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Acidity and Catalytic Activity of Nafion-H

Susan J. Sondheimer, Nigel J. Bunce,* Mary E. Lemke, and Colin A. Fyfe*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.
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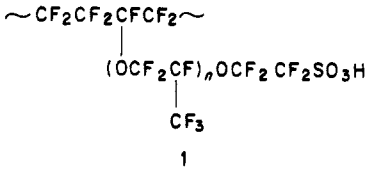
ABSTRACT: Studies with acid–base indicators have shown that suspensions of the fluorinated sulfonic acid polymer Nafion-H behave as an acid of strength comparable with CF_3SO_3H, but only in solvents capable of removing the water chemically from within the beads. The proton NMR spectra of Nafion-H samples swollen in benzene or cyclohexane show that the chemical shift of the hydroxylic protons moves downfield as the water content decreases. The observed chemical shift arises from fast exchange between H_2O and the Nafion-H and indicates that samples having the ratio $OH/SO_3^- \geq 3$ behave as $R_FSO_3^-\cdot H_3O^+$ ion pairs in the interior of the beads. Nafion-H samples similar to those used by other workers for catalysis of organic reactions have the approximate composition $R_FSO_3^-\cdot H_3O^+$, where the catalytically active species is the unsolvated $R_FSO_3^-\cdot H_3O^+$ ion pair. This explains the great acidity of these catalysts, which is comparable with concentrated (>95%) solutions of H_2SO_4. Catalysis of hydrogen–deuterium exchange in aromatic compounds by Nafion-D/D_2O is found to be of only limited application.

Introduction

Nafion-H, the acidic form of the polymeric fluorinated sulfonic acid 1, has been widely investigated as an acidic catalyst for organic reactions.[1] All indications are that



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the substance is a very strong Brønsted acid. Thus Nafion-H catalyzes the isomerization of dialkylbenzenes in the gas phase at elevated temperatures, with an activity intermediate between that of SiO_2/Al_2O_3 ($H_0 = -8$) and that of $AlCl_3$ in solution ($H_0 = -15$).[2] Similarly, in the formation of phenylphosphorus dichlorides from PCl_3 and substituted benzenes, Nafion-H has a catalytic activity comparable with that of Brønsted acids having $H_0 < -12$.[3] To date, no reports on the direct determination of an effective acidity constant for Nafion-H have appeared or on the effect of traces of water on its acidity. This is the purpose of this study.

Results and Discussion

Indicator Studies. The determination of an effective pK_a for Nafion-H is not straightforward because Nafion-H is not soluble in water or organic solvents at room temperature.[4] In a heterogeneous suspension of Nafion-H in water, the pH of the aqueous phase is not affected by the presence of Nafion-H. This can be shown by dipping a piece of pH paper into the slurry: a color change is observed only where the paper is in contact with the Nafion-H beads.

Protonation of Hammett indicators[5] by suspensions of Nafion-H was shown by observing the beads acquire the color of the protonated form of the indicator. For example, when a yellow aqueous solution of *p*-aminoazobenzene is shaken with Nafion-H, the beads become red and the solution decolorizes. Addition of aqueous NaOH to the separated aqueous phase effects no color change, but addition of the filtered beads to this reagent decolorizes the beads and regenerates yellow in the supernatant liquid.

In water, Nafion-H completely protonated bases at least as basic as *p*-nitroaniline ($pK_a = 1.0$), partially protonated *o*-nitroaniline ($pK_a = -0.3$), and did not protonate 4-chloro-2-nitroaniline ($pK_a = -1.0$) to a detectable extent. Homogeneous aqueous solutions of *p*-toluenesulfonic acid ($pK_a = -5$ to -7)[6] behaved similarly to the Nafion-H suspensions.

An experiment to determine an effective K_a for Nafion-H in water was carried out by partitioning a known amount of organic base (*o*-nitroaniline) between bulk water and the beads. The loss of dye from the bulk solution was measured spectrophotometrically. An order of magnitude estimate of K_a for Nafion-H was obtained from equilibria 1–3 by making the further assumptions (i) that the concentration of the uncharged indicator is the same in the "internal" water as it is in the bulk, (ii) that K_a for the indicator is the same in the internal environment, and (iii) that equilibrium is reached during the time of the experiment (~25 min). The equilibrium constant for reaction 3 was found to be 2.2, in remarkable agreement with the value of unity would be expected if the acidic species in 1 and 3 were actually H^+_{aq} and not the neutral R_FSO_3H.

$$R_FSO_3H + In \rightleftarrows R_FSO_3^- + HIn^+ \qquad K_1 = K_{obsd} \quad (1)$$

$$HIn^+ \rightleftharpoons H^+_{aq} + In \qquad K_2 = K_a \text{ for } HIn^+ \quad (2)$$

$$R_FSO_3H \rightleftharpoons R_FSO_3^- + H^+_{aq} \qquad K_3 = K_a \text{ for } R_FSO_3H = K_1K_2 \quad (3)$$

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Table I
Reactions of Nafion-H with Indicators in Different Media[a]

indicator	p-toluenesulfonic acid	Nafion suspension: beads	Nafion suspension: supernatent
	In Water or Acetic Acid		
p-aminoazobenzene	red	red	colorless
p-nitroaniline	colorless	colorless	colorless
o-nitroaniline	pale yellow	colorless[d]	pale yellow[d]
4-chloro-2-nitroaniline	yellow	colorless	yellow

indicator	CH_3SO_3H[b]	Nafion suspension: beads	Nafion suspension: supernatent
	In 20% Acetic Anhydride in Acetic Acid		
o-nitroaniline	colorless	colorless	colorless
4-chloro-2-nitroaniline	colorless	colorless	colorless
2,5-dichloro-4-nitroaniline	colorless	colorless	very pale yellow

indicator	fuming H_2SO_4[b]	CH_3SO_3H[b]	CF_3SO_3H[b]	Nafion suspension: beads	Nafion suspension: supernatent
		In Acetic Anhydride			
2,6-dichloro-4-nitroaniline	colorless	colorless		colorless	colorless
2,6-dinitroaniline	colorless	colorless		colorless	colorless
2-bromo-4,6-dinitroaniline	colorless	pale yellow		colorless[d]	colorless
anthraquinone	red	colorless	yellow	pale yellow	colorless
p-nitrotoluene		colorless	yellow[c]	colorless	colorless
		In Trifluoroacetic Anhydride			
anthraquinone	red	yellow	orange	dark yellow	colorless
p-nitrotoluene	yellow	colorless	yellow	yellow	colorless
2,4-dinitrotoluene	yellow		colorless	colorless	colorless

[a] All reactions complete after 5 min or less except where noted *d*. [b] One drop added unless otherwise noted. [c] Required several drops of acid to effect color change.

Further indicator experiments (Table I) showed that the acid strength of Nafion-H is greater than that of CH_3SO_3H and comparable with that of CF_3SO_3H. In glacial acetic acid, Nafion protonated only the same indicators that it protonated in water, a result ascribed to the water that is present in Nafion which has been dried open to the air of the laboratory (approximate composition $R_FSO_3H{\cdot}3H_2O$[7]). In acetic anhydride, which combines chemically with the water, Nafion-H protonated 2-bromo-4,6-dinitroaniline ($pK_a = 6.7$). CF_3SO_3H also protonated this indicator, but CH_3SO_3H did not. CF_3SO_3H partially protonated anthraquinone in acetic anhydride solution but Nafion-H and CH_3SO_3H did not.

In trifluoroacetic anhydride solution, all three of the above acids protonated anthraquinone ($pK_a = -8.3$), while Nafion-H and CF_3SO_3H both protonated *p*-nitrotoluene ($pK_a = -10.2$). None of these acids protonated 2,4-dinitrotoluene ($pK_a = -12.8$).

We therefore conclude that the acid strength of Nafion-H is comparable with that of CF_3SO_3H and greater than that of CH_3SO_3H. We cannot deduce the actual value of K_a for Nafion-H because of the different solvents used. Previous estimates of the acidities of sulfonic acids are CH_3SO_3H ($H_0 = -7.9$)[8] and CF_3SO_3H ($H_0 = -14.1$).[9] For comparison, a 96.5% by weight solution of H_2SO_4 in water has $H_0 = -10$, and a 100% solution has $H_0 = -12$.[10]

^{1}H NMR Studies. The proton NMR spectrum of a dilute aqueous solution of a strong acid shows only a single resonance, due to fast exchange between H_3O^+ and H_2O. This resonance moves downfield as the acid concentration increases, and the hypothetical limit of the downfield shift, which cannot be realized in practice, would be the chemical shift of pure, unsolvated H_3O^+, related, of course, to water as the solvent.

For mineral acids the chemical shift of the hydroxyl resonance may be related[11] to the concentration by plotting chemical shift against a parameter p, defined by

$$p = 3x/(2 - x) \tag{4}$$

In eq 4, x is the stoichiometric mole fraction of H_3O^+. The parameter p takes into account the three protons of H_3O^+ as opposed to the two of H_2O. Equation 5 gives the relationship between the chemical shift and p; S_{obsd} is the observed chemical shift of the hydroxyl resonance, expressed relative to pure water as zero, and $S_{H_3O^+}$ is the hypothetical chemical shift of the pure H_3O^+ ion. Linear relationships between S_{obsd} and p have been obtained[11,12] for HNO_3, HCl, and $HClO_4$ up to moderate concentrations. The slopes of these lines afford values for $S_{H_3O^+}$ of 11.82, 11.43, and 9.17 ppm, respectively.[12] At higher concentrations, the plots become curved because of the presence of additional species such as the ion pairs $H_3O^+X^-$ and the undissociated acids HX. Also, as the solvent composition begins to change, it can no longer be assumed that the chemical shifts of H_2O and H_3O^+ are independent of the composition of the mixture.

$$S_{obsd} = pS_{H_3O^+} \tag{5}$$

For weak acids, eq 5 is modified[13] to include the degree of dissociation, eq 6. $S_{H_3O^+}$ can be obtained at extremely low concentrations where the acid is completely dissociated ($\alpha = 1$). Values of $S_{H_3O^+}$ in the same range of 11–14 ppm

$$S_{obsd} = S_{H_3O^+}\alpha p + \tfrac{1}{3}S_{HX}(1 - \alpha p) \tag{6}$$

have been obtained for aqueous solutions of HIO_3,[14] CH_3SO_3H,[13] CF_3SO_3H,[15] *p*-toluenesulfonic acid,[16] and poly(styrenesulfonic acid), the latter in the restricted concentration range $0 < p < 0.02$. Measurements on cross-linked sulfonated poly(styrene-*co*-divinylbenzene) resins[17,18] gave a very complex relationship between S_{obsd} and p.

Figures 1 and 2 are plots of S_{obsd} vs. p for Nafion-H swollen in cyclohexane and benzene, respectively. The plots are linear in p to high mole fractions of H^+, comparable with those seen for strong acids,[11,12] but the values of $S_{H_3O^+}$ obtained from the limiting slopes are very much

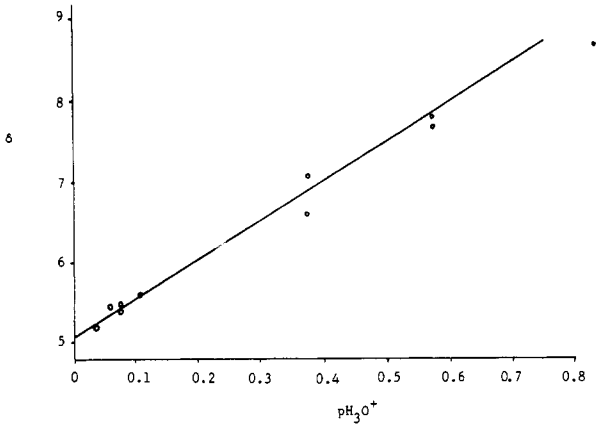

Figure 1. Chemical shift vs. parameter p related to mole fraction of H_3O^+ for samples of Nafion-H swollen in cyclohexane.

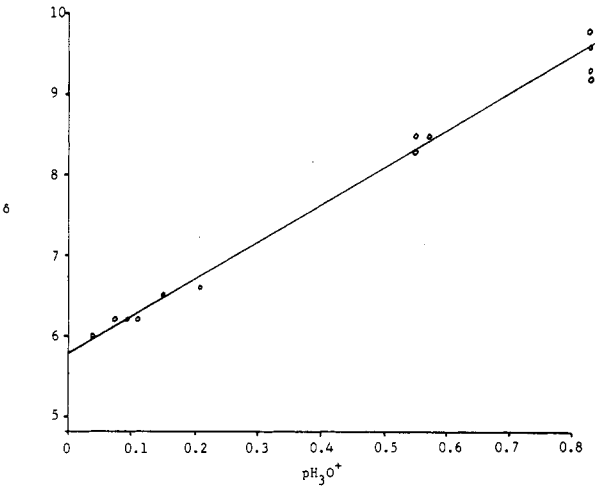

Figure 2. Chemical shift vs. parameter p related to mole fraction of H_3O^+ for samples of Nafion-H swollen in benzene.

smaller: 4.8 ppm for cyclohexane and 4.6 ppm for benzene as the swelling solvent.

In Figure 3 we show for comparison the results of Duplessix et al.[19] taken from a presentation of chemical shift vs. percent water for unswollen samples of Nafion-H. The data have been replotted in the format S_{obsd} vs. p. A linear relationship is obtained up to $p \sim 0.4$ with $S_{H_3O^+} \simeq 4.5$ ppm.

From the indicator experiments, we can assume that Nafion-H is intrinsically a strong acid. We must therefore explain why swollen Nafion-H samples show S_{obsd} vs. p plots with a slope of $\simeq$4.5 ppm while aqueous acids give values of the order of 10–12 ppm. One possible factor is a solvent effect since the extrapolations to $p = 0$ do not correspond to the chemical shifts of pure water (4.8 ppm relative to Me_4Si) when the polymer is swollen in either benzene (5.8 ppm) or cyclohexane (5.1 ppm). Another factor is the influence on the chemical shift of ion pairing between $R_FSO_3^-$ and H_3O^+. According to one popular model for Nafion structure, the SO_3H groups project in clusters into roughly spherical cavities containing the water.[20] Electrostatic repulsion demands that all the SO_3^- groups cannot be located around the periphery of a cluster with all the H_3O^+ ions in the center. We thus consider the equilibrium 7. The dissociation behavior of the ion pairs

$$nH_2O + R_FSO_3^-\cdot H_3O^+ \rightleftharpoons R_FSO_3^-(aq) + H_3O^+(aq) \quad (7)$$

might be analogous to that of a weak acid, in which case we would expect the plot of S_{obsd} vs. p to follow the form of eq 6. This explanation cannot account for the data because the degree of dissociation should be strongly

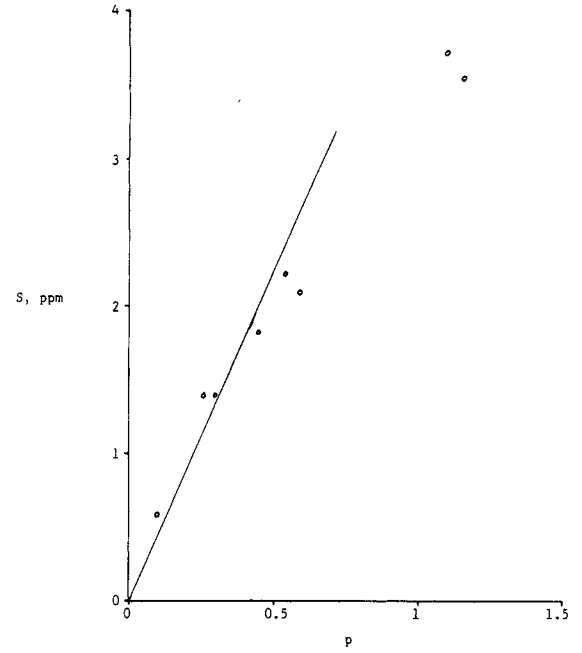

Figure 3. Chemical shift vs. parameter p related to mole fraction of H_3O^+ for dry Nafion-H powder (replotted with the data of ref 22).

concentration-dependent except in the limit $p \rightarrow 0$, and linear plots should not be observed.

We therefore postulate that the two main species that are in fast exchange by NMR are H_2O and the ion pair. Under all conditions the degree of dissociation of the ion pairs is small, and free $H_3O^+_{aq}$ is not a major contributor to the chemical shift. The predominant species detected by NMR are H_2O and $R_FSO_3^-\cdot H_3O^+$, and we can write eq 8 corresponding to eq 5. Hence the slope of the S_{obsd} vs.

$$S_{obsd} = pS_{ion\ pair} \quad (8)$$

p plot affords the chemical shift of the ion pair and not that of H_3O^+. On the δ scale, the chemical shift of the ion pair is close to 10 ppm. The similarity of the S values obtained from Figures 1, 2, and 3 shows the self-consistency of the explanation. Of course, for Nafion-H samples having less than one H_2O molecule per SO_3H, the resonance observed by ^1H NMR is a weighted average of R_FSO_3H and $R_FSO_3^-\cdot H_3O^+$ rather than $R_FSO_3^-\cdot H_3O^+$ and $H_3O^+_{aq}$, and the chemical shift under these conditions can be greater than 10 ppm on the δ scale.

Nafion-H as an Acid Catalyst. Nafion-H containing substantial amounts of water has just been shown to be composed principally of $R_FSO_3^-\cdot H_3O^+$ ion pairs and is potentially a source of H^+_{aq}. However, in its catalytic chemistry, the material behaves as a much stronger acid than H^+_{aq}. The composition of the material explains its catalytic behavior.

We have recently determined the absolute water content of Nafion-H samples by quantitative ^1H NMR spectroscopy.[7] Samples of Nafion-H dried in the open laboratory have a composition approximated by $R_FSO_3H\cdot(3\text{–}5)H_2O$, vacuum-drying at room temperature gives a material of composition $R_FSO_3H\cdot H_2O$ (or $R_FSO_3^-\cdot H_3O^+$), and vacuum-drying at temperatures above 100 °C gives a material whose composition is close to that of the free sulfonic acid R_FSO_3H. A similar conclusion for the material dried at elevated temperatures has recently been obtained from infrared measurements.[21]

When Nafion-H samples of composition $R_FSO_3H\cdot 3H_2O$ were heated overnight in a stream of N_2 at temperatures of either 130 or 190 °C, the resulting material had the

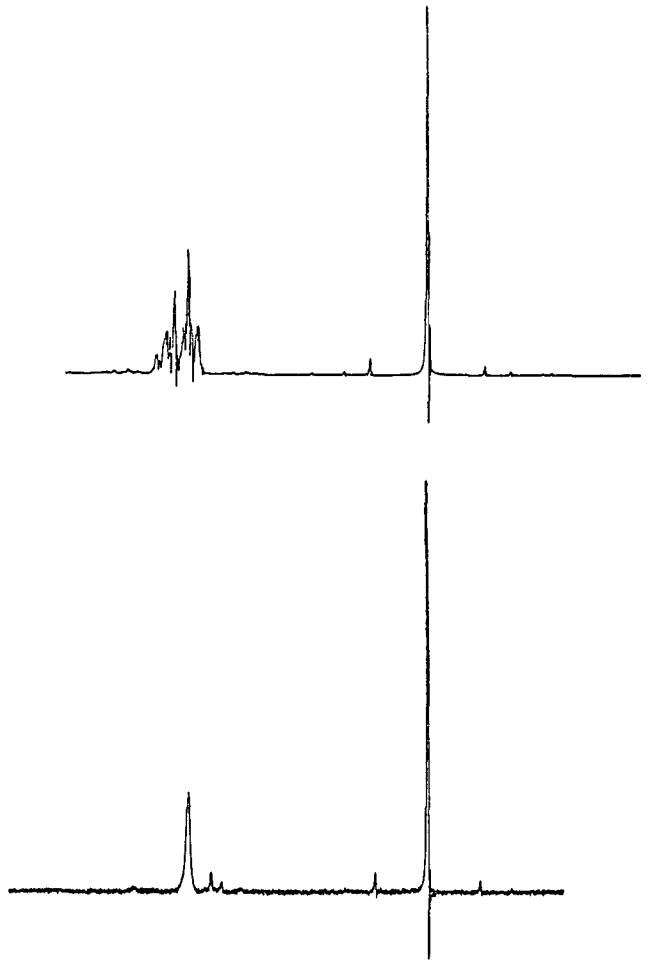

Figure 4. ^1H NMR spectrum of anisole (a) before, and (b) after exchange with D_2O/Nafion-H at 150 °C.

approximate composition $R_FSO_3H \cdot H_2O$ whether the N_2 stream had been dried by bubbling through concentrated H_2SO_4 or saturated with water. This suggests that under the conditions of typical gas-phase reactions the Nafion-H catalyst has a composition close to that of the H_3O^+ salt, even when steam is deliberately added to the feed (for examples, see ref 1b). There is thus no contradiction that this material should be a much stronger acidic catalyst than an aqueous mineral acid, i.e., H^+_{aq}, since in the Nafion material it is an unsolvated $R_FSO_3^- \cdot H_3O^+$ ion pair that is present. Indeed, 96.5% by weight H_2SO_4, which has $H_0 = -10$,[10] has as the major acidic species present H_3O^+ (mol fraction $x = 0.9$) and H_2SO_4 ($x = 0.1$). It thus appears that Nafion-H, which has the $R_FSO_3^- \cdot H_3O^+$ ion pair as the active acidic catalyst, may be even more acidic than solutions of H_2SO_4 in which the H_3O^+ ions are solvated by H_2SO_4 molecules.

Deuteration of Benzene Derivatives. Exploratory studies have been carried out to determine whether Nafion-D would be a useful catalyst for hydrogen–deuterium exchange in aromatic compounds. The potential attraction of the method is that inexpensive D_2O can be used to exchange the H_3O^+ sites, and the solid catalyst offers the advantage of an easy workup procedure by simply filtering the catalyst from the solution after reaction.

As an example, anisole was investigated under various conditions. No detectable exchange was seen when anisole was boiled ($T \sim 100$ °C) with D_2O/Nafion-D for several hours. At 150 °C, exchange of the o/p protons was almost complete, while the meta protons were unaffected (Figure 4). A similar result was obtained when anisole, acetic acid-*O*-*d*, and Nafion-H were heated to reflux.

Attempts were made to exchange the remaining meta hydrogens by the use of more vigorous conditions. At 200 °C, an anisole/D_2O/Nafion-D mixture reacted rapidly, but now, in addition to isotopically exchanged anisole, other products were obtained, including phenol and isomeric cresols. The gas-phase conversion of anisole to phenol and the cresols is catalyzed by Nafion-H.[22] Prolonged exchange of anisole with acetic acid-*O*-*d* and Nafion-D produced, in addition to isotopically exchanged material, phenol, phenyl acetate, and *p*-methoxyacetophenone. The last two products were obtained from independent reactions of phenol with acetic acid and Nafion-H (compare also ref 23).

Using the D_2O/Nafion-D exchange method, with temperatures ranging up to 250 °C, we made attempts to deuterate toluene and *tert*-butylbenzene (both gave partial exchange) and chlorobenzene and nitrobenzene (both unsuccessful). Styrene polymerized (cf. ref 24), as did cyclohexanol. We conclude that the D_2O/Nafion-D method is not a promising method of hydrogen–deuterium exchange.

Experimental Section

Nafion-501 powder was obtained from E. I. duPont de Nemours Co., Inc. as the potassium salt and was converted to the hydrogen form by successive exchanges with 2.5 M HCl followed by washing with deionized water until $AgNO_3$(aq) gave no precipitate with the washing. This material was deuterated, when necessary, by three exchanges with D_2O.

Procedures for preparing Nafion-H samples of known water content and for preparing the samples for the ^1H NMR experiments at 400 MHz have been described previously.[7]

Indicator Experiments. The qualitative experiments were carried out by adding a few crystals of the basic form of the indicator to 2–3 mL of the appropriate solvent. Nafion-H beads were added to half of this solution, and the other half was kept as a visual reference. In all cases, reversibility of the reactions was checked by separating the beads and adding them to aqueous NaOH when the color of the basic form of the indicator was regenerated. Table I summarizes the results.

An example of a quantitative experiment involving Nafion-H and *o*-nitroaniline is now given. To a sample of bench-dried Nafion-H ($nH_2O/SO_3H = 3$, equiv weight 1260, 83.5 mg) contained in a UV cuvette was added 2.0 mL of 2.86×10^{-4} M *o*-nitroaniline solution. The solution was stirred with a small magnetic stirring bar and the change in the absorbance of the aqueous phase monitored until no further change occurred (25 min). The absorbance (412 nm, $\epsilon = 5000$) changed from 1.43 initially to 0.43 at equilibrium. The calculation was carried out with the following values: (i) moles of $SO_3H = 0.0835$ g/1260 g mol^{-1} $= 6.63 \times 10^{-5}$ mol; (ii) volume of internal water in the swollen polymer = 21 mol H_2O per mol $SO_3H \times 0.018$ dm^3 mol^{-1} $= 2.51 \times 10^{-5}$ dm^3; (iii) equilibrium concentration of *o*-nitroaniline $= 8.6 \times 10^{-5}$ M; (iv) moles of *o*-nitroaniline consumed = moles of SO_3H consumed = $(2.86 \times 10^{-4} - 8.6 \times 10^{-5})$ mol dm^{-3} $\times 0.0020$ dm^3 $= 4.0 \times 10^{-7}$ mol; (v) moles of SO_3H remaining $= 6.59 \times 10^{-5}$ mol; (vi) moles of internal *o*-nitroaniline $= 8.6 \times 10^{-5}$ mol dm^{-3} $\times 2.51 \times 10^{-5}$ dm^3 $= 2.2 \times 10^{-9}$ mol

$$K(\text{eq } 1) = [R_FSO_3H][HIn^+]/[In][R_FSO_3^-] = 1.12$$

$$K(\text{eq } 3) = K(\text{eq } 1) \times K(\text{eq } 2) = 1.1 \times 2.0 = 2.2$$

A total of nine such experiments gave an average value of 2.1.

NMR Experiments. The experimental procedures and the raw data on which Figures 1 and 2 are based were given previously.[7] Table II gives details of the calculations needed to rework the data of ref 19.

Nafion-H of similar composition to that used for catalytic studies was obtained from bench-dried Nafion-H (approximate composition $R_FSO_3H \cdot 3H_2O$) or, alternatively, vacuum-dried Nafion-H (approximate composition $R_FSO_3H \cdot H_2O$), which was packed into a glass tube of 8-mm o.d. The tube was placed in the oven of a gas chromatograph, attached to the gas inlet with Swagelok fittings, and purged with dry or wet nitrogen while the

Table II
Chemical Shift of Water in Unswollen Nafion-H Powder Recalculated from the Data of Ref 22

δ_{H_2O},[a] Hz	S, ppm	% H_2O[a]	n_{H_2O}[b]	n_{Nafion}[b]	$x_{H_3O^+}$[c]	p[d]
213	3.55	2.6	0.144	0.081	0.56	1.16
223	3.72	2.8	0.156	0.081	0.52	1.05
126	2.10	4.3	0.239	0.080	0.33	0.59
133	2.22	4.9	0.272	0.079	0.29	0.54
110	1.83	5.5	0.306	0.079	0.26	0.45
84	1.40	7.5	0.417	0.077	0.18	0.30
84	1.40	8.5	0.472	0.076	0.16	0.26
36	0.60	19.1	1.061	0.067	0.063	0.10

[a] Measured from the printed figure. [b] In 100 g. [c] $x_{H_3O^+} = n_{Nafion}/n_{H_2O} \equiv n_{Nafion}/[(n_{H_2O} - n_{Nafion}) + n_{Nafion}]$ knowing that the Nafion is composed of $H_3O^+ \cdot R_FSO_3^-$ ion pairs. [d] equation 4.

Table III
Products from the Reaction of Anisole and Acetic Acid Catalyzed by Nafion-H

time at reflux, h	% $PhOCH_3$	% p-$CH_3OC_6H_4COCH_3$	% CH_3CO_2Ph	% PhOH
2	99	0.3		
4	98	2	0.3	
8	93	3	0.7	3
18	80	7	2	10

oven was heated to the appropriate temperature. The cooled samples were then analyzed by the method of ref 7.

Isotope Exchange Experiments. Two typical experiments are described.

(i) A mixture of Nafion-D (approximate composition, $R_FSO_3D \cdot 3D_2O$, 1.0 g), anisole (2.0 g), and D_2O (20 mL) was sealed into a glass ampule of ca. 30-mL capacity. The ampule was placed in a stainless steel bomb equipped with Teflon gaskets together with about 20 mL of ordinary water (outside the ampule). The assembly was heated to 150 °C in a muffle furnace for 16 h. The apparatus was cooled and opened carefully; the ampule was broken open and the Nafion, anisole, and aqueous phases separated. The ^1H NMR spectrum of the anisole remaining is shown in Figure 4.

(ii) A mixture of vacuum-dried Nafion-D, acetic acid-*O*-*d* (4.5 mL, prepared by reacting equimolar amounts of D_2O and acetic anhydride), and anisole (0.5 mL) was heated to reflux. Samples were removed periodically and examined by ^1H NMR. After 1 h, no further change in the spectrum was observable. This corresponded to ~80% deuteration of the ortho and para hydrogens.

Byproducts in the High-Temperature Exchange of Anisole with Nafion-D. The products were initially identified by comparing their gas chromatographic retention times with those of authentic samples. Confirmation was obtained by carrying out control reactions with Nafion-H as the catalyst and analyzing the mixtures by gas chromatography–mass spectrometry. The mass spectra were identical with those of authentic reference materials. Table III gives some data for the anisole–acetic acid system.

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Registry No. PhOH, 108-95-2; p-$CH_3OC_6H_4COCH_3$, 100-06-1; CH_3CO_2Ph, 122-79-2; $PhOCH_3$, 100-66-3; Nofion-H, 63937-00-8; Na acetic acid, 64-19-7; water, 7732-18-5.

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