^{\bullet}$ radicals and trapped by MNP, to locate the specific site of attack of hydroxyl radicals in the membranes and MCs, and to compare the adducts detected by ESR with the stable degradation species reported in ref 4 on some of these MCs. We used an important tool in the detection of early fragmentation events: addition of β-cyclodextrin (β-CD) for molecular recognition and selective encapsulation of adducts. The unique properties of the CDs are derived from their shape: a central hydrophobic cavity and a hydrophilic surface consisting of hydroxyl groups.[13] In a recent study we have reported that the presence of the hydrophobic β-CD host leads to increased lifetimes of some spin adducts of MNP, DMPO (5,5-dimethyl-1-pyrroline *N*-oxide), and PBN (*N*-tert-butyl-α-phenylnitrone); moreover, fluorine spin adducts were preferentially encapsulated in the host cavity.[14] As will be seen below, the presence of β-CD has a stabilizing effect on the short-lived adducts of oxygen-centered radicals (OCRs) and allows the detection of "very early events" in the fragmentation of the membranes and MCs shown in Chart 1.

EXPERIMENTAL SECTION

Materials. MNP and β-CD were purchased from Aldrich Chemical Co. Hydrogen peroxide (H_2O_2) was from Sigma Chemical Co. as a 3% aqueous solution. Stabilized Nafion was purchased from Aldrich Chemical Co. as a 10% wt water dispersion. The 3 M membrane was a gift from S.J. Hamrock of 3 M Co. as a ~15% wt water dispersion; the Aquivion membrane was purchased as a 20% wt. water dispersion from Ajedium Films, Newark, DE (a division of Solvay-Solexis). The MCs PFMHSA and PFEBSA were a gift from D. A. Schiraldi of Case Western Reserve University, who used the notation MC7 (for PFEBSA) and MC8 (for PFMHSA) in their study.[4] PFEESA was purchased from Alfa Aesar. Perfluoro-*n*-octanoic acid ($HOOC(CF_2)_6CF_3$, PFOA), also a gift from D. A. Schiraldi, was also studied, to provide the baseline for interpreting the adducts detected in the membranes and the MCs. All materials were used as received. Deionized "ultra pure" water with low conductivity and $\leq$10 ppb total organic carbon was provided by the Millipore Model Direct-Q UV system and used in the preparation of all aqueous samples. The hydroxyl radicals were generated by UV irradiation of aqueous solutions of hydrogen peroxide.[15]

Scheme 1. Spin Trapping by 2-Methyl-2-nitrosopropane (MNP)



Sample Preparation. Solutions of the membranes were prepared by mixing 0.2 mL of an aqueous solution of MNP (2×10^{-4} M) with 0.4 mL of stabilized Nafion (1×10^{-6} wt. %), Aquivion (0.01 wt. %), or 3 M (0.09 wt. %) and 0.05 mL of 3% H_2O_2, as described in ref 9. The MNP adducts of the MCs were prepared in a similar way by mixing 0.1 mL of an aqueous solution of MNP (0.2 mM) with 0.05 mL of H_2O_2 and 1 mL of the MCs at concentrations varying from 0.01 to 0.2 M for PFOA and 0.5 to 3 M for the other MCs. As described in the literature, the fluorinated MCs shown in Chart 1 are amphiphiles that may self-assemble into micelles or other types of aggregates, a process that can affect the magnetic parameters of the corresponding adducts.[16] For this reason the fragmentation process was studied at several MC concentrations, including the critical micellization concentrations (CMCs) reported for some of the MCs in the literature,[17,18] but no significant changes of the magnetic parameters for their MNP adducts were detected. The optimal results in terms of adduct intensities were obtained using the following concentrations: 0.1 M for PFOA, 1.5 M for PFEBSA, 3 M for PFMHSA, and 2 M for PFEESA. The pH of all solutions except PFEBSA was adjusted to 6.5−7.5 with NaOH, in order to reduce the intensity of di-*tert*-butyl nitroxide (DTBN), the degradation product of MNP;[12] the PFEBSA mixture generated optimal results at pH 3.5. In order to generate the MNP adducts, the mixtures containing membranes or MCs were irradiated in situ at 300 K, in quartz capillary tubes placed inside the ESR resonator using a 300 W ozone-free Xe arc from Oriel.

Samples containing membranes and β-CD were prepared by adding the appropriate amount of β-CD to obtain a final concentration of 2 mM in the MNP/membrane solution; the mixtures were then UV irradiated in situ for 5 min. Samples containing the MCs and β-CD were prepared by adding the appropriate amounts of β-CD to an aliquot of the MNP spin adduct obtained by UV irradiation for 5−10 min of the corresponding MNP/MC/H_2O_2 mixture at room temperature in quartz capillary tubes with a low-pressure mercury source (Mineralight model PCQX1); this procedure seemed to reduce the formation of DTBN encapsulated in the β-CD host (DTBN "in"). No radicals were detected by direct ESR in mixtures of MCs or membranes and β-CD at 100 K, even after 180 min of UV irradiation.

ESR Measurements. Spectra were recorded at 300 K using a Bruker X-band EMX spectrometer operating at 9.7 GHz and

100 kHz magnetic field modulation and equipped with the Acquisit 32 Bit WINEPR data system version 3.01 and the ER 4111 VT variable temperature unit. The microwave frequency was measured with the Hewlett-Packard 5350B microwave frequency counter. Typical parameters used for spectra acquisition were sweep width 150 G, microwave power 2 mW, modulation amplitude 1 G, receiver gain 5.02×10^4, 50 scans, and 2048 points. The hyperfine splittings of the spin adducts were determined by simulating the spectra using the WinSim (NIEHS/NIH) simulation package;[19] for spectra that consisted of a superposition of contributions from different adducts or radicals, the fitting also determined the relative intensity of each component with a typical margin of error of 5% in multicomponent spectra. The weak ^{13}C satellites in the ESR spectra of DTBN, indicated by downward arrows in Figure 2, were not included in the simulations.

RESULTS AND DISCUSSION

In this section we will present and discuss the following: Control experiments that were performed in order to validate our approach and conclusions; detection and identification of spin adducts from the membranes and MCs in the presence of hydroxyl radicals and the effect of β-CD on the nature and stability of the adducts; and implication of results for membrane degradation. We will focus on the effect of β-CD addition on the type of adducts detected, in an attempt to capture the earliest possible radicals generated in the fragmentation process.

Control Experiments. Four types of experiments were conducted for all systems. First, no radicals were detected by direct ESR at 100 K after irradiation times up to 180 min of membranes and MCs, and at 300 K for the systems containing both membranes or MCs and H_2O_2 in the absence of the spin trap. Second, UV irradiation of MNP or MNP/H_2O_2 solutions led to the formation of the DTBN radical with a_N = 17.1 G; in the presence of β-CD both the "out" form (a_N = 17.1 G), and the "in" form (a_N = 16.7 G) of DTBN were detected.[14] Irradiation of MNP/MCs, MNP/membranes, MNP/MCs/β-CD, and MNP/membranes/β-CD led also to the formation of DTBN ("out" form in the absence and both "in" and "out" forms in the presence of β-CD). Third, the absence of any MNP adducts in systems that did not contain H_2O_2 indicated that the $HO^\bullet$ radicals are initiating the fragmentation processes. Fourth, all mixtures (with or without β-CD) were irradiated for 4 h, and spectra were recorded immediately and also during 4 h after the UV irradiation was stopped; only the species detected initially were detected.

These control experiments indicated that the spin adducts identified in the membranes and MCs are generated by $HO^\bullet$ radicals attack and not by direct photolysis.

Fragmentation of PFOA. Experiments with PFOA ($HOOC-(CF_2)_6CF_3$) were performed in order to provide the baseline for identification of the radicals and spin adducts detected in the membranes and the MCs; in contrast to the other systems studied, PFOA has no ether groups.

The attack of $HO^\bullet$ radicals was studied in the concentration range 0.01−0.2 M (due to its low solubility in water) and at pH in the range 3−9. Optimal results (in terms of adduct intensity) were recorded for 0.01 M and at pH 7.4. The adduct was identified as the MNP adduct of the carbon-centered radicals (CCRs), MNP/CCR, with a_N = 13.4 G and a_F = 22.4 G (2F), as shown in Figure 1A. Similar hyperfine splittings were measured for the MNP/CF_2COOH adduct generated when CF_2HCOOH was exposed to $HO^\bullet$ radicals: a_N = 13.5 G and a_F = 22.5 G (2F).[9] As PFOA has no hydrogen atoms, the attack is expected at the COOH group. The DTBN radical, with a_N = 17.1 G, was also detected and is shown in Figure 1A. The relative intensity of MNP/CCR is low compared to that of DTBN, 21% vs 79%. No other MNP adducts were detected at these optimal conditions, even after 30 min of continuous UV irradiation.

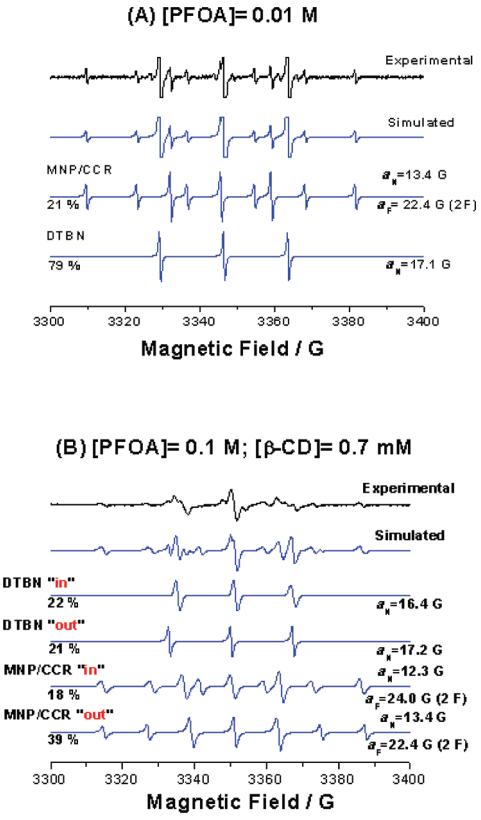


Figure 1. (A) Experimental and simulated spectra of the MNP/CCR adduct generated from PFOA at 300 K and pH 7.4; (B) Effect of β-CD addition: The "in" and "out" conformations for both DTBN and MNP/CCR adduct are detected. The host, β-CD, was added after the generation of the corresponding MNP adducts by UV irradiation in the presence of H_2O_2. The same species were detected when the irradiation was carried out in the presence of β-CD.

The effect of β-CD depends on its concentration. For [β-CD] < 0.7 mM an increase of the relative intensity of MNP/CCR to 56% was detected. For [β-CD] ≥ 0.7 mM, the spectra indicate "in" and "out" species for both the MNP/CCR adduct and DTBN, as seen in Figure 1B. The "in" species are recognized by the lower values for a_N: 16.4 G vs 17.2 G for DTBN and 12.3 G vs 13.4 G for the adduct. The relative intensities of "in" form of both DTBN and MNP/CCR increase with β-CD concentration; for [β-CD] > 0.9 mM only the "in" form of DTBN can be detected, whereas "in" and "out" forms of MNP/CCR are present even at the maximum β-CD concentration studied, 2 mM. This behavior suggests that both DTBN and MNP/CCR are encapsulated in the β-CD cavity. In addition, the half-life of the MNP/CCR adduct increases in the presence of β-CD: from 200 s in the absence of the host to 1400 s for [β-CD] = 0.9 mM. It is important to note the a_N value for MNP/CCR in the presence of β-CD is lower than in its absence, 12.3 G vs 13.4 G, indicating that the N−O group is also inside the hydrophobic environment of the host, not only the fluorinated CCR. A contrasting behavior

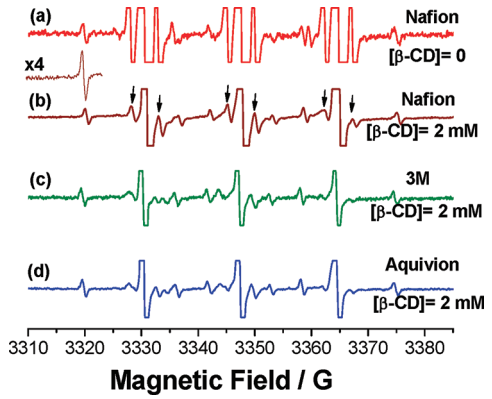


Figure 2. Experimental spectra of the MNP/OCR adduct generated in the absence (a) and in the presence of β-CD (b, c, d) for the indicated perfluorinated membranes [stabilized Nafion (a and b), 3M (c), and Aquivion (d)] in water solutions at 300 K and pH 7. The vertically enhanced (×4) low field segment in (b) indicates that the intensity of the MNP/OCR adduct is higher in the presence of β-CD by a factor of 4, within 10%, compared to (a). A similar ratio was also detected for 3 M and Aquivion membranes. Downward arrows in (b) point to the ^{13}C satellites (1.1%) that were not included in the simulations.

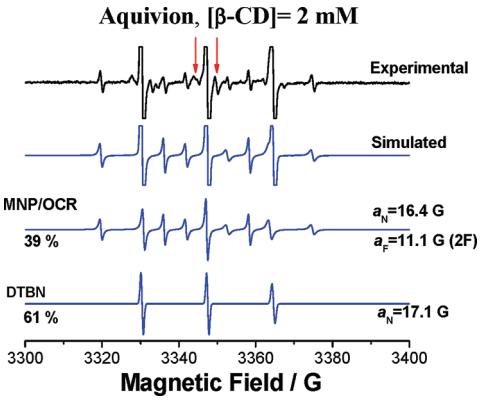


Figure 3. Experimental and simulated spectra of the MNP/OCR adduct generated in the presence of Aquivion (0.01 wt. %) and β-CD. For this β-CD concentration the DTBN radicals are in the "out" conformation (a_N = 17.1 G).

was detected for the DMPO/OH: The half-life increased in the presence of β-CD, but no effect was detected for a_N, suggesting that the N−O group is outside the hydrophobic host.[14]

As demonstrated for the fragmentation of CF_3COOH in an earlier paper,[9] attack of $HO^\bullet$ on $HOOC(CF_2)_6CF_3$ is expected at the carboxylic group, leading to the generation of $CF_3(CF_2)_6COO^\bullet$ and further to CO_2 and $CF_3(CF_2)_5CF_2^\bullet$. The formation of the CCR adduct is a result of the instability of the $CF_3(CF_2)_6COO^\bullet$ radical, which loses CO_2 before spin trapping and generates the CCR radical that is trapped by MNP.[20] This process explains the presence of the MNP/CCR adduct, Figure 1. The presence of β-CD, Figure 1B, does not change the nature of the species detected but leads to encapsulation of the adduct and of DTBN in the host and to "in" and "out" species for both; the magnetic parameters are presented in Figure 1B. It is important to note that essentially the same results were obtained when the radicals were generated by UV irradiation in the presence of β-CD.

Recently ^1H and ^{19}F NMR chemical shifts in aqueous solutions have provided evidence for the presence of inclusion complexes of PFOA in β-CD.[21] To the best of our knowledge no data have been published on complexes of PFOA adducts in the cyclodextrin host.

Membrane Fragmentation. The ESR spectra for systems containing the membranes are shown in Figures 2 and 3. The ESR spectrum for stabilized Nafion in Figure 2a indicates the presence of DTBN with a_N = 17.1 G and of an MNP adduct with a_N = 16.4 G and a_F = 11.1 G (2F), which is assigned to an adduct of an OCR, MNP/OCR. The hyperfine splittings for the adduct are similar to the values reported for the MNP/OCF_2CF_2R adduct detected for PFEESA, a_N = 16.6 G and a_{F1} = 11.5 G (2F), a_{F2} = 0.5 G (2F).[9] The ^{19}F hyperfine splitting of 0.5 G detected in ref 9 was not detected in the membranes, most likely because of broader signals in the polymer dispersions compared to solutions of MCs. The same results were obtained for the three membranes (stabilized Nafion, Aquivion, and classic 3M). No other adducts were detected even after 4 h of UV irradiation. Lines b−d in Figure 2 show the results for the three membranes in the presence

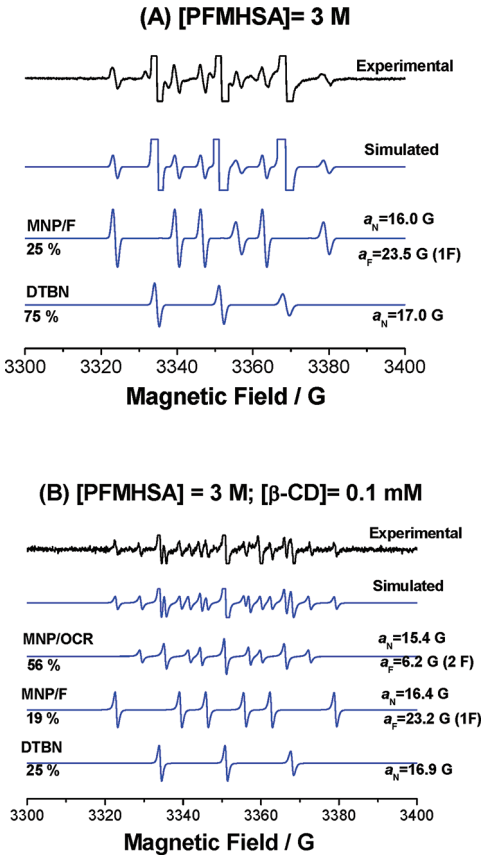


Figure 4. (A) Experimental and simulated ESR spectra of the MNP/F adduct generated in the MNP/H_2O_2/PFMHSA system at 300 K and pH 6.5. (B) Effect of β-CD addition: Note the appearance of the MNP/OCR adduct and the lower relative intensities of both DTBN and MNP/F.

of [β-CD] = 2 mM; we note that the intensity of the MNP/OCR adduct is significantly enhanced, typically by a factor of 4, as deduced from the vertically enhanced low-field portion of the spectra shown in Figure 2b; the enhancement was performed in order to compare ESR spectra with the same signal/noise ratio.

The experimental ESR spectra for the Aquivion system in the presence of β-CD, and the deconvolution into the two components,

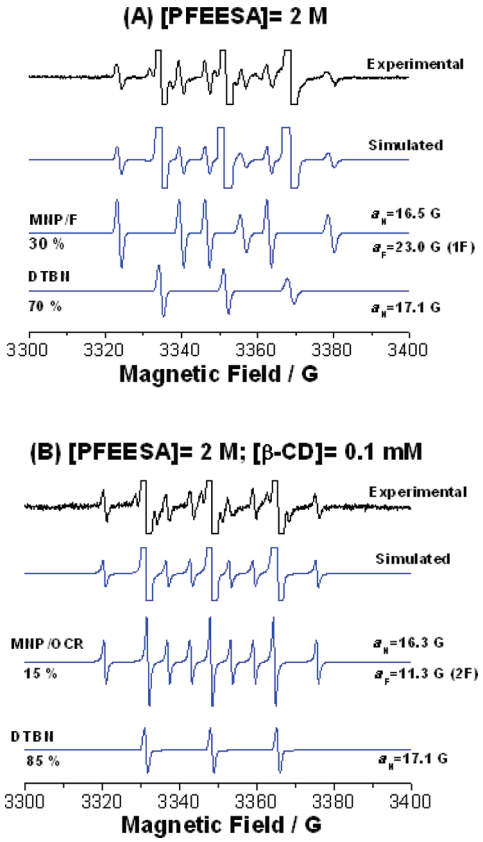


Figure 5. (A) Experimental and simulated ESR spectra of the MNP/F adduct generated in the MNP/H_2O_2/PFEESA system at 300 K and pH 7.2. (B) Effect of β-CD addition: Note the appearance of the MNP/OCR adducts. In both (A) and (B) the DTBN radical is in the "out" conformation (a_N = 17.1 G).

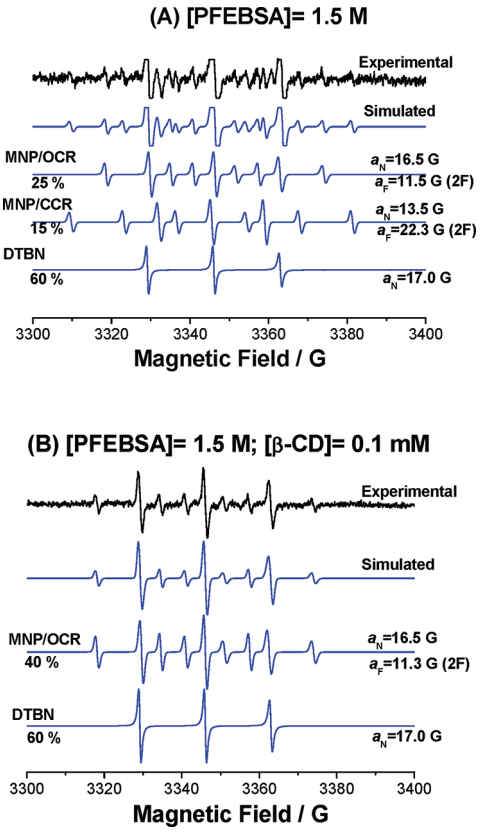


Figure 6. Experimental and simulated ESR spectra of the MNP/OCR and MNP/CCR adducts generated in the MNP/H_2O_2/PFEBSA system at 300 K and pH 3.5. (A) In the absence of β-CD. (B) In the presence of β-CD.

MNP/OCR and DTBN, are presented in Figure 3. The relative intensity of the adduct is 39%, an enhancement compared to solutions in the absence of β-CD, where its relative intensity is only 9%. The DTBN radicals are detected in the "out" form (a_N = 17.1 G). The increase of the relative intensities of MNP adducts in the presence of β-CD is at this stage assigned to the stabilization process of MNP/OCR adducts[22] by their selective encapsulation in β-CD. Similar results were obtained for the other membranes. The formation of the same adduct, MNP/OCR, for the three membranes suggests the vulnerability of the side chain to $HO^{\bullet}$ radical attack in the initial fragmentation stages.

PFMHSA Fragmentation. The effect of hydroxyl radicals on this MC, which is considered as the model compound for the side chain of Nafion membrane, was studied in a wide range of concentrations, 0.5−3 M, and pH values, 3−8. The ESR spectra are shown in Figure 4A. For all of these conditions only one adduct was detected, with a_N = 16.0 G and a_F = 23.5 G (1F); this adduct is assigned to MNP/F, based on reported hyperfine splittings.[9] The addition of β-CD, Figure 4B, leads to the detection of an additional MNP adduct, with a_N= 15.4 G and a_F= 6.2 G, which is assigned to an MNP/OCR adduct, and a high relative intensity, 56%; this result is important because oxygen-centered radicals are not easily detectable. Until now only indirect proof for their formation was presented in the literature.[23,24] Even at higher concentration of β-CD no DTBN "in" was detected, suggesting that the inclusion of DTBN inside β-CD cavity is hindered in the presence of MNP/OCR adducts, which are preferred for selective encapsulation. We note that the hyperfine splittings for the MNP/OCR adduct are slightly different compared to the membranes, most likely because of the sensitivity of magnetic parameters for fluorinated radicals, depending on the details of their conformations.[25] A study of the effect of the detailed geometry on the hyperfine splittings of the MNP/OCR adducts by density functional theory (DFT) is planned, based on methods that allowed us to make a distinction between OCR and CCR species in a direct ESR study of Nafion fragmentation.[26]

PFEESA Fragmentation. This system was studied at a concentration of 2 M, and the results are shown in Figure 5A. In the absence of β-CD, Figure 5A, only one adduct, with a_N = 16.5 G and a_F = 23.0 G (1F), was detected and assigned to MNP/F. Results in the presence of β-CD (concentration 0.1 mM) are presented in Figure 5B. Only one adduct was detected, with a_N = 16.3 G and a_F = 11.3 G (2F), which is assigned to the MNP/OCR adduct. Even at higher concentrations of β-CD no other MNP adducts were detected. No "in" and "out" conformations of the DTBN radicals were detected as previously observed in the case of PFOA, indicating the selective encapsulation of MNP/OCR adducts.

PFEBSA Fragmentation. The ESR spectra in the absence of β-CD are shown in Figure 6A and consist of two adducts: The adduct with a_N = 13.5 G and a_F = 22.3 G (2 F) is assigned to the MNP/CCR adduct, based on the similarity of the adduct detected in PFOA: low a_N and hyperfine splittings from two

Table 1. Magnetic Parameters of MNP Adducts and Effect of β-CD Addition on MNP Adducts and DTBN Radicals Generated in the Systems Below

Model Compound	Spin Adduct	a_N/G	a_F/ G
$HOOC(CF_2)_6CF_3$ (PFOA)	*MNP/CCR* [a]	13.4	22.4 (2F)
$CF_3CF_2OCF_2CFO(CF_2)_2SO_3H$ (PFMHSA) with CF_3	*MNP/F* [b]	16.0	23.5 (1 F)
	MNP/OCR [c]	15.4	6.2 (2 F)
$CF_3CF_2OCF_2CF_2SO_3H$ (PFEESA)	*MNP/F* [d]	16.5	23 (1 F)
	MNP/OCR [e]	16.3	11.3 (2 F)
$CF_3CF_2O(CF_2)_4SO_3H$ (PFEBSA)	*MNP/OCR* [f]	16.5	11.5 (2F)
	MNP/CCR [g]	13.5	22.3 (2F)

[a] β-CD enhanced both the relative intensity of MNP/CCR adducts comparing with DTBN radicals and their stability, detection of "in" and "out" conformations for MNP adducts and DTBN. [b] Addition of β-CD resulted in a small increase of the relative intensity of MNP/F. No "in" and "out" conformations for MNP/F or DTBN were detected. [c] Addition of β-CD resulted in the detection of a new adduct, MNP/OCR, which was not observed in the absence of β-CD. The relative intensity of this adduct is dominant in the ESR spectra. [d] Addition of β-CD resulted in the total disappearance of MNP/F adducts. No "in" and "out" conformations for DTBN were detected. [e] Addition of β-CD resulted in the detection of MNP/OCR, an adduct that was not detected in the absence of CD. [f] β-CD stabilized MNP/OCR, described as unstable and determined the increase of their relative intensity. [g] β-CD determined the total disappearance of MNP/CCR adducts in the presence of MNP/OCR adducts. No "in" and "out" forms for neither MNP/CCR nor DTBN were detected when MNP/OCR adducts was also detected in the system.

^{19}F nuclei. The adduct with a_N = 16.5 G and a_F = 11.5 G (2F) is assigned to MNP/OCR, as in the case of PFEESA as the MC. In the presence of β-CD, Figure 6B, the oxygen-centered radical adduct MNP/OCR and DTBN are detected, but no trace of MNP/CCR is presented in Figure 6A. The addition of 0.1 mM β-CD leads to a significant increase of the relative intensity of MNP/OCR (from 25% in the absence of β-CD to 40% in the presence of CD) to the total disappearance of the MNP/CCR adduct. As in the case of PFMHSA and PFEESA as MCs, the "in" form of DTBN radicals cannot be detected even for [β-CD] = 2 mM.

Table 1 presents the magnetic parameters of MNP adducts and the effect of β-CD addition on MNP adducts and DTBN radicals generated in the systems studied.

In summary, the stabilization of MNP/OCR adducts in the presence of β-CD in the membranes and MCs is clearly documented in Figures 1−6. The hyperfine splittings of the MNP/OCR adducts are slightly different in the different systems reported above, but close enough for the same assignment of this adduct. The a_N value for all MNP/OCR adducts is in the range 15.4 to 16.5 G, suggesting that the N−O group is in a polar environment, and outside the β-CD host. This result is in contrast to the a_N value of the MNP/CCR adduct, which is 12.3 G for the "in" form of PFOA, Figure 1; the a_N value for the "out" form of this adduct is 13.4 G (Figure 1, data for PFOA) or 13.5 G (Figure 6, data for the PFEBSA as the MC).

In addition, the a_N value of the DTBN radicals in the "out" form varies in a narrow range in the systems above, 16.9−17.1 G; these values reflect the slightly different local polarities.

Implication for Membrane Degradation. The spin adducts of MNP as the spin trap detected in the perfluorinated membranes (Nafion, 3M, and Aquivion) and in their corresponding MCs discussed above can bring new insights on the very early events occurring due to hydroxyl radicals attack.

The OCR adducts detected in the membranes indicate the susceptibility of ether bridges to fragmentation and the generation of oxygen centered radicals; these radicals are highly unstable and undergo rapid transformation to carbon centered radicals.[23,24] The addition of β-CD leads to the stabilization of the MNP/OCR adducts, and their relative intensity increases by a factor of 4 in the presence of β-CD for all three membranes studied. No other adducts can be detected in the absence or presence of β-CD, suggesting that cleavage of the ether bridge occurs in the very early degradation phase.

The results for the corresponding MCs support this hypothesis, as the fragmentation of MCs with one ether bridge (PFEESA and PFEBSA) and two ether bridges (PFMHSA) in the presence of β-CD leads also to the detection of MNP/OCR adducts. Cleavage of the ether bridge is also supported by ref 4 (by MS-LC) (for MCs) and ref 27 (for Nafion); the results presented above provide direct evidence of oxygen centered radicals generation in the initial degradation stages. The results for PFOA as a control provide additional support for this conclusion: The hydroxyl radical's attack leads to the generation of CCRs and MNP/CCR adducts in the absence or presence of β-CD, via attack of the COOH groups: a mechanism that leads to the unzipping mechanism of the perfluorinated membranes fully described in the literature.[2,3]

The stable fragmentation species generated by the hydroxyl radical's attack on fluorinated model compounds and perfluorinated membranes have been studied by fluoride ion concentration measurements, ^{19}F NMR and liquid chromatography−mass spectroscopy methods (LC-MS).[4] This paper has correctly assumed that ether linkages, which connect the ionomeric side chains groups to perfluorinated backbone, are susceptible points of attack and can lead to side chain cleavage, especially when the concentration of COOH at the chain ends is negligible. The results described in this study provide the evidence for the fragmentation of the side chain in the membrane and the generation of OCRs in the very early stages, and the transformation of these radicals into the more stable radicals, CCRs.

CONCLUSIONS

The detection of MNP/CCR adducts in $HOOC(CF_2)_6CF_3$ (PFOA) aqueous solutions in the absence or presence of β-CD suggests the attack of hydroxyl radicals on the carboxylic group, and provides the mechanistic model for the unzipping mechanism of nonstabilized Nafion.[2,3] The detection of MNP adducts of oxygen-centered radicals, MNP/OCR, as the main components in the ESR spectra of the perfluorinated membranes (stabilized Nafion, Aquivion, and 3M) and corresponding model compounds with one (PFEESA and PFEBSA) or two ether bridges (PFMHSA) demonstrates that cleavage of the ether bridge by hydroxyl radicals is the very early event.

The oxygen-centered radicals, OCRs, are short-lived and are transformed into carbon-centered radicals, CCRs. Addition of β-CD leads to an increased stability of OCRs and their selective encapsulation of the MNP/OCR adducts in the model compounds PFMHSA, PFEESA, and PFEBSA. In the perfluorinated membranes the transformation of OCRs to CCRs is slower, but the stability of the OCRs is increased in the presence of β-CD.

The radical di-*tert*-butyl nitroxide (DTBN) is also detected in the systems studied, from spin trap decomposition. In PFOA

both "in" and "out" forms of DTBN in the presence of β-CD were detected.

Spin trapping ESR experiments with MNP as the spin trap suggest that the very early event in the presence of hydroxyl radicals is the attack on the ether bridges in the model compounds and in the perfluorinated membranes.

AUTHOR INFORMATION

Corresponding Author

*Telephone: 1-313-404-9757 (mobile). Fax: 1-313-993-1144. E-mail: schlicks@udmercy.edu.

ACKNOWLEDGMENT

This research was supported by grants from the Polymers Program of the National Science Foundation. We are grateful to D. A. Schiraldi for the gift of some model compounds and PFOA and to S. J. Hamrock for the 3M membrane dispersion.

REFERENCES

(1) Roduner, E.; Schlick, S. In *Advanced ESR Methods in Polymer Research*; Schlick, S., Ed.; Wiley: Hoboken, NJ, 2006; Chapter 8, pp 197−228.

(2) Curtin, D. E.; Lousenberg, R. D.; Henry, T. J.; Tangeman, P. C.; Tisack, M. E. *J. Power Sources* **2004**, *131*, 41–48.

(3) Healy, J.; Hayden, C.; Xie, T.; Olson, K.; Waldo, R.; Brundage, A.; Gasteiger, H.; Abbott, J. *Fuel Cells* **2005**, *5*, 302–308.

(4) Zhou, C.; Guerra, M. A.; Qiu, Z. M.; Zawodzinski, T.; Schiraldi, D. A. *Macromolecules* **2007**, *40*, 8695–8707.

(5) Danilczuk, M.; Perkowski, A. J.; Schlick, S. *Macromolecules* **2010**, *43*, 3352–3358.

(6) Ghassemzadeh, L.; Marrony, M.; Barrera, R.; Kreuer, K. D.; Maier, J.; Muller, K. *J. Power Sources* **2009**, *186*, 334–338. Ghassemzadeh, L.; Kreuer, K. D.; Maier, J.; Müller, K. *J. Power Sources* **2011**, *196*, 2490–2497.

(7) Ghassemzadeh, L.; Kreuer, K. D.; Maier, J.; Muller, K. *J. Phys. Chem. C* **2010**, *114*, 14635–14645.

(8) Chen, C.; Fuller, T. F. *Polym. Degrad. Stab.* **2009**, *94*, 1436–1447.

(9) Danilczuk, M.; Coms, F. D.; Schlick, S. *Fuel Cells* **2008**, *8* (6), 436–452.

(10) Danilczuk, M.; Coms, F. D.; Schlick, S. *J. Phys. Chem. B* **2009**, *113*, 8031–8042.

(11) Danilczuk, M.; Schlick, S.; Coms, F. D. *Macromolecules* **2009**, *42*, 8943–8949.

(12) Madden, K. P.; Taniguchi, H. *J. Am. Chem. Soc.* **1991**, *113*, 5541.

(13) Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743–1754.

(14) Spulber, M.; Schlick, S. *J. Phys. Chem. A* **2010**, *114*, 6217–6225.

(15) Bednarek, J.; Schlick, S. *J. Phys. Chem.* **1991**, *95*, 9940–9944.

(16) Matsouka, K; Moroi, Y. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 227–236.

(17) Lin, I. J. *J. Phys. Chem.* **1972**, *14*, 2019–2023.

(18) Tomasic, V.; Chittofrati, A.; Kally, N. *Colloids Surf. A* **1995**, *104*, 95–99.

(19) The WinSim software can be accessed at: http://www.niehs.nih.gov/research/resources/software/tools/index.cfm.

(20) Han, Y.; Tuccio, B.; Lauricella, R.; Villamena, F. A. *J. Org. Chem.* **2008**, *73*, 7108–7117.

(21) Karoyo, A. H.; Borisov, A. S.; Wilson, L.; Hazendonk, P. *J. Phys. Chem. B* **2011**, *115*, 9511–9527and references therein.

(22) Franchi, P.; Lucarini, M.; Pedulli, G. F. *Curr. Org. Chem.* **2004**, *8*, 1831–1849.

(23) Faucitano, A.; Buttafava, A.; Karolczack, S.; Guarda, P. A.; Marchionni, G. *J. Fluorine Chem.* **2004**, *125*, 221–241.

(24) Faucitano, A.; Buttafava, A.; Caporiccio, G; Viola, C. T. *J. Am. Chem. Soc.* **1984**, *106*, 4172–4174.

(25) (a) Kispert, L. D.; Rogers, M. T. *J. Chem. Phys.* **1971**, *54*, 3326–3335. (b) Bogan, C. M.; Kispert, L. D. *J. Phys. Chem.* **1973**, *77*, 1491–1496.(c) Kispert, L. D. In *Fluorine-Containing Free Radicals Kinetics and Dynamics of Reactions*; Root, J. W., Ed.; ACS Symposium Series No. 66; American Chemical Society: Washington, DC, 1978; Chapter 13, pp 349−385.

(26) Lund, A.; Macomber, L.; Danilczuk, M.; Stevens, J.; Schlick, S. *J. Phys. Chem. B* **2007**, *111*, 9484–9491.

(27) Ramaswamy, N.; Hakim, N.; Mukerjee, S. *Electrochem. Acta.* **2008**, *53*, 3279–3295.